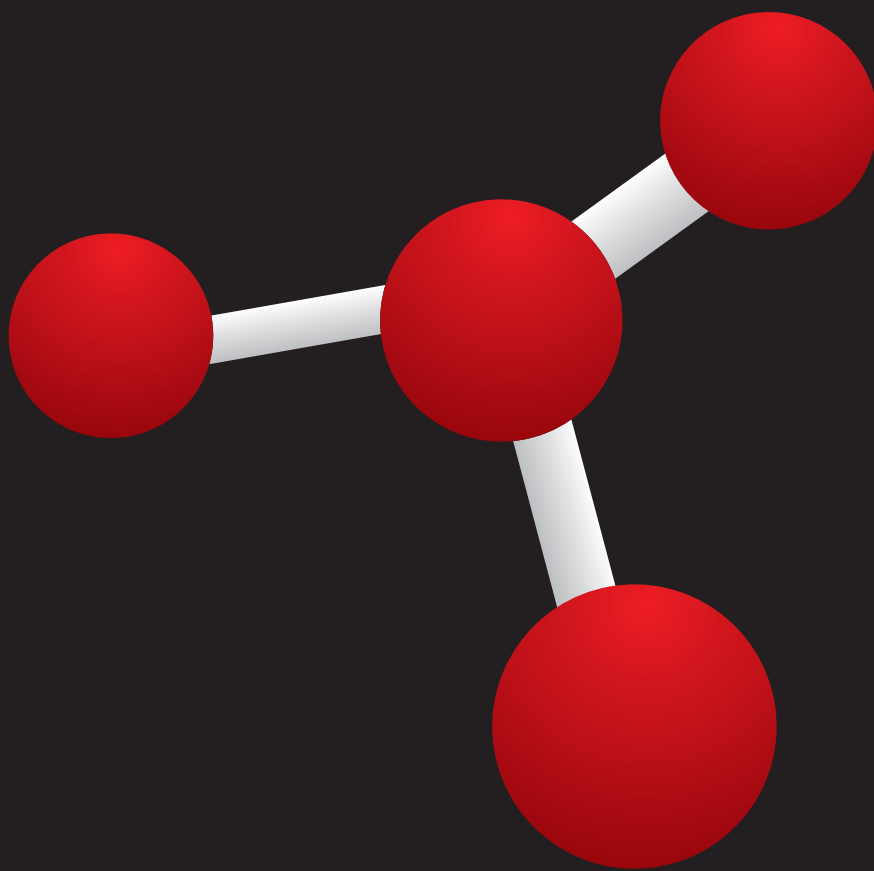


BASIC CONCEPTS OF
INORGANIC
CHEMISTRY

D. N. SINGH

SECOND EDITION



BASIC CONCEPTS OF INORGANIC CHEMISTRY

(Second Edition)

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ISBN 9788131768617

eISBN 9788131798683

Head Office: A-8(A), Sector 62, Knowledge Boulevard, 7th Floor, NOIDA 201 309, India

Registered Office: 11 Local Shopping Centre, Panchsheel Park, New Delhi 110 017, India

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"MY GURUS"*

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Preface

Inorganic Chemistry is the least taught portion of Class 12 Chemistry course.

Good part about the questions from the inorganic portion is that they are solely based on the principles. But the books already available in the market talk least of the principles and more about the experimental details and other things. This book mainly deals with the principles of inorganic chemistry and uses experimental conditions only when it is needed.

This book has been written to meet the needs of students from different courses and different boards like CBSE, ICSE and various State boards.

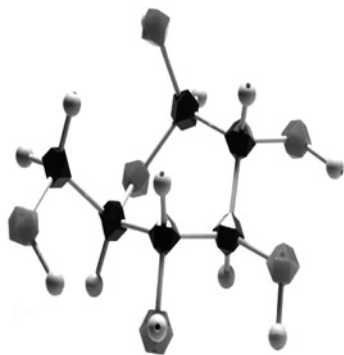
I am indebted to several of my colleagues for their suggestion and criticism. I am also thankful to my family members for encouragement, especially my daughter, Shiva, in the final draft.

I sincerely appreciate the help of Mr Lalit Kumar Gupta in the preparation of the manuscript.

I hope the readers will appreciate this book and any comments/suggestions towards improving the text would be welcome.

D. N. Singh

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Periodic Table and Periodicity of Properties

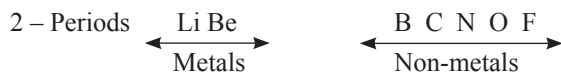
In 19th century, (before 1869) many pseudoscientific arrangement of elements were proposed. But none withstood the test of time and so were rejected. During 1869, first of all, Mendeleev (Russian chemist) realized that atomic weights of elements are related with their properties. On this observation, he proposed a law for the arrangement of elements.

MENDELEEV'S PERIODIC LAW

This law states that properties of elements and their compounds are the periodic function of their atomic weights. He, then arranged the elements in increasing order of their atomic weights. It resulted into a tabular form, so it is called Mendeleev's periodic table. Only 63 elements were known when this classification was presented.

Important features of the Table

- (i) Mendeleev's Periodic table forms vertical columns and horizontal rows for elements.
- (ii) Vertical columns are called groups. There are eight groups in the table (Group I to Group VIII). Elements of a group are similar in properties.
- (iii) All groups from I to VII are divided into sub-groups A and B (i.e., I_A , I_B , II_A , II_B etc.). Group VIII has no sub-groups.
- (iv) Horizontal rows are known as periods. There are seven periods (1 to 7).
- (v) Elements of the same period differ in properties.



- (vi) Sub-group elements also differ in properties.

I_A Na (highly reactive metal)
 I_B Cu (noble metal)

Merits of Mendeleev's Periodic Table

- (i) Correction of atomic weights: Many doubtful atomic weights were corrected using Mendeleev's periodic table, Example, Be.
- (ii) Vacant places for undiscovered elements: Mendeleev left vacant places in his table for elements to be discovered, (Ga, Ge etc.). Not only that, he also predicted properties of those elements which were found true when the elements were actually discovered. For example, Ga and Ge were not known

when Mendeleev proposed his periodic table. He named these elements EKAAluminium (Ga) and EKASILICON (Ge) because he believed that they would be similar to Al and Si. Mendeleev's predictions were found to be true.

Defects of Mendeleev's Periodic Table

- (i) H has got two places in Mendeleev's periodic table, in Group I (alkali metals) and Group VII (halogens).
- (ii) Some elements are in reverse order of atomic weights like Ar (39.9)–K (39.1), Co (58.9)–Ni (58.7), Te (127.6)–I (126.9).
- (iii) Highly reactive alkali metals (Li to Cs) are with noble coinage metals (Cu, Ag, Au).
- (iv) Gr VIII has three elements at a place (Fe, CO, Ni), (Ru, Rh, Pd) and (Os, Ir, Pt), instead of one element.
- (v) Metals like Mn, Tc, Re are placed with non-metals and halogens (F to I) in Group VII.
- (vi) Isotopes have got no places in Mendeleev's periodic table.
- (vii) There are 15 lanthanides in the same Group III.

MODERN PERIODIC TABLE

Mosley (1914), on the basis of his experiment observed that atomic number is the fundamental property of an element. This concept changed the basis of Periodic Table from atomic weight to atomic number. Mosley proposed his own periodic law, known as Modern Periodic Law. It states "Properties of elements and their compounds are the periodic function of their atomic numbers". Elements were, then, arranged in increasing order of their atomic numbers. The resultant table is known as Modern Periodic Table. In this table sub groups are separated and so the table becomes longer in size. Therefore, it is also known as long form of the periodic table.

Main Features of the Modern Periodic Table

- (i) It has groups and periods like Mendeleev's Periodic table.
- (ii) It has nine groups, I to VIII and zero group. (Noble gases were known when the table was made)
- (iii) Zero groups contains noble gases (He, Ne, Ar, Kr, Xe and Rn)
- (iv) Groups from I to VII are divided into sub-groups A and B.
- (v) Zero group and group VIII has no sub-groups.
- (vi) This table has seven periods.
- (vii) Elements from atomic number 84 (Polonium) onwards are radioactive. A few others having lower atomic number are also radioactive, T_c (it is synthetic also).
- (viii) Elements after atomic number 92 (Uranium) are all synthetic or man made. They have been produced by nuclear reactions.

Table 1.1

| Period | Nature | Elements |
|--------|-----------------|--|
| 1 | Shortest period | 2 H and He |
| 2 | Short period | 8 $_{(3)}\text{Li}$ to $_{(10)}\text{Ne}$ |
| 3 | Short Period | 8 $_{(11)}\text{Na}$ to $_{(18)}\text{Ar}$ |
| 4 | Long Period | 18 $_{(19)}\text{K}$ to $_{(36)}\text{Kr}$ |
| 5 | Long Period | 18 $_{(37)}\text{Rb}$ to $_{(54)}\text{Xe}$ |
| 6 | Longest Period | 32 $_{(55)}\text{Cs}$ to $_{(86)}\text{Rn}$ |
| 7 | Incomplete | 23 $_{(87)}\text{Fr}$ to $_{(111)}\text{Rg}$ |

IUPAC TABLE

It is simply a changed version of the long form of the periodic table. It was recommended in 1984 by IUPAC committee.

Main Features

- (i) This table has 18 groups, 1 to 18.
- (ii) The notation IA – VII_A, I_B – VII_B and VIII has been dropped.
- (iii) Elements of group 1 and group 2 and 13 to 17 have all their inner shells completely filled. These are s- and p- block elements.
- (iv) Elements of group 18 are noble gases. They have all their orbitals completely filled.
- (v) Elements belonging to group 3 to group 12 have their inner (n-1)d or (n-2)f orbital partially filled (these are d- and f-block elements).

Periodic Table and Aufbau Principle

Electron configuration of elements and the modern periodic table (or IUPAC table) correspond with each other. The electronic configuration of atoms follows Aufbau principle. It states that electrons should be placed, one at a time, in the lowest energy orbital. When an orbital is fully filled then the electron should occupy next higher energy orbital. The sequence followed is $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s$ etc. Thus, addition of each electron in an orbital makes an element.

Formation of other elements can be seen in the same way.

In the modern periodic table, the first period has 2 elements and it is due to gradual filling of 1s orbital, $1s^1$ and $1s^2$ i.e., H and He.

The second period contains 8 elements only due to gradual filling of 2s 2p orbital i.e., $2s^1$, $2s^2$, $2s^2 2p^1$, $2s^2 2p^2$, $2s^2 2p^6$.

Note

- In 3rd period, there are 8 elements only due to gradual filling of 3s3p orbitals. The 3d orbital has higher energy than 4s and when 4s filled period is changed. Thus period of an element corresponds to highest orbit present in electron configuration of the atom of that element.
- Similarly fifth period has only 18 elements due to filling of 5s 4d and 5p orbitals.
- In the 6th period, orbitals filled are $6s^2 4f^{14} 5d^{10}$ and $6p^6$. So there are 32 elements.

Therefore, it may be said that the modern periodic table is a consequence of Aufbau principles.

Determination of group and period of an element

Group and period

Table 1.3

| Modern Period Table | IUPAC Table |
|---|--|
| Group group = total valence electrons | s-block, group = total valence electron |
| Sub-group A = when valence orbital are s or s and p | p-block, group = total valence electron + 10 |

(Continued)

Table 1.2

| Period | Electron Configuration | Number of Elements |
|--------|---------------------------------------|--------------------|
| 1 | $1s^1$ to $1s^2$ | 2 |
| 2 | $2s^1$ to $2s^2 2p^6$ | 8 |
| 3 | $3s^1$ to $3s^2 3p^6$ | 8 |
| 4 | $4s^1$ to $3d^{10} 4s^2 4p^6$ | 18 |
| 5 | $5s^1$ to $4d^{10} 5s^2 5p^6$ | 18 |
| 6 | $6s^1$ to $4f^{14} 5d^{10} 6s^2 6p^6$ | 32 |

| Modern Period Table | IUPAC Table |
|--|---|
| Sub-group B = when valence orbitals are (n-1)d ns. | d-block, group = total valence electrons. |
| Period: Equals highest orbit number present in electron configuration of atom of the element | Same as in modern periodic table. |

Note:

- The f-block elements are placed in group 3rd (modern and IUPAC table both)
Lanthanides in 6th period and actinides in 7th period.

Relationships in the Periodic Table**(1) Group relation**

Elements of a group are similar.

Group1 \longrightarrow Li Na K Rb Cs

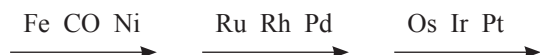
Group2 \longrightarrow Be Mg Ca Sr Ba etc., are similar. However, first elements of each main group (i.e., s and p-block) differ from rest of the group members, Example, Li, Be, B, C, N, O, and F differ from their higher group members respectively.

Li differ from Na, Be from Mg, etc. This difference is due to:

- Small size (of the first member)
- High electronegativity (of the first member)
- Non-availability of d orbitals in the valence shell of these elements i.e., 2nd period elements).
Valence orbitals are s and p only.

(2) Horizontal relationship

- Elements of Group VIII (or 8, 9 and 10 of IUPAC table) have horizontal similarity



- Transition elements form a horizontal series.
Ti, V, Cr, Mn, Fe, Co, Ni, etc and are similar
- Lanthanides i.e., elements from Ce to Lu, are similar in many ways.

(3) Diagonal relationship

Some elements placed diagonally in the table are similar.

Table 1.4

| Gr \rightarrow | 1(I _A) | 2(II _A) | 3(III _A) | 4(IV _A) |
|------------------|--------------------|---------------------|----------------------|---------------------|
| Elements | Li | Be | B | C |
| | Na | Mg | Al | Si |

Li is similar to Mg, Be to Al and B to Si. It is known as diagonal relationship.
Diagonal similarity is due – either

- To similar ionic radii
 $\text{Li}^+ = 0.76\text{\AA}$, $\text{Mg}^{2+} = 0.72\text{\AA}$
- or to similar ionic potential

Ionic pot. = Charge/ionic radius

$\text{Be}^{2+} = 6.6$, $\text{Al}^{+3} = 6.0$

Classification of Elements

Different concepts can be applied for classification of elements. Example, properties, electron configuration, physical state of elements, atomicity etc.

(A) Properties and Type of Elements

Elements are of the following four types:

(I) Normal or Representative Elements

Elements belonging to groups I_A to VII_A of the modern periodic table. (or 1, 2, and 13 to 17 of IUPAC table) are called 'Normal Elements'. Some of the groups have got special names.

Note:

- (i) Alkali metals because oxides and hydroxides are basic and water soluble.
- (ii) Alkaline earth because oxides and hydroxides are partially soluble like earth (soil).
- (iii) Pnictogens because some compounds have very bad odour.
- (iv) Chalcogens because they form ores.
- (v) Halogens because they form salt like compounds.

Table 1.5

| Group | Name | Electron-configuration |
|-------|-----------------------|------------------------|
| IA | Alkali metals | ns^1 |
| IIA | Alkaline earth metals | ns^2 |
| IIIA | No special name | ns^2np^1 |
| IVA | No special name | ns^2np^2 |
| VA | Pnictogens | ns^2np^3 |
| VIA | Chalcogens | ns^2np^4 |
| VIIA | Halogens | ns^2np^5 |

(II) Noble gases

Elements of zero group (or 18th group of IUPAC) are known as "Noble Gases". They are also called 'Rare Gases' or 'Inert Gases'. The gases are ${}_{(2)}\text{He}$, ${}_{(10)}\text{Ne}$, ${}_{(18)}\text{Ar}$, ${}_{(36)}\text{Kr}$, ${}_{(54)}\text{Xe}$ and ${}_{(86)}\text{Rn}$. These elements have their outermost orbitals full filled.

He $1s^2$, Ne to Rn – ns^2np^6 .

(III) Transition Elements

Elements having partially filled $(n-1)$ d orbitals in their atoms or ions are known as 'Transition Elements'.

General electron configuration $(n-1)d^xns^2$ or $(n-1)d^xns^1$ [$x = 1$ to 10].

There are four such series in the table:

All these elements are metals. The only member liquid is Hg, rest are solids. They have many common characteristics (Cf Tr elements).

Table 1.6

| Series | Elements | No. of Elements |
|-----------------|---|-----------------|
| 1st series (3d) | ${}_{21}\text{Sc}$ to ${}_{30}\text{Zn}$ | 10 |
| 2nd series (4d) | ${}_{39}\text{Y}$ to ${}_{48}\text{Cd}$ | 10 |
| 3rd series (5d) | ${}_{57}\text{La}$, ${}_{72}\text{Hf}$ to ${}_{80}\text{Hg}$ | 10 |
| 4th series (6d) | ${}_{89}\text{Ac}$, ${}_{104}\text{Rf}$ to ${}_{111}\text{Rg}$ [incomplete] | 7 |

(IV) Inner Transition Elements

Elements which have incompletely filled $(n-2)f$ and $(n-1)d$ are called 'Inner Transition Elements'.

General e-configuration – $(n-2)f^x (n-1)d^1 ns^2$, $x = 1$ to 14

However, there is variation in the electron configuration of these elements (it will be discussed in Lanthanides).

There are two such series in the table, corresponding to filling of 4f and 5f orbitals.

Lanthanides (4f) (La) $_{58}\text{Ce}$ to $_{71}\text{Lu}$

Actinides (5f) (Ac) $_{90}\text{Th}$ to $_{103}\text{Lw}$

Elements after $U_{(92)}$ are synthetic and known as 'Transuranic Elements'.

(B) Electron-Configuration and Type of Elements**(I) s-block elements**

When last electron of the configuration is added to s - orbital, the element belongs to s-block.

Gr 1 (ns^1) Li Na K Rb Cs Fr and Gr 2 (ns^2) Be Mg Ca Sr Ba Ra elements are s-block elements. These elements are most electropositive and highly reactive.

(II) p-block elements

In these elements last electron is added to a p-orbital. This block has variety of elements.

Table 1.7

| ns^2np^1 III _A (13) | ns^2np^2 IV _A (14) | ns^2np^3 V _A (15) | ns^2np^4 VI _A (16) | ns^2np^5 VII _A (17) | ns^2np^6 Zero (18) |
|-------------------------------------|------------------------------------|-----------------------------------|------------------------------------|-------------------------------------|-------------------------|
| | | | | | He |
| B | C | N | O | F | Ne |
| Al | Si | P | S | Cl | Ar |
| Ga | Ge | As | Se | Br | Kr |
| In | Sn | Sb | Te | I | Xe |
| Tl | Pb | Bi | Po | At | Rn |

- Elements below the line joining B to At are metals, (Al to Tl; Sn and Pb and Bi; and Po).
- Elements above the line joining B to At are non-metals (B, C, N., O, F, P, S, Cl, Br, I).
- Elements falling on the line or very near to it are metalloids (Si, Ge, As, Sb, Se, Te).
- Noble gases are also taken as non-metals.

(III) d-block elements

The last electron in the configuration is filled in $(n-1)d$ orbitals.

General configuration – $(n-1)d^x ns^2$ or $(n-1)d^x ns^1$ [$x = 1$ to 10].

There are four such series in the periodic talbe (3d, 4d, 5d and 6d); i.e., transition elements are d-block elements. These elements have common properties (details in the chapter general properties of transition elements).

Periodic table

| <div>1</div> <div>H</div> <div>1.008</div> | | | | | | | | | | | | | | | | | | <div>Atomic number, Z</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|----|--------|----|----|--------|-------|----|-------|-----|----|--------|-----|----|--------|-----|----|--------|--|----|--------|-----|----|--------|-----|----|--------|-----|----|--------|-----|----|--------|--------------|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|----|----|--------|
| <div>2</div> <div>He</div> <div>4.00</div> | | | | | | | | | | | | | | | | | | <div>Element symbol</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>3</div> <div>Li</div> <div>6.94</div> | | | | | | | | | | | | | | | | | | <div>Relative atomic mass, A_r</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>4</div> <div>Be</div> <div>9.01</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>11</div> <div>Na</div> <div>22.99</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>12</div> <div>Mg</div> <div>24.31</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>3</div> <div>4</div> <div>5</div> <div>6</div> <div>7</div> <div>8</div> <div>9</div> <div>10</div> <div>11</div> <div>12</div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 19 | K | 39.10 | 20 | Ca | 40.08 | 21 | Sc | 44.96 | 22 | Ti | 47.90 | 23 | V | 50.94 | 24 | Cr | 52.01 | 25 | Mn | 54.94 | 26 | Fe | 55.85 | 27 | Co | 58.93 | 28 | Ni | 58.69 | 29 | Cu | 63.54 | 30 | Zn | 65.41 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 37 | Rb | 85.47 | 38 | Sr | 87.62 | 39 | Y | 88.91 | 40 | Zr | 91.22 | 41 | Nb | 92.91 | 42 | Mo | 95.94 | 43 | Tc | 98.91 | 44 | Ru | 101.07 | 45 | Rh | 102.91 | 46 | Pd | 106.42 | 47 | Ag | 107.87 | 48 | Cd | 112.40 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 55 | Cs | 132.91 | 56 | Ba | 137.34 | La–Lu | | | 72 | Hf | 178.49 | 73 | Ta | 180.95 | 74 | W | 183.85 | 75 | Re | 186.21 | 76 | Os | 190.23 | 77 | Ir | 192.22 | 78 | Pt | 195.08 | 79 | Au | 196.97 | 80 | Hg | 200.59 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 87 | Fr | 223 | 88 | Ra | 226.03 | Ac–Lr | | | 104 | Rf | [261] | 105 | Db | [262] | 106 | Sg | [266] | 107 | Bh | [264] | 108 | Hs | [277] | 109 | Mt | [268] | 110 | Ds | [271] | 111 | Rg | [272] | Uub [285] | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <div>Lanthanoids</div> | | | | | | | | | | | | | | | | | | 57 | La | 138.91 | 58 | Ce | 140.12 | 59 | Pr | 140.91 | 60 | Nd | 144.24 | 61 | Pm | 146.92 | 62 | Sm | 150.36 | 63 | Eu | 151.96 | 64 | Gd | 157.25 | 65 | Tb | 158.92 | 66 | Dy | 162.50 | 67 | Ho | 164.93 | 68 | Er | 167.26 | 69 | Tm | 168.93 | 70 | Yb | 173.04 | 71 | Lu | 174.97 |
| | | | | | | | | | | | | | | | | | | <div>Actinoids</div> | | | | | | | | | | | | | | | | | | 89 | Ac | 227.03 | 90 | Th | 232.04 | 91 | Pa | 231.04 | 92 | U | 238.03 | 93 | Np | 237.05 | 94 | Pu | 239.05 | 95 | Am | 241.06 | 96 | Cm | 244.07 | 97 | Bk | 249.08 |

(IV) f-block elements

The last electron in the configuration is added to $(n-2)f$ orbitals.

General configuration – $(n-1)f^x (n-1)d^1ns^2$ [$x = 1$ to 14].

Lanthanides and Actinides are f-block elements. All elements are metals. All elements of actinide series are radioactive. Elements after U (92) are synthetic. These are gr III_B (3 of IUPAC) elements of the table. However, to keep the symmetry of the table scientific, the elements are placed at the bottom of the table.

Atomicity and Elements of the Periodic Table**Monoatomic Elements**

Noble gases He, Ne, Ar, Kr, Xe and Rn, are monoatomic in their standard state. It is because noble gases have closed shell electron configuration ($1s^2$ or ns^2np^6), and are not in a position to form bond with each other. However, in excited states species like He^+_2 can exist, such species are known as “Exonomers”. In the vapour state, Hg ($5d^{10} 6s^2$) is also monoatomic.

Diatomic molecules: ($H_2, D_2, HD, HT, DT, T_2, N_2, O_2, F_2, C_2, Br_2, I_2$).

Diatomicity is also related with electron configuration. Hydrogen and halogens achieve stable electron – configuration by forming a single electron – pair bond in a diatomic molecule. For Nitrogen ($2s^2 2p^3$) and Oxygen ($2s^2 2p^4$), multiple bonding gives stable e – configuration, so diatomicity, i.e., H_2, X_2, N_2, O_2 .

Phosphorus and Sulphur also form P_2 and S_2 at high temperature but not at $25^\circ C$.

Discrete Polyatomic molecules: (P_4, S_8, Se_8 etc.)

Dinitrogen (N_2) and dioxygen (O_2) are stable due to very effective π bonding involving p – orbitals i.e., (p – p) π bonding. For the third period elements (p – p) π bonding is not effective due to larger size of p – orbitals of P, S etc., and more core electrons (8 es).

Therefore, these elements, instead, form discrete polyatomic molecules like P_4, S_8 . White phosphorus P_4 is tetrahedral. Each ‘P’ forms three bonds, with the P – P distance 2.21 \AA and P – P – P angles 60° .

This small angle is associated with considerable strain in the ring structure. Therefore, white phosphorus is highly reactive. Arsenic and antimony are As_4 and Sb_4 .

The most common form of S is S_8 . The S_8 has crown ring structure, (given below) such rings are stacked over each other in the solid structure S is sp^3 in the S_8 ring and the angle SSS is around 108° . Selenium is Se_8 like S_8 .

Carbon also form polyatomic molecules, C_{60} called “Fullerenes”. The C_{60} has soccer ball structure (details in allotropy).

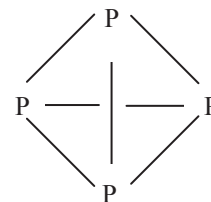


Figure 1.1

Giant molecules

Elements which can form 2, 3, 4 etc covalent bonds can also form giant (or macromolecular) species. Thus p – block elements have this property like B, C, P, S etc. have this properties.

B is inert and has very high m. p. It is due to the fact that boron exists as B_{12} , icosahedral structure.

Other macromolecular species include

- (i) Diamond,
- (ii) Graphite,

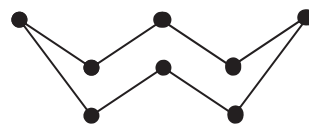


Figure 1.2

- (iii) SiC,
- (iv) Black phosphorus,
- (v) Catena sulphur, chain form of sulphur. It is present in plastic sulphur.

Periodicity in the Periodic Table

Effective Nuclear Charge

In a multielectronic atom electrons of the inner shells put a screen of negative charge on the nucleus. Therefore, outer electrons experience lesser attractive effect of nucleus. The actual nuclear charge an outer electron experiences is called 'Effective Nuclear Charge' (Z^*).

It is given as, $Z^* = Z - \sigma$, where Z = atomic number, σ = screening (or shielding) constant.

Thus, if σ is known, Z^* can be calculated. It is calculated using Slater's rule. The rules are:

- (i) Orbitals are grouped in the following way
(1s) (2s,2p) (3s3p) (3d) (4s4p) etc.
- (ii) $\sigma = 0$, for e in question (i.e., e of nth orbit) or electrons in the higher group (i.e., $n + 1$)
- (iii) $\sigma = 0.35$ per electron for rest of the group electrons.
- (iv) $\sigma = 0.3$, for a 1s electron screening another 1s electron.
- (v) $\sigma = 0.85$ per electron for all electrons in $(n - 1)$ th group.
- (vi) $\sigma = 1$, per electron for all electrons in $(n - 2)$ or lower groups.
- (vii) In case of electron being shielded of nd or nf, all electrons lying to the left of nd or nf gr, $\sigma = 1$ per electron.

The above rules are summarized in the table below:

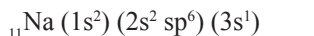
Table 1.8

| Electron group | All higher groups | Same group | Group with $(n - 1)$ | Group with $(n - 2)$ |
|----------------|-------------------|------------|----------------------|----------------------|
| 1s | 0 | 0.30 | 0 | 0 |
| ns, np | 0 | 0.35 | 0.85 | 1.00 |
| nd, nf | 0 | 0.35 | 1.00 | 1.00 |

The screening power of different orbitals follows the order: $s > p > d > f$

Examples

- (a) Z^* for valence electron of Na



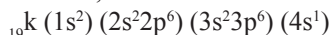
$$\sigma = 1 \times 2 + 0.85 \times 8 + 0.35 \times 0$$

$$= 2 + 6.8 + 0$$

$$= 8.8$$

$$Z^* = 11.0 - 8.8 = 2.2$$

- (b) Z^* for k, valence electron



$$\sigma = 1 \times 10 + 0.85 \times 8 + 0.35 \times 0$$

$$= 10 + 6.8 + 0$$

$$= 16.8$$

$$Z^* = 19.0 - 16.8 = 2.2$$

- (c) Li Z^*



$$\sigma = 0.85 \times 2 + 0.35 \times 0$$

$$= 1.70 + 0$$

$$= 1.7$$

$$Z^* = 3.0 - 1.7 = 1.3$$

- (d) Z^* Be



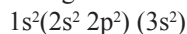
$$\sigma = 0.85 \times 2 + 0.35 \times 1$$

$$= 2.05$$

$$Z^* = 4.00 - 2.05$$

$$= 1.95$$

- (e) Z^* Mg



$$\begin{aligned}\sigma &= 1 \times 2 + 0.85 \times 8 + 0.35 \times 1 \\ &= 2 + 6.8 + 0.35 \\ &= 9.15 \\ Z^* &= 12.00 - 9.15 \\ &= 2.85\end{aligned}$$

$$\begin{aligned}\text{(f) } Z^* \text{ for 10th d – electron of Zn}_{(30)} \\ {}_{30}\text{Zn} = 1s^2 (2s^2 2p^6) (3s^2 3p^6) 3d^{10} 4s^2 \\ \sigma = 1 \times 18 + 0.35 \times 9 + 2 \times 0 \\ = 18 + 3.15 \\ = 21.15 \\ Z^* = 30.00 - 21.15 \\ = 8.85\end{aligned}$$

Variation of Z^* in the Periodic Table

- (i) Z^* remains constant in a group (except the first member)

| | | | | |
|-----------|-----|-----|-----|-----|
| Li | Na | K | Rb | Cs |
| $Z^* 1.3$ | 2.2 | 2.2 | 2.2 | 2.2 |

- (ii) Z^* increases in a period from left to right

| | | | | | | |
|-----------------------|------|-----|------|-----|------|-----|
| Li | Be | B | C | N | O | F |
| $Z^* \rightarrow 1.3$ | 1.95 | 2.6 | 3.25 | 3.9 | 4.55 | 5.2 |

Atomic and Ionic Size

Wave mechanical model of atom shows that a precise boundary around an atom can not be drawn, because electron probability distribution never becomes exactly zero. Therefore, radius of an atom is difficult to determine. Radii of atoms are determined in different combined states and so defined as:

- (i) Covalent radius
- (ii) Van der Waal's radius
- (iii) Crystal radius

(i) Covalent Radius

Half of the bond length between two similar covalently bonded atoms is defined as covalent radius. It is based on the assumption that atoms are spherical. The Cl–Cl bond length is found 1.988 \AA , so covalent radius of chlorine is 0.99 \AA .

$$\text{Thus, } r_{\text{covalent}} = \text{Bond length}/2$$

$$\text{Bond length} = 1.988 \text{ \AA}$$

$$\text{Covalent radius} = 1.988/2 = 0.99 \text{ \AA}$$

In a similar way radii of other atoms are determined

Covalent radii are commonly referred to as atomic radii.

Elements may have multiple bonds and they are always shorter than the corresponding single bonds,

$$\text{C} - \text{C} (1.54 \text{ \AA}), \text{C} = \text{C} (1.33 \text{ \AA}), \text{C} \equiv \text{C} (1.2 \text{ \AA})$$

$$\text{N} - \text{N} (1.45 \text{ \AA}), \text{N} = \text{N} (1.25 \text{ \AA}), \text{N} \equiv \text{N} (1.10 \text{ \AA})$$

Therefore, double and triple bond radii are also defined (half the double bond length and triple bond length), e.g.,

$$\text{Double bond radius of C} = 1.33/2 = 0.665 \text{ \AA}$$

$$\text{Triple bond radius of N} = 1.10/2 = 0.55 \text{ \AA}$$

The double and triple bond radii of an atom are approximately 0.87 and 0.78 times the single bond radii, respectively.

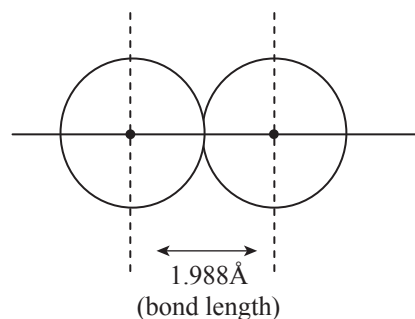


Figure 1.3

Table of Radii

Covalent radii of the elements (Å)

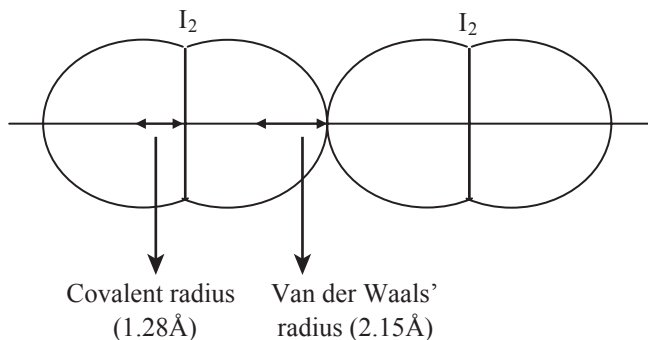
| Period | Group 1 | | | | | | | | | | | | | | | | | Group 13 | Group 14 | Group 15 | Group 16 | Group 17 | Group 18 | | |
|--------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|------------|------------|------------|-----------|-----------|------------|------------|--|
| 1 | H 0.37 | | | | | | | | | | | | | | | | | | | | | | He 1.4 | | |
| 2 | Li 1.34 | Be 1.25 | | | | | | | | | | | | | | | | | B 0.90 | C 0.77 | N 0.74 | O 0.74 | F 0.72 | Ne 1.54 | |
| 3 | Na 1.57 | Mg 1.45 | Group | | | | | | | | | | | | | | | | Al 1.25 | Si 1.17 | P 1.10 | S 1.04 | Cl 0.99 | Ar 1.92 | |
| 4 | K 2.03 | Ca 1.74 | Sc 1.44 | Ti 1.32 | V 1.22 | Cr 1.17 | Mn 1.17 | Fe 1.17 | Co 1.16 | Ni 1.15 | Cu 1.17 | Zn 1.25 | | | | | | | | | | | | | |
| 5 | Rb 2.16 | Sr 1.91 | Y 1.62 | Zr 1.45 | Nb 1.34 | Mo 1.29 | Te - | Ru 1.24 | Rh 1.25 | Pd 1.28 | Ag 1.34 | Cd 1.41 | In 1.50 | Sn 1.40 | Sb 1.41 | Te 1.37 | I 1.33 | Xe 2.18 | | | | | | | |
| 6 | Cs 2.35 | Ba 1.98 | La 1.68 | Hf 1.44 | Ta 1.34 | W 1.30 | Re 1.28 | Os 1.26 | Ir 1.26 | Pt 1.29 | Au 1.34 | Hg 1.44 | Tl 1.55 | Pb 1.46 | Bi 1.52 | Po - | At - | Rn - | | | | | | | |
| 7 | Fr | Ra | Ac | | | | | | | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|------------|------------|------------|------------|---------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Lanthanide | Ce 1.65 | Pr 1.64 | Nd 1.64 | Pm - | Sm 1.66 | Eu 1.85 | Gd 1.61 | Tb 1.59 | Dy 1.59 | Ho 1.58 | Er 1.57 | Tm 1.56 | Yb 1.70 | Lu 1.56 |
|------------|------------|------------|------------|---------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|

*Radii of group 18 elements is Van der Waals' radii.

Van der Waal's Radii

Let us first consider solid iodine. When I_2 molecules pack together, their approach to one another is limited due to short range repulsive forces which result due to interaction of the electron clouds around the atoms. In this situation radius of an atom is defined as 'Van der Waals radius'. It is defined as half the distance between nearest neighbour atoms in different molecules.

Covalent and Van der Waals' radii for iodine**Figure 1.4**

Van der waals radius is, thus, larger than covalent radius for an atom.

Van der Waals radii of some atoms (Å)

| | | | | | | | |
|----|-----------|----|------|----|------|----|------|
| H | 1.1 – 1.3 | O | 1.40 | F | 1.35 | He | 1.40 |
| N | 1.5 | S | 1.85 | Cl | Ne | Ne | 1.54 |
| P | 1.9 | Se | 2.00 | Br | 1.95 | Ar | 1.92 |
| As | 2.0 | Te | 2.20 | I | 2.15 | Kr | 1.98 |
| Sb | 2.2 | | | | | Xe | 2.18 |

Van der Waals radii are roughly similar for isoelectronic species. Thus in crystalline Br_2 Van der Waals' radius is 1.95Å which is almost equal to Van der radius of solid Kr, 1.98Å . It is because when Br is bonded to any other atom is isoelectronic to Kr atom.

Crystal Radii or Metallic Radii

Metals have crystal structure. Crystal constituents are metal atoms. The half the distance between the nuclei of two adjacent atoms is defined as crystal radius of the atom.

Covalent, Van der waals and crystal radii for the same atom differ. Example,

| | | |
|----|-----------------|----------------|
| | Covalent Radius | Crystal Radius |
| Na | 1.54Å | 1.6Å |

Variation of Atomic Radii in the Periodic Table

Atomic radii (covalent or crystal or van der Waal's) is controlled by orbit number (i.e., energy level) and Z^* .

Group Elements and Atomic Radii

Atomic radii increase in a group from top to bottom. It is due to the following facts.

- Higher orbits are added with increase in atomic number i.e., on going down the group.
- Z^* remains constant.

Table 1.9

| Elements | Li | Na | K | Rb | Cs |
|-----------------------------------|--------|--------|--------|--------|--------|
| Highest orbit number i.e., period | 2 | 3 | 4 | 5 | 6 |
| Configuration | $2s^1$ | $3s^1$ | $4s^1$ | $5s^1$ | $6s^1$ |
| Z^* | 1.3 | 2.2 | 2.2 | 2.2 | 2.2 |
| Radii (Å) | 1.34 | 1.54 | 2.03 | 2.16 | 2.35 |
| ————— Increases —————→ | | | | | |

Period Elements and Atomic Radii

Atomic radii decrease in a period from left to right. The reasons are –

- No new orbit is added with increase in atomic number.
- Z^* increases from left to right. Therefore, nucleus has greater attractive effect on outer electrons resulting into decrease in radii.

Table 1.10

| | Li | Be | B | C | N | O | F |
|------------------------|--------|--------|-------------|-------------|-------------|-------------|-------------|
| Configuration | $2s^1$ | $2s^2$ | $2s^2 2p^1$ | $2s^2 2p^2$ | $2s^2 2p^3$ | $2s^2 2p^4$ | $2s^2 2p^5$ |
| Orbit number | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Z^* | 1.3 | 1.95 | 2.6 | 3.25 | 3.9 | 4.55 | 5.2 |
| Radii (Å) | 1.34 | 1.25 | 0.90 | 0.77 | 0.74 | 0.73 | 0.71 |
| ————— Decreases —————→ | | | | | | | |

Exceptions

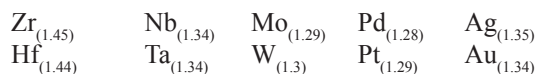
At several points in the periodic table the above trends are not followed. Those are –

- Radii of Al and Ga are similar (1.25 Å). It is due to presence of ten transition elements between Al and Ga. In transition elements $(n-1)d$ orbitals are filled. The screening power of d orbitals is very low (screening power $s > p > d > f$).
Therefore, the nucleus has stronger attractive effect on outer electrons (electrons of Ga), reducing its size. It may be called d – orbital contraction.
- Atomic radii of Zr and Hf are almost equal (~ 1.44 Å). It is due to lanthanide contraction.
- Variation of radii among transition series is small due to filling of electrons in inner orbitals, $(n-1)d$.

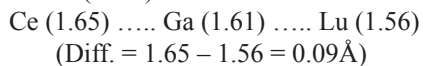
Table 1.11

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---------|------|------|------|------|------|------|------|------|------|------|
| r (Å) | 1.44 | 1.32 | 1.22 | 1.17 | 1.17 | 1.77 | 1.16 | 1.15 | 1.17 | 1.25 |

- (iv) Radii of 3rd transition series elements are almost equal to 2nd transition series elements due to lanthanide contraction.



- (v) Change in the radii of lanthanides is very small. It is due to the fact that electrons are filled in deep seated $(n-2)f$ orbitals and f orbitals are least screening.



Ionic radii

Cations

Cations are produced when atoms lose electrons



In a cation number of protons is greater than electrons. The Z^* of cation is also greater than neutral atom. Therefore, remaining electrons are attracted more towards the nucleus and the size of a cation is smaller than its corresponding atoms.

Table 1.12

| | Na | Na ⁺ |
|------------------|------|-----------------|
| es | 11 | 10 |
| ps | 11 | 11 |
| Z^* | 2.2 | 6.85 |
| $r (\text{\AA})$ | 1.57 | 0.95 |

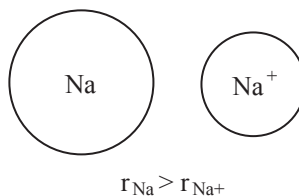
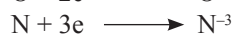
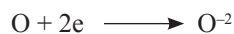


Figure 1.5

Anions

When electrons are added to an atom, anion is produced.



In an anion number of electrons is larger than protons. In addition to this Z^* of an anion is smaller than its neutral atom. Therefore, nucleus exerts lesser attractive force on outer electrons and size of an anion is larger than the neutral atom.

Table 1.13

| | F | F ⁻ |
|------------------|------|----------------|
| es | 9 | 10 |
| ps | 9 | 9 |
| Z^* | 5.2 | 4.85 |
| $r (\text{\AA})$ | 0.71 | 1.35 |

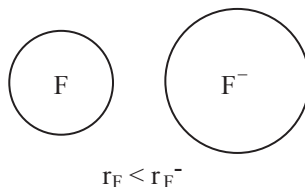
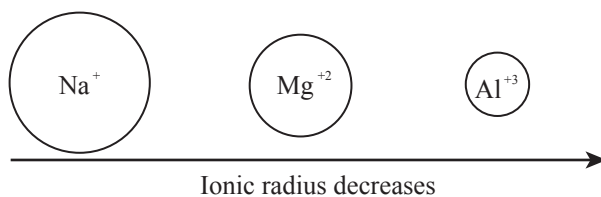


Figure 1.6

Important Conclusions

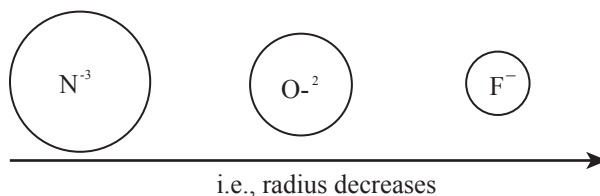
- (i) Among isoelectronic cations the cation which has highest charge is smallest in size,
 $\text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}$ (10 es)

$$r_{\text{Na}^+} > r_{\text{Mg}^{2+}} > r_{\text{Al}^{3+}}$$

**Figure 1.7**

- (ii) Among isoelectronic anions, the anion which has highest charge is largest in size.

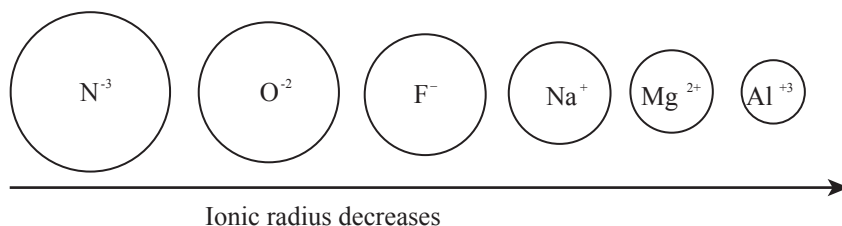
| | | | | |
|---------|-----------------|-----------------|--------------|--------|
| Anions | N^{3-} | O^{2-} | F^- | (10es) |
| r (Å) | 1.71 | 1.4 | 1.35 | |

**Figure 1.8**

- (iii) Among isoelectronic cation and anion both, radii decreases with increase in nuclear charge.

Table 1.14

| 10es | N^{3-} | O^{2-} | F^- | Na^+ | Mg^{+2} | Al^{+3} |
|---------|-----------------|-----------------|--------------|---------------|------------------|------------------|
| Protons | 7 | 8 | 9 | 11 | 12 | 13 |
| r (Å) | 1.71 | 1.4 | 1.35 | 1.02 | 0.72 | 0.53 |

**Figure 1.9**

Ionic radii are calculated using internuclear distance between positive and negative ions in an ionic crystal.

Pauling's Method

This method considers isoelectronic cation and anion (Na^+ & F^- , 10es). Pauling proposed that the ratio of the ionic radii should be inversely proportional to the ratio of effective nuclear charge, i.e.

$$r_{\text{Na}^+} / r_{\text{F}^-} = 4.85/6.85 [Z_{\text{Na}}^* = 6.85, Z_{\text{F}}^* = 4.85]$$

The interionic distance between NaF, from X-ray diffraction, is 2.31 \AA ,

$$\text{i.e., } r_{\text{Na}^+} + r_{\text{F}^-} = 2.31$$

From the above equation, $r_{\text{F}^-} = 1.35 \text{ \AA}$ and $r_{\text{Na}^+} = 0.96 \text{ \AA}$

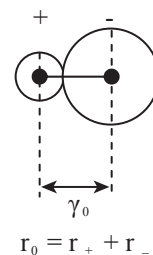


Figure 1.10

Variation of Ionic Radii in the Periodic Table

Like atomic radii. Ionic radii follow the same trend in the periodic table. Important points –

- (i) Ionic radii increase in a group from top to bottom,
- (ii) Ionic radii decrease in a period from left to right.

Exceptions

- (a) Ionic radii of Al^{+3} and Ga^{+3} are similar (d orbital effect).
- (b) Ionic radii of Zr^{+4} and Hf^{+4} are almost equal (lanthanide contraction effect),
- (c) Variation of ionic radii in transition series elements is small.,
- (d) Radii of tripositive (M^{+3}) lanthanide ions decrease regularly along the series.

Table 1.15 Some ionic radii (\AA)

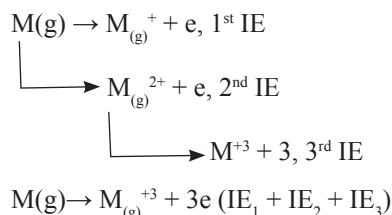
| Ion | Radii | Ion | Radii | Ion | Radii | Ion | Radii | Ion | Radii |
|------------------|-------|------------------|-------|------------------|-------|------------------|-------|-----------------|-------|
| Li^+ | 0.76 | Be^{+2} | 0.45 | Mn^{+2} | 0.83 | H^- | 2.08 | N^{-3} | 1.71 |
| Na^+ | 1.02 | Mg^{+2} | 0.72 | Fe^{+2} | 0.78 | F^- | 1.35 | P^{-3} | 2.12 |
| K^+ | 1.38 | Ca^{+2} | 0.99 | Co^{+2} | 0.65 | Cl^- | 1.81 | | |
| Rb^+ | 1.52 | Sr^{+2} | 1.18 | Ni^{+2} | 0.69 | Br^- | 1.95 | | |
| Cs^+ | 1.69 | Ba^{+2} | 1.35 | Cu^{+2} | 0.72 | I^- | 2.16 | | |
| Cu^+ | 0.77 | Zn^{+2} | 0.74 | Fe^{+3} | 0.64 | O^{2-} | 1.40 | | |
| Ag^+ | 1.15 | Cd^{+2} | 0.97 | Ti^{+4} | 0.61 | S^{2-} | 1.84 | | |
| Au^+ | 1.37 | Pb^{+2} | 1.20 | Sn^{+4} | 0.71 | Te^{2-} | 2.21 | | |
| Tl^+ | 1.49 | Hg^{+2} | 1.10 | Ce^{+4} | 0.87 | Se^{2-} | 1.98 | | |
| Au^{3+} | 0.85 | Sn^{+2} | 1.10 | Pb^{+4} | 0.78 | | | | |

Ionization Energy (or Potential) (IE OR IP)

The amount of energy needed to remove an electron from a free gaseous atom is known as “Ionization energy”.



It is, thus, an endothermic process. If only one electron is removed from the neutral gaseous atom, the energy needed is called “first IE”. If the electron is removed from $\text{M}_{(\text{g})}^+$, it is called “second IE” and so on.



Ionization energy is an experimental quantity. It is obtained either from the spectra of the gaseous species or by discharge tube experiment technique. For all elements, successive values of IE increases i.e.,

$$\text{IE}_1 < \text{IE}_2 < \text{IE}_3 < \text{IE}_4 \dots \dots \dots \text{etc.}$$

It is due to the fact that the removal of each electron decreases number of electrons consequently effective nuclear charge (Z^*) increases, therefore, nuclear attraction on remaining electrons increases successively resulting into increase in IE.

Table 1.16

| | Al | Al ⁺ | Al ⁺² | Al ⁺³ |
|-----------|-----|-----------------|------------------|------------------|
| Electrons | 13 | 12 | 11 | 10 |
| Z^* | 3.5 | 3.85 | 4.20 | 8.85 |

Ionization energy depends on many factors, viz

- Atomic size i.e., distance between the electron and the nucleus,
- Effective nuclear charge (Z^*),
- Nature of orbital from which electron is removed,
- Stability of electron configuration.

Variation of Ionization Energy in the Periodic Table

(1) IE and group elements

Ionization energy decreases in a group from top to bottom. In a group, with increase in atomic number, the distance between the electron being removed and nucleus increases due to addition of higher electronic orbits in the configuration. Therefore, attractive forces between the electron and the nucleus decreases (attractive force is inversely proportional to the square of the distance, $F \propto 1/r^2$, the inverse square law). It result into decrease in IE.

Table 1.17

| | Li | Na | K | Rb | Cs |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| V.Shell | 2s ¹ | 3s ¹ | 4s ¹ | 5s ¹ | 6s ¹ |
| IE (ev) | 5.39 | 5.14 | 4.34 | 4.18 | 3.89 |

Note:

Other controlling factors of IE are similar in a group

(2) Ionization Energy and Period Elements

Ionization energy does not change regularly in a period although it has a tendency to increase. It is because all factors controlling ionisation energy change in a period from left to right.

Table 1.18

| | Li | Be | B | C | N | O | F |
|-----------------|-----------------|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Configuration | 2s ¹ | 2s ² | 2s ² 2p ¹ | 2s ² 2p ² | 2s ² 2p ³ | 2s ² 2p ⁴ | 2s ² 2p ⁵ |
| Type of orbital | s | s | p | p | p | p | p |
| Radii (Å) | 1.34 | 1.25 | 0.90 | 0.77 | 0.74 | 0.73 | 0.71 |
| Z* | 1.30 | 1.95 | 2.6 | 3.25 | 3.90 | 4.55 | 5.20 |
| IE (ev) | 5.39 | 9.32 | 8.29 | 11.26 | 14.53 | 13.62 | 17.42 |

Important Facts**(a) First IE of Be is greater than the first IE of B**

The reason is difference in the nature of valence orbitals. The valence orbitals of Be is 2s² and that of B is 2s²2p¹. An s orbital is more penetrating and less shielded whereas a p – orbital is less penetrating and more shielded. Therefore, attractive effect is larger on s- electron than on p – electron. Beryllium, so has higher IE than B.

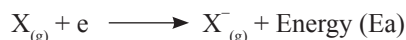
(b) The first IE of N is greater than Oxygen

In this case, the reason is difference in the stability of electron configuration. Nitrogen has full filled 2s orbital and half filled 2p orbitals i.e., both are extra stable. Oxygen has full filled 2s orbital but its p – orbitals are neither half nor full filled i.e., not extra stable. Therefore, removal of p – electron of oxygen is easy and its 1st IE is lower than N.

- (c) The first IE of Al and Ga are almost equal (reason, equal radii)
- (d) Variation of 1st IE along each transition series is small (reason, small difference in radii)
- (e) The first IE of third transition series elements is larger than second transition series elements (reason – lanthanide contraction)
- (f) The change in first IE for lanthanide elements is small (reasons, small change in the radii of lanthanide elements from Ce to Lu).

Electron Affinity (Ea)

The energy released when an electrons is added to an isolated neutral atom is called “Ea”. It corresponds to the reaction,



Energy in the above process is released due to attraction between the nucleus of X and the electron being added.

Electron affinity depends on atomic radius. When the atom is small the attraction between the nucleus of the atom and e is large and Ea is high. But in the case of large atoms the distance between the nucleus of the atom and electron is large, attraction is small and so Ea is also small.

Electron affinity can be measured by analysis of the ionization spectra of X[−].

The process of addition of electron may be endothermic



It is due to the fact that in the second step, the e has to be added to O^- , which naturally will repel the electron. Thus, the formation of N^{3-} , P^{3-} , S^{2-} etc., are all endothermic process.

Variation of Ea in the Periodic Table

(1) Ea and Gr elements

Ea depends on atomic radius. Smaller the radius of the atom larger the Ea and vice versa.

Atomic radius increases in a group from top to bottom. Therefore, Ea decreases in group from top to bottom.

(2) Ea and Period elements

Atomic radius decreases in a period from left to right. Therefore, Ea increases along a period from left to right.

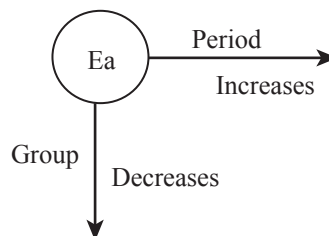


Figure 1.11

Table 1.19 Ionization Energies of the Atom of Selected Elements (eV)

| z | Elements | IE ₁ | IE ₂ | IE ₃ |
|----|----------|-----------------|-----------------|-----------------|
| 1 | H | 13.599 | — | — |
| 2 | He | 24.588 | — | — |
| 3 | Li | 5.392 | 75.641 | — |
| 4 | Be | 9.323 | 18.211 | — |
| 5 | B | 8.298 | 25.156 | 37.92 |
| 6 | C | 11.260 | 24.383 | 47.87 |
| 7 | N | 14.534 | 29.602 | 47.43 |
| 8 | O | 13.618 | 35.118 | 54.89 |
| 9 | F | 17.423 | 34.987 | — |
| 10 | Ne | 21.565 | — | — |
| 11 | Na | 5.139 | 47.304 | — |
| 12 | Mg | 7.646 | 15.035 | 80.12 |
| 13 | Al | 5.986 | 18.828 | 28.44 |
| 14 | Si | 8.152 | 16.342 | 33.46 |
| 15 | P | 10.487 | 19.73 | 30.16 |
| 16 | S | 10.360 | 23.35 | — |
| 17 | Cl | 12.968 | 23.80 | — |
| 18 | Ar | 15.760 | — | — |
| 19 | K | 4.341 | 31.820 | — |
| 20 | Ca | 6.113 | 11.871 | 51.21 |
| 21 | Sc | 6.562 | 12.80 | 24.75 |

(Continued)

| z | Elements | IE ₁ | IE ₂ | IE ₃ |
|----|----------|-----------------|-----------------|-----------------|
| 22 | Cr | 6.765 | 16.50 | 31.0 |
| 23 | Mn | 7.435 | 15.640 | 33.69 |
| 24 | Fe | 7.893 | 16.183 | 30.64 |
| 25 | Co | 7.87 | 17.06 | 33.49 |
| 26 | Ni | 7.635 | 18.15 | 35.16 |
| 27 | Cu | 7.726 | 20.292 | 36.83 |
| 28 | Zn | 9.394 | 17.964 | 39.70 |
| 29 | Ga | 6.09 | 20.514 | 30.70 |

Exceptions

- (i) The Ea of F is lower than Cl (although Cl is below F in 17th group).

Explanation

Fluorine is very small in size. Its electronic shell is compact. Therefore, there is large electron – electron repulsion between added electron and electrons of the F atom. Hence, F has low Ea. This large repulsion is observed in the expansion of the size of fluoride (F⁻) ion. $r_F = 0.71\text{\AA}$ and $r_{F^-} = 1.35\text{\AA}$ i.e., an increase of about 88%.

- (ii) Like F and Cl, the Ea of O is lower than S (the reason is the same).

Ea of Few Elements (ev)**Table 1.20**

| Elements | Ea | Elements | Ea | Elements | Ea |
|----------|-------|----------|------|----------|------|
| H | 0.756 | O | 1.47 | F | 3.45 |
| Li | 0.6 | S | 2.07 | Cl | 3.61 |
| K | 0.5 | Se | 2.01 | Br | 3.36 |
| Rb | 0.3 | | | I | 3.07 |

Electronegativity (χ , Chi)

The dipolemoment of HF (1.91) is greater than HCl (1.03). This shows that polarity in HF bond is larger than HCl bond (dipolemoment, $\mu = qxr$, q = charge at either end and r = bond length). That is F has higher tendency to attract bond pair electrons than Cl. This property of bonded atom was called electronegativity by L. Pauling. It may be defined as – “the tendency of an atom in a molecule to attract bond pair electrons towards itself is called electronegativity.

(1) Pauling's Method

This method uses bond energy to calculate electronegativity. The difference in electronegativity between tow atoms A and B is given as,

$$\chi_A - \chi_B = 0.102\sqrt{\Delta}$$

Where $\Delta = (\text{Bond energy of A-B}) - (\text{geometric mean of the bond energies A – A and B – B})$.

For example,

$$E_{\text{H-F}} = 566 \text{ kJ mol}^{-1}$$

$$E_{\text{H-H}} = 436 \text{ kJ mol}^{-1}$$

$$E_{\text{F-F}} = 158 \text{ kJ mol}^{-1}$$

$$\Delta = 566 - \sqrt{(158 \times 436)}$$

Therefore, if χ of one atom is known χ of the other can be evaluated. Pauling assigned an arbitrary value of 4.0 for χ of F and calculated χ of other atoms.

(2) Mulliken Method

This method utilizes IE and Ea to evaluate χ . The following equations can be used

$$\chi = \text{IE} + \text{Ea} / 5.6 \text{ (when IE and Ea are taken in eV)}$$

$$\chi = \text{IE} + \text{Ea} / 540 \text{ (when IE and Ea are taken kJmol}^{-1}\text{)}$$

Thus χ of an element in different oxidation states can be calculated. But as Ea of only a few elements are known the method has limited use.

(3) Allred and Rochow Scale

This method starts with the idea that an atom will attract electron in its valence shell according to Coulomb's law i.e.,

$$F = (Z^* \cdot e)e / r^2$$

Where F = force of attraction, Z^* = effective nuclear charge, e = electronic charge, r = covalent radius of the atom.

On the basis of the above concept an equation was developed to evaluate electronegativity. It is,

$$\chi = 0.359 Z^* / r^2 + 0.744$$

This method is simple and easy to operate as Z^* and r for many atoms are known.

χ of some elements

Table 1.21

| Li | Be | B | H | C | N | O | F |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.0 | 1.5 | 2.0 | 2.1 | 2.5 | 3.0 | 3.5 | 4.0 |
| Na | Mg | Al | | Si | P | S | Cl |
| 1.0 | 1.3 | 1.5 | | 1.8 | 2.1 | 2.5 | 2.9 |
| | | | | | | | Br |
| | | | | | | | 2.8 |
| | | | | | | | I |
| | | | | | | | 2.2 |

All the methods described above show that χ overall depends on atomic radii.

Variation of χ in the Periodic Table**(i) χ and group elements**

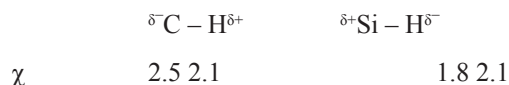
χ decreases in a group from top to bottom (reason is increase in atomic radii down the group).

(ii) χ and period elements

χ increases from left to right in a period. It is because atomic radii decrease across a period.

Important Points

- (a) F is most electronegative ($\chi_F = 4.0$) and Cs is least electronegative (0.7) elements.
- (b) Difference in electronegativity show bond polarity, negative end being more electronegative element



- (c) $\Delta\chi$ is useful in the explanation of hydrolysis of covalent molecules
- (d) χ can explain bond angle (VSEPR)
- (e) In the estimation of oxidation number of an atom
- (f) χ and dipole moment: (it is discussed in chemical bonding chapter)

Physical Properties and the Periodic Table

Physical properties such as melting point, boiling point, density, molar volume, depend on several factors. The main ones are—

- (a) Bonding in an element
- (b) Packing of the structural units
- (c) Physical state

Since the above factors do not change systematically along the group or the period, properties change abruptly.

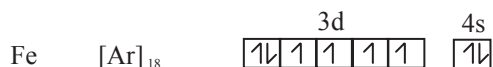
Melting and Boiling Points

The mp of a substance is the temperature at which solid and its liquid are in equilibrium at atmospheric pressure. It very much depends on structure and bonding.

Metals have lattice structure. Lattice contains metal ions and delocalized valence electrons. Thus, lattice stability and so mp increases with increase in the number of valence electrons and decrease in the size of the metal.

| | | | |
|----------|--|--------|-------------|
| | Na | Mg | Al |
| mp | 98 | 650 | 660 |
| V_{es} | $3s^1$ | $3s^2$ | $3s^2 3p^1$ |
| r | \longrightarrow decreases (valence es and size factor) | | |

In case of transition metals in addition to electrostatic force there are covalent bonds in the lattice due to unpaired electrons in their $(n-1)d$ orbitals.



This situation makes lattice more stable and mp is higher than non-transition metals.

Table 1.22

| Elements | K | Ca | Fe |
|----------|-----------------|-----------------|---------------------------------|
| Ves | 4s ¹ | 4s ² | 3d ⁶ 4s ¹ |
| mp (°C) | 64 | 842 | 1535 |

(Valence electron factor)

In the case of metals, most of the metallic bonding exists even in the liquid state. The metal atoms must be separated to a large distance in the forming the vapour. This requires complete breakage of the metal bonds. Therefore, bp of metals is much higher than their mp.

Table 1.23

| | Li | Ca | Sn | Fe | Ce |
|------|------|------|------|------|------|
| Mp°c | 179 | 851 | 232 | 1535 | 795 |
| Bp°c | 1337 | 1440 | 2623 | 2750 | 3257 |

(Metallic bonds in liquid state also)

Non-metals are either covalent solids (giant structures) or molecular solids. Non-metals having giant structure have high mp. The binding force in molecular solids is weak van der Waal's force. Therefore, such solids have low mp.

Table 1.24

| | Li | Be | B | C | N | O | F |
|---------|------------------------|------|----------------------|------|----------------------|--------|------|
| | ← Metallic structure → | | ← Giant structures → | | ← Discrete species → | | |
| mp (°c) | 179 | 1280 | 2000 | 3500 | -210 | -218.9 | -223 |
| bp (°c) | 1337 | 1500 | 3700 | 4200 | -195.8 | -182.9 | -187 |
| Trends | Increases abruptly | | | | Decreases abruptly | | |

Table 1.25

| | Na | Mg | Al | Si | P | S | Cl |
|--------|---------------------|------|------|----------------|----------------------|-------|-------|
| | ← nature metallic ↓ | | | ← Giant str. → | ← Discrete species ↓ | | |
| mp(°c) | 98 | 650 | 660 | 1420 | 44.1 | 119 | -102 |
| μo(°c) | 880 | 1100 | 2660 | 2600 | 280.0 | 444.6 | -34.6 |
| | Abrupt increase | | | | Abrupt decrease | | |

In p-block elements, there is change in the nature of elements, non-metal → metalloid → metal. This change is followed with change in structure and bonding. Therefore, melting point and boiling point also change abruptly.

Table 1.26

| Elements | C | Si Ge | | Sn Pb | |
|----------|-----------|-----------|------|--------|------|
| Nature | Non-metal | Metalloid | | Metals | |
| mp(°C) | 3500 | 1420 | 959 | 232 | 327 |
| bp (°C) | 4200 | 2600 | 2700 | 2623 | 1751 |

Halogens in gaseous state exist as X_2 (F_2 , Cl_2 , Br_2 , I_2). In the liquid and solid states X_2 molecules are joined by weak Van der waal's force. This force increases with increase in the number of electrons in the system. This is the reason that F_2 and Cl_2 are gas, bromine is liquid and iodine is solid. Therefore, melting point and boiling point increase down the group.

Table 1.27

| Molecules | F_2 | Cl_2 | Br_2 | I_2 | |
|----------------------|-------|--------|--------|-------|-----------|
| At No | 9 | 17 | 35 | 53 | |
| Electrons | → | | | | Increases |
| Van der waal's force | → | | | | Increases |
| Physical stats | Gas | Gas | Liquid | Solid | |
| mp (°C) | -223 | -102 | -7.3 | 114 | Increases |
| bp (°C) | -187 | -34.4 | 58.8 | 183 | Increases |

Density

Mass per unit volume is called "Density". It depends on atomic mass, atomic radius and crystal structure of the substance.

Across a period density increases and reaches a maximum for the central members. It is due to increase in atomic mass and decrease in atomic radius. However, for elements at the right hand side, density is low, in spite of having higher mass and lower atomic radii. It is because they form discrete molecules which are only weakly bonded by Van der waal's force.

Table 1.28

| Na | Mg | Al | Si | P | S | Cl |
|------|------|------|------|------------|------|------|
| 0.97 | 1.74 | 2.74 | 2.42 | 2.2 | 2.07 | 1.51 |
| K | Ca | Sc | Ti | V | Cr | Mn |
| 0.87 | 1.54 | 2.4 | 4.5 | 4.96 | 6.92 | 7.42 |
| Fe | Co | Ni | Cu | Zn | Ga | Ge |
| 7.8 | 8.9 | 8.9 | 8.93 | 7.15 | 5.91 | 5.47 |
| | | As | Se | Br(liquid) | | |
| | | 5.73 | 4.8 | 2.97 | | |

Atomic Volume

Atomic volume (or Molar Volume) is the volume occupied by one mole of an element (or the volume occupied by 6.02×10^{23} atoms of an element).

A plot of atomic volumes against atomic numbers

The above plot shows the following features:

- (d) The ascending portions are occupied by non-metals (electronegative elements)
- (e) The descending portions are occupied by metals (electropositive elements).

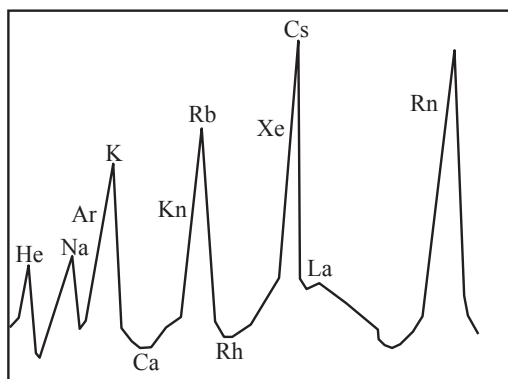


Figure 1.12

Overall observation in the change of atomic volume shows that it mainly depends on structure. For example, phosphorus has larger volume than Si although radius of Si is smaller than P. It is because Phosphorus contains weakly bonded P_4 whereas Si is strongly bonded macromolecule (diamond structures).

Metallic and Non-metallic Properties in the Periodic Table

Atomic properties such as IE, radii, electronegativity can be used to decide metallic and non-metallic nature of an element.

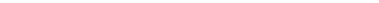
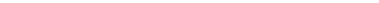
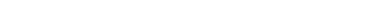
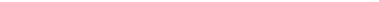
| Metals | | Non-metals | |
|---------------|-------|-------------------|-------|
| (i) r | large | (i) r | small |
| (ii) IE | low | (ii) IE | high |
| (iii) χ | low | (iii) χ | high |

It is clear from above facts that, large radius and low χ makes an element metal (metals are said electropositive) and small radius and high χ makes an element non-metal.

More and more the χ , more non-metallic the element and less and less the χ more metallic the element.

Therefore, (a) metallic nature increases and non-metallic nature decreases from top to bottom in a group. (b) metallic nature and non-metallic nature increases, from left to right in a period.

Group Elements

| | Li | Na | K | Rb | Cs | |
|---------------------|---|----|---|----|----|-----------|
| r |  | | | | | Increases |
| χ |  | | | | | Decreases |
| Metallic nature |  | | | | | Increases |
| Non-metallic nature |  | | | | | Decreases |

Period Elements

| | Li | Be | B | C | N | O | F | |
|---------------------|----|----|---|---|---|---|---|-----------|
| r | | | | | | | | Decreases |
| χ | | | | | | | | Increases |
| Metallic nature | | | | | | | | Decreases |
| Non-metallic nature | | | | | | | | Increases |

Oxidizing and Reducing Properties of the elements and the Periodic Table

Metals are reducing agents and non-metals are oxidizing agents (C, H are reducing also). Therefore, (a) increase in metallic nature or decrease in non-metallic nature leads to increase in reducing power (decrease in O. power), (b) decrease in metallic nature or increase in non-metallic nature leads to increase in oxidizing power (and decrease in R. power).

Period elements

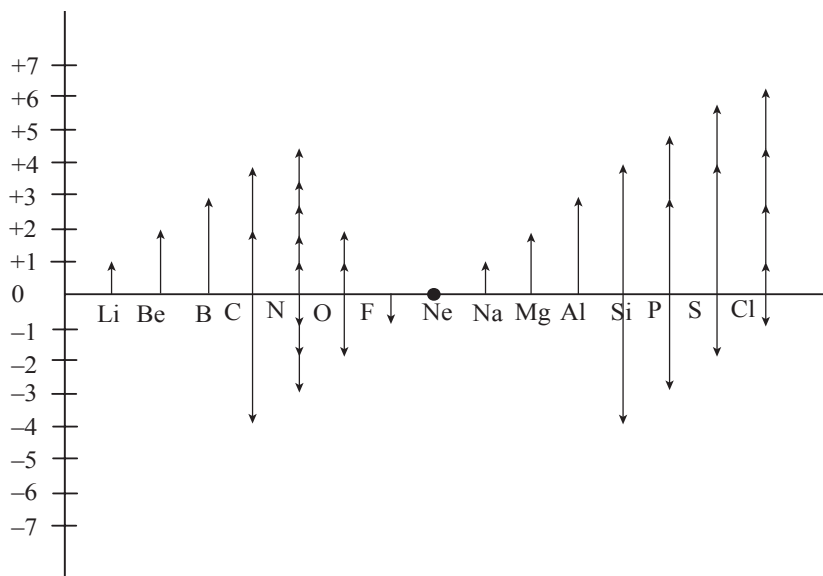
| | Li | Be | B | C | N | O | F | |
|---------------------|----|----|---|---|---|---|---|-----------|
| Metallic nature | → | → | → | → | → | → | → | Decreases |
| Non-metallic nature | → | → | → | → | → | → | → | Increases |
| R. power | → | → | → | → | → | → | → | Decreases |
| O. power | → | → | → | → | → | → | → | Increases |

Group Elements

| | F | Cl ₂ | Br ₂ | I ₂ | |
|---------------------|---|-----------------|-----------------|----------------|-----------|
| Metallic nature | → | → | → | → | Increases |
| Non-metallic nature | → | → | → | → | Decreases |
| O. power | → | → | → | → | Decreases |

Conclusions

- Oxidizing power increases in a period from L to R
- Reducing power increases in a group from top to bottom. (Li is also strong reducing agent).

Oxidation Numbers, its Patterns and Binary Compounds**Figure 1.13**

Every arrow head represent an oxidation number.

Formulas of Hydrides, Chlorides and Oxides**Table 1.29**

| Period 2 | Li | Be | B | C | N | O | F |
|-----------|-------------------|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------|-------------------------------|
| Hydrides | LiH | BeH ₂ | BH ₃ | CH ₄ | NH ₃ | H ₂ O | HF |
| Chlorides | LiCl | BeCl ₂ | BCl ₃ | CCl ₄ | NCl ₃ | Cl ₂ O | ClF |
| Oxides | Li ₂ O | BeO | B ₂ O ₃ | CO | N ₂ O | O ₂ | O ₂ F ₂ |
| | | | | CO ₂ | NO | | OF ₂ |
| | | | | C ₃ O ₂ | N ₂ O ₃ | | |
| | | | | | NO ₂ | | |
| | | | | | N ₂ O ₅ | | |

Table 1.30

| Period 3 | Na | Mg | Al | Si | P | S | Cl | Ar |
|-----------|-------------------|-------------------|---------------------------------|-------------------|--------------------------------|--------------------------------|--------------------------------|----|
| Hydrides | NaH | MgH ₂ | AlH ₃ | SiH ₄ | PH ₃ | H ₂ S | HCl | – |
| | | | | | PCl ₃ | SCl ₂ | | |
| Chlorides | NaCl | MgCl ₂ | Al ₂ Cl ₆ | SiCl ₄ | | | Cl ₂ | – |
| | | | | | PCl ₅ | S ₂ Cl ₂ | | |
| Oxides | Na ₂ O | MgO | Al ₂ O ₃ | SiO ₂ | P ₄ O ₆ | SO ₂ | Cl ₂ O | – |
| | | | | | P ₄ O ₁₀ | SO ₃ | Cl ₂ O ₇ | |

Pattern in the Properties of Oxides

Periodic pattern is seen in the structure, bonding and properties.

Oxides of second period elements**Table 1.31**

| Formula | Li ₂ O | BeO | B ₂ O ₃ | CO ₂ | N ₂ O, NO, N ₂ O ₃ , NO ₂ , N ₂ O ₅ | OF ₂ |
|---|-------------------|----------------|--------------------------------|---|--|-----------------------|
| State at 20°C | Solid | Solid | Solid | Gas | Gases (N ₂ O ₅ solid) | Gas |
| Structure | Giant structure | | Discrete molecular structure | | | |
| Conduction by liq. oxides | Good | Moderate | V. Poor | Nil | Nil | Nil |
| Enthalpy changes of formation at 25°C. (KJ/mol) | –596 | –611 | –1273 | –394 (CO ₂) | + 33 (NO ₂) | + 22 |
| Effect of adding water | LiOH | Does not react | H ₃ BO ₃ | H ₂ CO ₃ (not stable) | HNO ₂ HNO ₃ | O ₂ and HF |
| Nature of oxide | Basic (alkaline) | Amphot-eric | Acidic | | | |

Oxides of third period elements**Table 1.32**

| Formula | Na ₂ O | MgO | Al ₂ O ₃ | SiO ₂ | P ₄ O ₁₀ | SO ₃ | Cl ₂ O ₇ OCl ₂ |
|---------------------------------|-------------------|---|--------------------------------|------------------------------|---|-------------------------|--|
| State at 20°C | Solid | Solid | Solid | Solid | Solid | Liquid Gas | Liquid Gas |
| Structure | Giant structure | | | Discrete molecular structure | | | |
| Conduction | Good | Good | Good | V. Poor | Nil | Nil | Nil |
| ΔH _f at 25°C (KJmol) | – 416 | –602 | – 1676 | –910 | –2984 P ₄ O ₁₀ | –395 SO ₃ | +80 Cl ₂ O |
| Nature of oxide | Basic (alkaline) | Basic | Amphoteric | Acidic | | | |
| Effect of adding water | NaOH(aq) | Mg(OH ₂) Weakly alkaline | Amphoteric | Acidic | | | |

Chlorides of third period elements**Table 1.33**

| Formula | NaCl | MgCl ₂ | Al ₂ Cl ₆ | SiCl ₄ | PCl ₃ PCl ₅ | SCl ₂ |
|--------------------------------|-------------------------|-------------------|---------------------------------|------------------------------|--------------------------------------|------------------|
| State at 20°C | Solid | Solid | Solid | Liquid | Liquid (solid) | Liquid |
| Structure | Giant structure | | | Discrete molecular structure | | |
| Conduction by liquid chloride | Good | Good | V. Poor | Nil | Nil | Nil |
| ΔH _f at 25°C KJ/mol | –411 | –642 | –1408 | –640 | –320 | –60 |
| Effect of adding water | Solid dissolves readily | | | HCl fumes are produced | | |

Artificial elements

Enrico Fermi (1934), proposed that new elements could be made by bombarding the nucleus of an atom by neutrons. Segre (Italy), in 1936, bombarded Mo(atomic no. 42) by deuterons and obtained the first man – made element Technetium (Tc, atomic no. 43). The next man made element was a trans – uranium element 93. It was obtained by bombarding U (atomic no. 92) with neutrons. The element 93 was named Neptunium by the discoverers Abelson and Mcmillan (1940) at the University of California, Berkeley (USA).

During 1940 – 1950 many elements were made by G. T. Seaborg and Coworkers at Berkeley. They are Plutonium (Pu, 94), Americium (Am, 95), Californium (Cf, 98), Einsteinium (Es, 99) and Fermium (Fm, 100).

Today many more elements are known. Some are given with place and year of discovery.

Table 1.34

| Atomic no. | Elements | Symbol | Place (year) |
|------------|---------------|--------|---|
| 101 | Mendelevium | Md | Berkeley (1955) |
| 102 | Nobelium | No | Dubna, Russia (1965) |
| 103 | Lawrencium | Lr | Berkeley (1961) |
| 104 | Rutherfordium | Rf | Dubna, Berkeley (1964) |
| 105 | Dubnium | Db | Dubna, Berkeley (1970) |
| 106 | Seaborgium | Sg | Berkeley (1974) |
| 107 | Bohrium | Bh | Darmstadt, Germany, Dubna (1974 – 1989) |
| 108 | Hassium | Hs | Darmstadt (1980's) |
| 109 | Meitnerium | Mt | Darmstadt (1980's) |
| 110 | Darmstadtium | – | Darmstadt (after 1993) |

Certain isotopes of elements are more stable than the other. It depends upon the number of neutrons and protons (the magic numbers, 2, 8, 20, 28, 50, 82, 126). The isotope of element – 114 with 184 neutrons is expected to be stable. Scientists, therefore, think of an island of nuclear stability.

Some records of Periodic Table

- | | | |
|-----|---|---|
| 1. | Smallest atom | Hydrogen (H) |
| 2. | Largest atom | Cesium (Cs) |
| 3. | Heaviest atom | U (isotope 238) |
| 4. | Most dense elements | Osmium (Os) |
| 5. | Element of lowest b.p. | He, -269°C |
| 6. | Elements of highest b.p. | Rhenium (Re) 5596°C |
| 7. | Elements having largest liq. range | Galium (Ga) m.p. 30°C , b.p. 2250°C |
| 8. | Liquid elements | Hg and Bromine (Br_2) |
| 9. | Most abundant elements in the universe | H and He |
| 10. | Most abundant element on earth | Oxygen |
| 11. | Most abundant element in the human body | Oxygen |
| 12. | Highest heat of atomization | Tungsten (W) |
| 13. | Least electronegative (or most electropositive) | Cs |
| 14. | Most electronegative | F |
| 15. | Strongest oxidizing elements | F |
| 16. | Strongest reducing agent | Li |
| 17. | Highest density of any element | Ir |

PRACTICE QUESTIONS

- A. Fill in the blanks.
- The electron affinity of F is _____ than Cl.
 - The radius of fluoride is _____ than Na^+ .
 - Least electronegative element in the periodic table is _____.
 - Largest atom in the periodic table is _____.
 - Elements having highest Ea belong to group _____ and lowest Ea belong to group _____.
 - Moving down the group 13, unipositive ion becomes _____ stable than the ytripositive ion.
 - There are _____ elements in each of the inner – transition series.
 - Covalent radius of an atom is _____ than the Van der Waals' radius.
 - The +2 oxidation state of lead is more stable than +4 state due to _____.
 - The most electropositive elements in the periodic table is _____.

OBJECTIVE-TYPE QUESTIONS

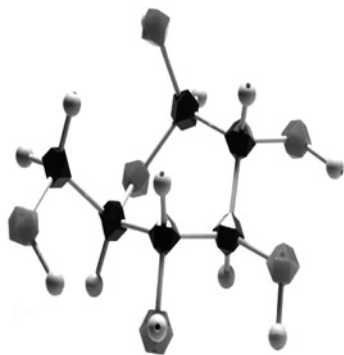
- The correct order of radii is
 - $\text{N} < \text{Be} < \text{B}$
 - $\text{F}^- < \text{O}_2^- < \text{N}_3^-$
 - $\text{Na} < \text{Li} < \text{K}$
 - $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}^{4+}$
- K^+ , Cl^- , Ca^{2+} , S^{2-} ions are isoelectronics. The decreasing order of their size is
 - $\text{S}^{2-} > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$
 - $\text{Ca}^{2+} > \text{K}^+ > \text{Cl}^- > \text{S}^{2-}$
 - $\text{K}^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{S}^{2-}$
 - $\text{Cl}^- > \text{S}^{2-} > \text{Ca}^{2+} > \text{K}^+$
- The correct order of ionic radii is
 - $\text{I}^+ > \text{I}^- > \text{I}$
 - $\text{I} > \text{I}^+ > \text{I}^-$
 - $\text{I} > \text{I}^- > \text{I}^+$
 - $\text{I}^- > \text{I} > \text{I}^+$
- The correct order of ionic radii is
 - $\text{Fe} > \text{Fe}^{2+} > \text{Fe}^{3+}$
 - $\text{O}^{2-} > \text{O}^- > \text{O}^+$
 - $\text{I}^- > \text{I} > \text{I}^+$
 - All of these
- The electron affinity of the members of oxygen family follow the order
 - $\text{O} > \text{S} > \text{Se}$
 - $\text{S} > \text{O} > \text{Se}$
 - $\text{S} > \text{Se} > \text{O}$
 - $\text{Se} > \text{O} > \text{S}$
- The electron affinity order for halogens is
 - $\text{F} > \text{Cl} < \text{Br} > \text{I}$
 - $\text{F} > \text{Cl} < \text{Br} > \text{I}$
 - $\text{F} < \text{Cl} > \text{Br} > \text{I}$
 - $\text{F} > \text{Cl} > \text{Br} > \text{I}$
- The correct order of second ionization potential of Carbon, Nitrogen, Oxygen and Fluorine is
 - $\text{C} > \text{N} > \text{O} > \text{F}$
 - $\text{O} > \text{N} > \text{F} > \text{C}$
 - $\text{O} > \text{F} > \text{N} > \text{C}$
 - $\text{F} > \text{O} > \text{N} > \text{C}$
- Ionization potential of Na would numerically be the same as
 - Electron affinity of Na^+
 - Electronegativity of Na^+
 - Electron affinity of He
 - Ionization potential of Mg
- The electronegativity of the following elements increases in the order
 - C, N, Si, P
 - N, Si, C, P
 - Si, P, C, N
 - P, Si, N, C
- The first ionization potential of Na, Mg, Al and Si are in the order
 - $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$
 - $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$
 - $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$
 - $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$
- The correct order of electron affinity is
 - $\text{F} > \text{Cl} > \text{Br}$
 - $\text{F} > \text{Cl} < \text{Br}$
 - $\text{F} < \text{Cl} > \text{Br}$
 - $\text{F} < \text{Cl} < \text{Br}$
- The correct order of first ionization energy is
 - $\text{C} > \text{N} > \text{O}$
 - $\text{C} > \text{N} < \text{O}$
 - $\text{C} < \text{N} > \text{O}$
 - $\text{C} < \text{N} < \text{O}$
- Which of the following configuration is expected to have maximum difference in second and third ionization energies?

- (a) $1s^2 2s^2 2p^2$
 (b) $1s^2 2s^2 2p^6 3s^1$
 (c) $1s^2 2s^2 2p^6 3s^2$
 (d) $1s^2 2s^2 2p^1$
14. In the periodic table, the metallic character of elements
 (a) Increases from left to right across a period and on descending a group.
 (b) Decreases from left to right across a period and on descending a group.
 (c) Increases from left to right across a period and decreases on descending a group.
 (d) Decreases from left to right across a period and increases on descending a group.
15. Which of the following elements is metalloid?
 (a) C (b) As
 (c) Pb (d) Mg
16. Which of the following elements has the highest value of electron affinity?
 (a) O (b) S
 (c) Se (d) Te
17. The correct order of ionization energy is
 (a) $\text{Cu} > \text{Ag} > \text{Au}$ (b) $\text{Cu} < \text{Ag} < \text{Au}$
 (c) $\text{Au} > \text{Cu} < \text{Ag}$ (d) $\text{Cu} < \text{Ag} > \text{Au}$
18. Most basic oxide is
 (a) Na_2O (c) MgO
 (c) Al_2O_3 (d) Fe_2O_3
19. The correct order of decreasing first ionization energy is
 (a) $\text{C} > \text{B} > \text{Be} > \text{Li}$
 (b) $\text{C} > \text{Be} > \text{B} > \text{Li}$
 (c) $\text{B} > \text{C} > \text{Be} > \text{Li}$
 (d) $\text{Be} > \text{Li} > \text{B} > \text{C}$
20. Property of the alkaline earth metals that increases with their atomic number is
 (a) Ionization energy
 (b) Solubility of their hydroxides
 (c) Solubility of their
 (d) Electronegativity
21. The correct order of second ionization energy is
 (a) $\text{C}^+ > \text{B}^+ > \text{Be}^+$ (b) $\text{B}^+ > \text{C}^+ > \text{Be}^+$
 (c) $\text{B}^+ > \text{Be}^+ > \text{C}^+$ (d) $\text{Be}^+ > \text{C}^+ > \text{B}^+$
22. The most electronegative elements is represented by
 (a) ns^2np^4 (b) ns^2np^3
 (c) ns^2np^5 (d) ns^2np^6

ANSWERS

1. (b) 2. (a) 3. (d) 4. (d) 5. (c) 6. (c) 7. (d) 8. (a) 9. (c) 10. (a)
 11. (c) 12. (c) 13. (c) 14. (d) 15. (b) 16. (b) 17. (c) 18. (a) 19. (b) 20. (b)
 21. (b) 22. (c).

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Chemical Bonding and Molecular Structure

CHEMICAL BONDING AND MOLECULAR STRUCTURE

The force which binds atoms together in a molecule is called a chemical bond. Bond formation is always an energy releasing process i.e., an exothermic process. It is shown in the graph below:

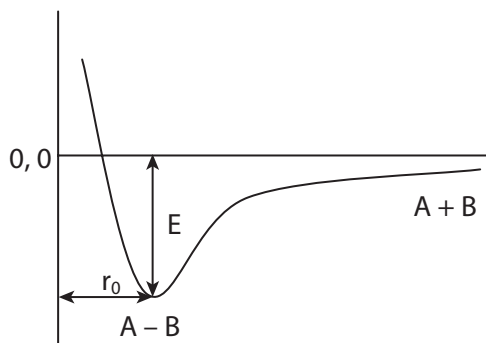


Figure 2.1

$A + B$ are isolated atoms

$A - B$ is molecule formed from A and B

r_0 is bond length in $A - B$

E is bond energy

Different types of chemical bonds

A. Strong bonds

- I. Ionic (or Electrovalent) bond
- II. Covalent bond
- III. Coordinate covalent bond.

B. Metallic bond

Metallic bond strength ranges from very weak (in alkali metals) to very strong (in transition metals.).

C. In addition to the above, some very weak forces may operate between molecules. They are termed as secondary forces,

- I. H – bond and
- II. Van der Waals' force

D. Multi-centre covalent bonding.

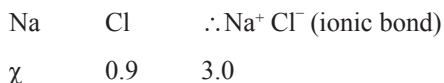
Summary of bond types

Table 2.1

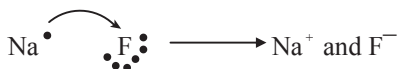
| Types of bond | Mechanism of formation | General properties |
|----------------------|---|---|
| Ionic | Electron loss – gain and electrostatic forces between ions | Solids, brittle, crystalline. High mp and bp soluble in polar solvents. Conduct electricity (with decomposition) in solution or when fused |
| Covalent | Electron sharing to form an electron pair bond | Either (a) discrete molecules (CH_4 , CO_2 etc.), volatile, low mp and bp, insulator and soluble in non-polar solvents or (b) giant molecules, SiC , SiO_2 etc, Hard, high mp and bp, insoluble in most solvents. May conduct electricity in solid state without decomposition. |
| Metallic | Metal ions held in a crystal lattice by delocalized electrons. | High coordination number (8 or 12). Crystalline (BCC, hcp or ccp). High to low melting and high bp. Conducts electricity in solid state without decomposition. |
| H – bond | Weak attraction between polar H and electron rich center, $\delta^- \text{Y} - \text{H}^{\delta+} \cdots \text{X}(\text{e} - \text{rich})$ | Effect on physical and chemical properties Solubility, stability of chemical species. |
| Van der waals' force | Deformation force | Present in every chemical system. Leads to volatility. Low mp and bp Soluble in non-polar solvents. |
| Multicentre bond | Less of electrons are involved to join more of atoms (i.e., not a $2\text{c} - 2\text{e}$ bond). | It is import to explain bonding in boron hydrides and some other electron deficient species, BeH_2 , $\text{Al}(\text{CH}_3)_3$ etc. |

Ionic or electrovalent bond

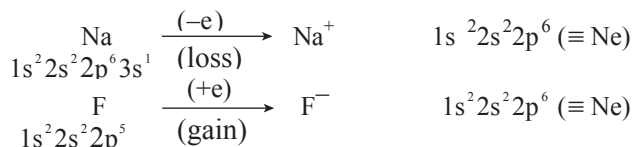
A bond formed by transfer of electron/s from one atom to another is called an ionic bond. It becomes possible when two combining atoms differ widely in their electronegativity.



Transfer of electron (or electrons) from less to more electronegative atom produces ions having opposite charge.



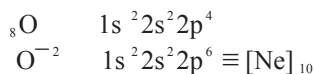
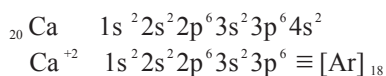
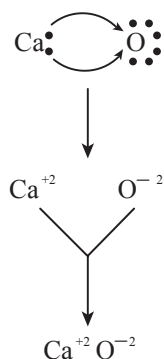
Transfer of electron from sodium gives sodium cation (Na^+) and gain of electron by fluorine forms negative ion (F^-). These ions have stable electron configurations.



These configurationally stable oppositely charged ions attract each other resulting into the formation of an ion-pair molecule, Na^+F^- . The electrostatic attraction is chemical bond. As electrostatic attraction is basically non-directional an ionic bond is also non-directional.

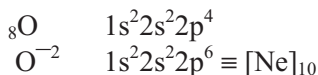
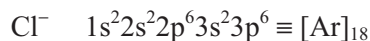
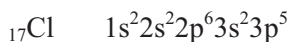
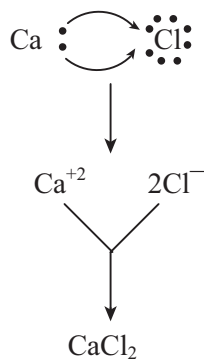
Some more examples

(i) Formation of CaO



Both ions have stable electrons-configuration (octet)

Figure 2.2



Both ions have stable electrons-configuration (octet)

Figure 2.3

Many other compounds such as KCl , KBr , K_2O , MgO , Na_2S , CaS etc., are formed due to transfer of electrons from less electronegative metals (i.e., electropositive elements) to more electronegative non-metals.

Therefore, ionic compounds are formed by electropositive metals and non-metals.

Note:

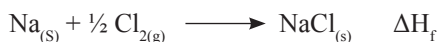
- (i) H – ionic compounds, hydrides, contain H^- , e.g., MH , ($M = Li$ to Cs) and MH_2 ($M = Ca, Sr, Ba$).
- (ii) N – compounds, nitrides (N^{3-}), e.g., Li_3N , M_3N_2 ($M = Ca, Sr, Ba$).
- (iii) P – compounds, phosphides (P^{3-}), e.g., Mg_3P_2 , Zn_3P_2 etc.
- (iv) O – compounds, oxides details in group – 16).
- (v) S – compounds, sulphides (S^{2-}), Na_2S , CaS , ZnS etc.
- (vi) Halogen compounds halides (X^- , $X = F, Cl, Br, I$), e.g., NaF , $CaCl_2$, $CaBr_2$ etc.

Table 2.2

| Electropositive metals | Electronegative non-metals |
|--|----------------------------|
| Gr – 1, Li to Cs | H |
| Gr – 2, Ca, Sr, Ba | N, O, F |
| Zn | P, S, Cl, Br, I |
| Transition metals in +2 oxidation state, V^{+2} , Cr^{+2} , Fe^{2+} , Ni^{2+} , Cu^{+2} etc. | |

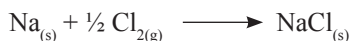
Factors favouring formation of ionic compounds

Formation of ionic compounds involves formation of ions. Let us consider formation of $NaCl$,



Energy change in the above reaction is enthalpy of formation, ΔH_f . The above overall reactions can be broken down into the following steps:

- (i) $Na_{(s)} \longrightarrow Na_{(g)} \quad \Delta H_{sub}$ – Sublimation energy
- (ii) $Na_{(g)} \longrightarrow Na_{(g)}^+ + e^- \quad IE$ – Ionization energy
- (iii) $\frac{1}{2} Cl_{2(g)} \longrightarrow Cl_{(g)} \quad \frac{1}{2} \Delta H_{Diss}$ – Dissociation energy
- (iv) $Cl_{(g)} + e^- \longrightarrow Cl_{(g)}^- \quad E_a$ – Electron affinity
- (v) $Na_{(g)}^+ + Cl_{(g)}^- \longrightarrow NaCl_{(s)} \quad U_o$ – Lattice energy



Thus, in the formation of $NaCl$, energetics involved are ΔH_{sub} , IE , $1/2\Delta H_{Diss}$, E_a and U_o . Energy is absorbed in the steps (i), (ii) and (iii) (i.e., these are endothermic steps) and energy is released in the steps (iv) and (v) (i.e., these are exothermic steps).

The ΔH_f quantity decides formation and stability of ionic compounds.

If,

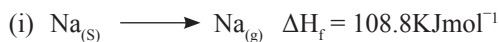
- (i) $\Delta H_f = \ominus$ ive, ionic compound is formed and is stable also.
- (ii) $\Delta H_f = \oplus$ ive, the ionic compound is not formed.

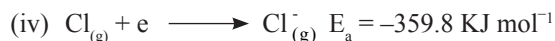
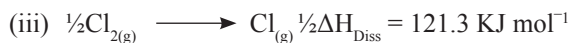
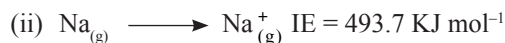
Therefore, in the above example,

If,

- (a) $(i) + (ii) + (iii) < (iv) + (v)$, ΔH_f is \ominus ive and $NaCl$ is formed and,
- (b) $(i) + (ii) + (iii) > (iv) + (v)$, ΔH_f is \oplus ive and $NaCl$ will not be formed.

Actual, energy changes are as:





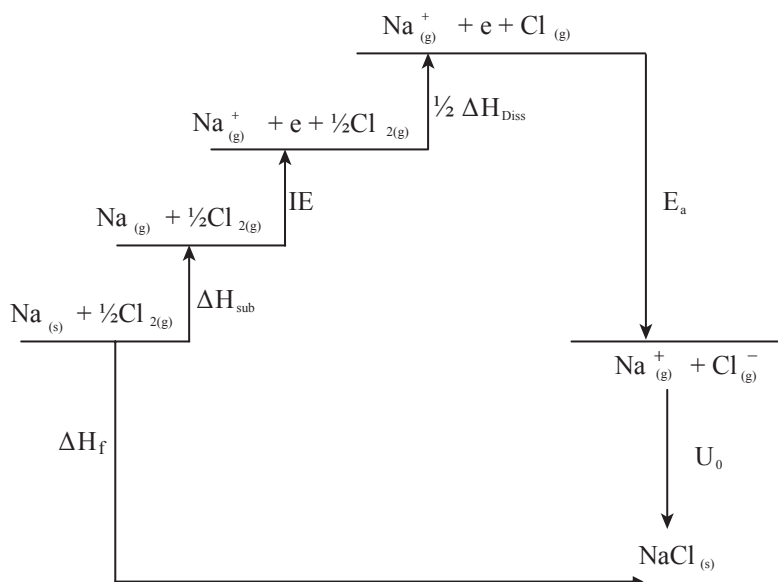
$$\therefore \Delta H_f = 108.8 + 493.7 + 121.3 - 359.8 - 775.0$$

$$= -411.0 \text{ KJ mol}^{-1}$$

Thus, NaCl formation is favoured as ΔH_f is negative.

Born-Haber cycle

Energy changes involved in the formation of ionic compounds can be represented in a cyclic form. It is called Born-Haber cycle. The B-H cycle for the formation of NaCl is shown below:



Therefore, from energy conservation principle (or Hess's law)

$$\Delta H_f = \Delta H_{\text{sub}} + \text{IE} + \frac{1}{2}\Delta H_{\text{Diss}} + E_a + U_o$$

(These terms have meaning as given above).

The above equation can be used to:

(a) Decide stability of an ionic compound

For stable ionic compounds, ΔH_f should be negative. It is negative when

$$\overbrace{\Delta H_{\text{sub}} + \text{IE} + \frac{1}{2}\Delta H_{\text{Diss}}}^{\text{Endothermic steps}} < \overbrace{E_a + U_o}^{\text{Exothermic steps}}$$

- (b) Compare stability of different ionic compounds. The compound for which ΔH_f is more negative is more stable and vice versa. For example,

Table 2.3

| Compounds \rightarrow | MgCl | MgCl ₂ | MgCl ₃ |
|--------------------------------------|------|-------------------|-------------------|
| ΔH_f (KJ mol ⁻¹) | -62 | -611 | +825 |

Note:

- (i) ΔH_f is most negative for MgCl₂, so it is magnesium chloride.
 - (ii) ΔH_f is positive for MgCl₃, so it is not possible to be formed (The third IE of Mg is very high).
 - (iii) ΔH_f is much less negative for MgCl so it is not stable.
- (c) Calculate any of the quantities in the R.H.S. if rest others are known.
- (d) Calculate lattice energy of ionic compounds.
- (e) Calculate enthalpy of formation of some ions, e.g., the ΔH_f of gaseous CN⁻ ion can be calculated from the B – H cycle for NaCN. The ΔH_f for CN⁻_(g) has been found 29 KJmol⁻¹.

Cations of stable electron configuration

Cations having noble gas core are stable. In addition to that 18 and (18 + 2) core electron containing cations are also stable.

Transition metal cation which have neither of the above core are also stable.

Table 2.4

| Core electrons | Cations |
|--------------------|--|
| 2 – electrons | Li ⁺ , Be ⁺² |
| 8 – electrons | Na ⁺ , Mg ²⁺ , Ca ⁺² , Al ⁺³ |
| 18 – electrons | Cu ⁺ , Ag ⁺ , Zn ⁺² , Cd ⁺² , Hg ⁺² |
| (18 + 2) electrons | Tl ⁺ , Bi ⁺³ , Pb ⁺² , Sn ⁺² |

Table 2.5

| | |
|------------------|--------------------|
| V ⁺² | 11 – Electron core |
| Fe ²⁺ | 14 – Electron core |
| Fe ³⁺ | 13 – Electron core |
| Ni ²⁺ | 16 – Electron core |
| Cu ²⁺ | 17 – Electron core |

Stable negative ions always have noble gas core

H⁻ 2 – electron core

N⁻³, O⁻², F⁻, Cl⁻, S⁻² etc 8 – electron core

Polarization and its effects**1. Covalent nature in ionic compounds**

No bond is 100% ionic or 100% covalent. There is covalency in ionic bonds (and ionicity in covalent bonds).

Two main causes for covalency in ionic bonds are:

- (a) Size of the ions, and
- (b) Core electrons of the cation.

Table 2.5

| Size of ion and core electrons | Covalent nature in ionic bond | Example |
|--------------------------------|-------------------------------|--|
| Small cation | More covalent | LiCl is more covalent than NaCl because $r_{\text{Li}^+} < r_{\text{Na}^+}$ |
| Large cation | Less covalent | |
| Large anion | More covalent | CaI_2 is more covalent than CaCl_2 because $r_{\text{I}^-} > r_{\text{Cl}^-}$ |
| Small anion | Less covalent | |
| More core electrons | More covalent | ZnCl_2 is more covalent than CaCl_2 Zn^{+2} – 18 core electrons Ca^{+2} – 8 core electrons |
| Less core electrons | Less covalent | |
| | | |

The basic reason for covalency in ionic bond is polarization effect. Cations, in general, are small and their effective nuclear charge (Z^*) is high. Anions are large in size and their Z^* is relatively small, ($Z^*_{(\text{Na}^+)} = 6.85$ and $Z^*_{(\text{F}^-)} = 4.85$). Cations, thus, have compact electronic shell and practically are not polarizable i.e., deformed. In stead they are polarizing i.e., can cause polarization. The larger anions do not hold their outer electrons firmly (Z^* low). Therefore, when a small cation approaches an anion, the anion is easily deformed i.e., polarized (i.e., anion is polarizable). In this way a cation may share some electron density with the anion resulting into covalency in ionic bonds.

Fajan has summerized the above facts which is known as Fajan's Rule. They are

- Small cations favour covalence
- Large anions favour covalence
- High charge on either or both the ions favour covalency. Thus AlN (aluminium nitride) has enough covalency, as both have high charge, (Al^{+3} and N^{-3}).

Polarizing power of a cation also depends on its core electrons. Cations having more of core electrons are more polarizing and vice versa. Therefore, they favour covalency.

Table 2.6

| Ions | Core Electrons | Effect |
|--|----------------|------------------|
| Na^+ , Mg^{+2} , Ca^{+2} | 8 | Ionic |
| Zn^{+2} , Hg^{+2} , Cd^{+2} | 18 | Favour covalency |
| Tl^+ , Pb^{+2} , Sn^{+2} | $18 + 2$ | Favour covalency |
| Fe^{3+} | 13 | Favour covalency |
| Cr^{+3} | 11 | Favour covalency |
| Ni^{2+} | 16 | Favour covalency |

2. Polarization and melting points

Polarization has profound effect on melting points. Compound having more polarizing cation has lower mp, (Covalent nature in compound).

Table 2.7

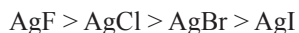
| Compounds | Mp ($^{\circ}\text{C}$) | Order of polarizing power |
|-----------------|---------------------------|---|
| NaBr | 755 | $\text{Al}^{+3} > \text{Mg}^{2+} > \text{Na}^+$ |
| MgBr_2 | 700 | (related to size) |
| AlBr_3 | 91.5 | |

(Continued)

| Compounds | Mp (°C) | Order of polarizing power |
|-------------------|---------|---|
| CaCl ₂ | 772 | Hg ²⁺ > Ca ²⁺ |
| HgCl ₂ | 276 | (related to size) |
| LiF | 870 | Polarizability of X ⁻ |
| LiCl | 613 | I ⁻ > Br ⁻ > Cl ⁻ > F ⁻ |
| LiBr | 547 | (related to size) |
| LiI | 446 | |

3. Polarization and solubility

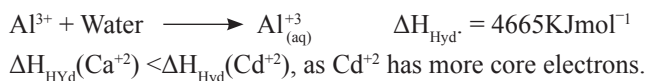
Polarization has effect on solubility. For example, solubility of silver halides. The solubility order is:



Chloride, bromide and iodide are practically insoluble (in water). The fluoride ion (F⁻) is small and is least polarizable whereas I⁻ is largest in size and is most polarizable. Therefore, AgI lattice is more stable and it is insoluble. The factor responsible for solubility of AgF is high hydration energy of the small F⁻ ion (513 KJmol⁻¹).

4. Polarization and hydration energy

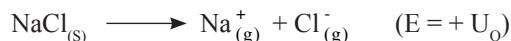
The cations, which are more polarizing, have high hydration energy. It is affected by radius as well as core electrons of the metal ions. One very clear example is very high hydration energy of Al³⁺.



Lattice Energy

Ionic compounds are solids and have crystalline structure. Crystals contain alternate arrangement of ions i.e., + - + - etc., in all the three dimensions. It results into attractive and repulsive forces both in the lattice. But calculations show that attractive force is always greater than the repulsive force. This situation brings stability to the structure.

Lattice energy is defined as: Energy required to separate one mole crystal into gaseous ions is called lattice energy.



Or conversely, Energy releases when one mole crystal is produced from its gaseous ions is called lattice energy.



Theoretically, lattice energy is given by Born – Lande equation. It is,

$$U_{\text{O}} = \frac{NMZ^{+}.Z^{-}.e^2}{r_{\text{O}}} \left[1 - \frac{1}{n} \right]$$

Where,

N = Avogadro's number

M = Madelung constant, it depends on crystal structure.

Z⁺ and Z⁻ = Charges on cation and anion

e = Charge on electron

r₀ = r₊ + r₋ [(r₊ = radius of cation), (r₋ = radius of anion)]

n = Born constant, it depends upon electron configuration of the ions.

For an ionic compound, Born constant (n) is average of the ions of the compound, e.g.,

$$\text{NaCl}, n = (7 + 9)/2 = 8$$

The value of Madelung constant (M) depends on crystal structure.

Table 2.9

| Crystal type | M |
|--------------|---------|
| NaCl | 1.74756 |
| CsCl | 1.76267 |
| ZnS | 1.63806 |

In SI unit's lattice energy equation is

$$U_o = \frac{NMZ^+ \cdot Z^- e^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{1}{n} \right]$$

Where ϵ_0 is dielectric constant and it has the value (of a vacuum)
 $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2\text{m}^{-1}\text{J}^{-1}$

Some conclusions from Born equation

- (i) The contribution of the term $(1 - 1/n)$ is small to lattice energy.
- (ii) $U_o \propto 1/r_0$ i.e., larger the ions lesser the lattice energy and vice versa.
- (iii) $U_o \propto Z^+ \cdot Z^-$ i.e., larger the product of the ionic charges greater the lattice energy.

| | $r_0(\text{\AA})$ | $Z^+ \cdot Z^-$ | $U_o (\text{KJmol}^{-1})$ |
|-----|-------------------|------------------|---------------------------|
| LiF | 2.01 | $1 \times 1 = 1$ | -1004 |
| MgO | 2.10 | $2 \times 2 = 4$ | -3933 |

- (iv) Crystals having higher L.E. usually melt at high temperature.

| Crystal | L.E (KJmol ⁻¹) (from Born eq.) | mpt (°C) |
|---------|---|----------|
| LiCl | - 825 | 614 |
| NaCl | - 764 | 800 |
| KCl | - 686 | 770 |

Melting point of LiCl, is low, inspite of higher L.E. It is due to covalent nature in LiCl.

(v) Lattice energy and water solubility

Solubility of ionic compounds depends on (a) L.E., and (b) Hydration energy. The conditions are

- (a) If $LE - HE = \ominus$ ive, the substance is soluble.
- (b) If $LE - HE = \oplus$ ive, the substance is insoluble.

Table 2.8

| e – configuration | Ions | n |
|-------------------|--|----|
| He | $\text{Li}^+, \text{Be}^{2+}, \text{H}^-$ | 5 |
| Ne | $\text{Na}^+, \text{Mg}^{2+}, \text{F}^-, \text{O}^{2-}$ | 7 |
| Ar | $\text{K}^+, \text{Ca}^{2+}, \text{Cl}^-, \text{S}^{2-}$ | 9 |
| Kr | $\text{Rb}^+, \text{Sr}^{2+}, \text{Br}^-$ | 10 |
| Xe | Cs^+, I^- | 12 |

Hydration energy: Ions in water do not exist isolated. They are surrounded by water molecules having weak attraction. It is called hydration.

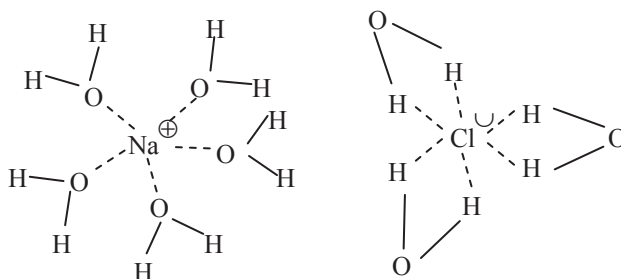


Figure 2.4

The energy released in this attractive interaction is called hydration energy. This depends on charge/radius ratio of the ion i.e., charge density,

$$\text{Charge density} = \text{Charge/radius}$$

When charge density is high interaction with water is more and hydration energy is high.

(vi) Lattice energy and core electrons

Lattice energy also depends on core electrons. It is because ions having more core electrons are more polarizing. Polarization effect adds to lattice energy. Thus, CdCl_2 has high lattice energy over CaCl_2 . It is because Cd^{+2} has more core electrons (18) than Ca^{+2} (8 electrons). Both these ions have almost equal ionic radii ($r_{\text{Ca}^{+2}} \sim r_{\text{Cd}^{+2}} \sim 0.9 \text{ \AA}$).

Table 2.10

| Ion | Charge density | Hydration energy (KJmol^{-1}) |
|------------------|----------------|--|
| Na^+ | 1.1 | – 422.0 |
| Mg^{2+} | 2.9 | – 1954.0 |
| Al^{+3} | 5.2 | – 4665.0 |
| F^- | 1/1.33 | – 513.0 |
| Cl^- | 1/1.84 | – 370.0 |

General properties of ionic compounds

- All ionic compounds are solids, hard and brittle.
- Ionic solids have crystal structure.
- Ions in the solid are arranged alternately. e.g.,

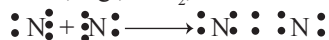
$$\begin{array}{cccccccc} + & - & + & - & + & - & + & - \\ - & + & - & + & - & + & - & + \\ + & - & + & - & + & - & + & - \\ - & + & - & + & - & + & - & + \end{array}$$
- Ionic compounds have high melting point (due to lattice structure)
- Ionic compounds are generally soluble in water. The solution contains ions. Therefore, solution of ionic compounds is electrolyte.
- Ionic compounds in fused state are also conductor. It is due to the fact that melt contains free ions.
- Ionic compounds in solid state are insulators as ions are held at fixed points in the lattice structure and can not move on application of pot. difference.

Covalent bonding

A covalent bond is formed by the sharing of one (or more) pairs of electrons with opposite spin between two atoms. It gives stable electron configuration (either 2 – electron, duct or 8 – electron i.e., octet) to each atom. The electron pairs remain somewhere between the two nuclei of the combining atoms. It is, therefore,

attracted by both the nuclei simultaneously resulting into bonding. Thus, the bond in H_2 results from the sharing of hydrogen electrons between the two atoms $H^\bullet + H^\bullet \longrightarrow H \parallel H (H-H)$.

Due to sharing of electrons both H atoms achieve electron configuration of He. Two or three pairs may also be shared, e.g., in N_2 ,



Both N atoms achieve octet configuration due to sharing of three pairs of electrons between them. The above presentation of a molecule is called Lewis structure (or Dot structure). [G. N. Lewis was the first to put forward an electronic interpretation of the chemical bond].

Electrons of atoms are present in atomic orbitals (s, p, d etc.). Thus sharing of electrons involves interaction of atomic orbitals. Orbital interaction in chemical terms is called overlap of orbitals. Therefore, a covalent bond is formed by overlap of orbitals. As no more than two electrons can occupy an orbital, only half-filled atomic orbitals can take part in overlap. The larger is the overlap stronger is the bond. The model described above is Valence Bond Model for covalent bonding.

σ and π bonds

Orbitals can overlap in two distinct ways,

- (i) At an axis (or linearly or head on) and,
- (ii) Side-ways (or laterally)

The above situations give different type of covalent bonds.

σ -bond

When two orbitals overlap at an axis, the bond formed is called ' σ -bond'. The axis taken is internuclear axis (or bond axis) i.e., the axis on which both the nuclei lie.

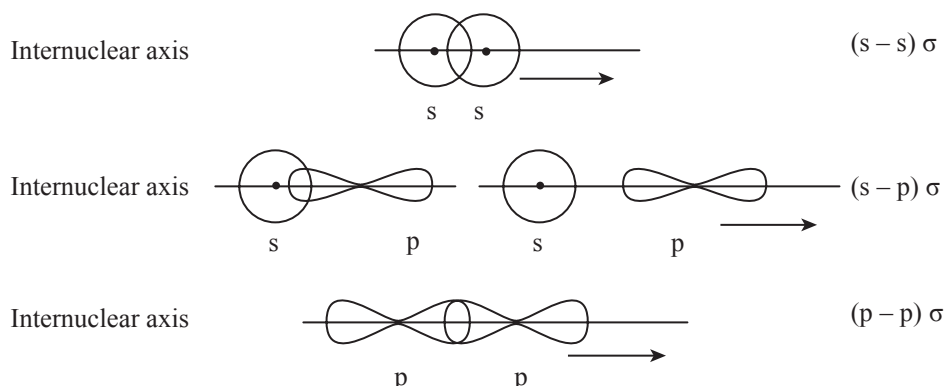


Figure 2.5

The degree of overlap is large, so, a σ -bond is stronger. [Hybrid orbitals also can form σ -bond].

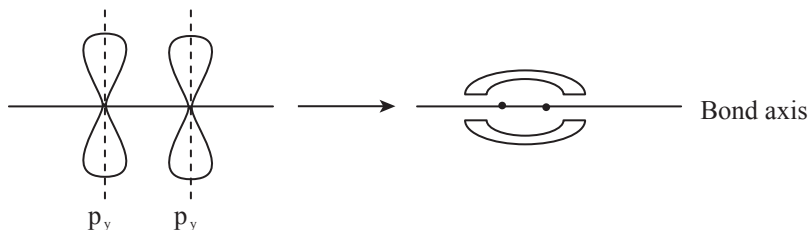
A σ -bond orbital is symmetrical around the bond axis. In such bonding rotation of one atom relative to the other about the bond axis does not change the extent of overlap. Therefore, free rotation is possible about a σ -bond.

π -bond

When two orbitals overlap side by side (or sideways or laterally) a π bond is formed. A π bond may involve two p orbitals (or d and p orbitals or d and d orbitals).

(p – p) π bond

When two p orbitals centered at two atoms overlap side by side a (p – p) π bond is formed. For most effective overlap the orbitals should lie perpendicular to the bond axis.

**Figure 2.6**

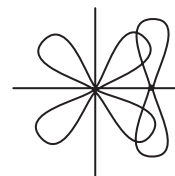
A π – bond orbital is divided in two parts by the bond axis i.e., it is not symmetrical about the bond axis. It has a nodal plane in the plane of the molecule. Free rotation about a π bond is not possible because it would break the π – bond.

As degree of overlap is small a π – bond is weaker than a σ – bond. The second period elements (B, C, N, O, F) form very strong (p – p) π bonds. Molecules like N_2 , O_2 , CO_2 , NO_2 , BF_3 etc. all have strong (p – p) π bonds. The (p – p) π bonding is not effective in third period elements (Si, P, S, Cl etc.). It is because of the fact that

- (i) 3p orbitals are large and,
- (ii) The elements have more of core electrons (8 electrons).

(d – p) π bond

A π bond may also involve d and p orbitals.

**Figure 2.7**

Such bonding is important in the compounds containing third (or higher) period elements (Si, P, S, Cl etc.). These elements have vacant 3d orbitals. These vacant d – orbital form (d – p) π bonding when Si, P, S etc., are bonded with N, O, F which have lone pair electrons in their p – orbitals. Molecules like SO_2 , SO_3 , SiF_4 , $N(SiH_3)_3$ etc. all have effective (d – p) π bonds.

Comparison of σ and π bond**Table 2.11**

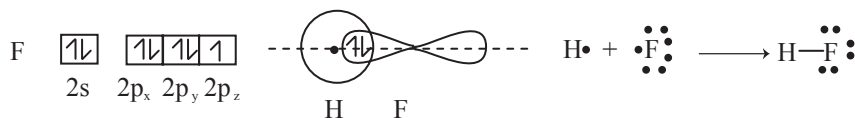
| Properties | σ -bond | π -bond |
|------------------------|---|--|
| 1. Nature of overlap | Linear overlap of orbitals | Side by side overlap of orbitals. |
| 2. Extent of overlap | Large | Small |
| 3. Bond strength | Strong bond | Relatively weak bond |
| 4. Symmetry | σ – bond orbital symmetrical around the bond axis. | π – bond orbital not symmetrical about the bond axis. |
| 5. Nodal plane | No nodal plane | There is nodal plane which lies in the plane of the molecule [(p – p) π bond]. |
| 6. Rotational property | Free rotation about σ bond axis is possible | No free rotation about π – bond axis is possible. |
| 7. Polarizability | Least polarizable | Most polarizable. |

Formation of molecules having σ bonds only

- (a)
- H_2
- : It is formed by overlap of 1s orbitals of H atoms.

**Figure 2.8**

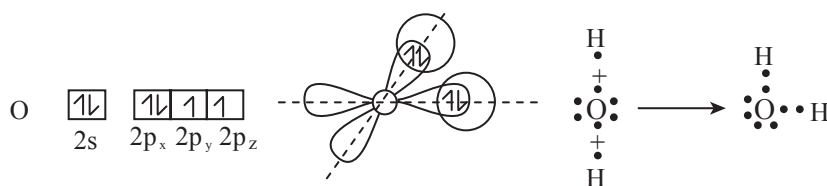
- (b)
- HF
- : It is formed by overlap of 1s orbital of H with half-filled
- $2p_z$
- orbital of F.

**Figure 2.9**

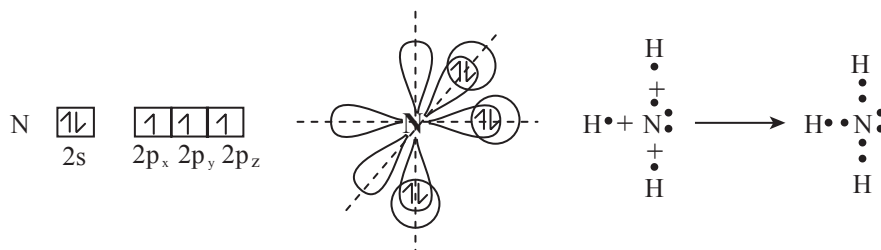
- (c)
- F_2
- : It is formed by overlap of half-filled
- $2p_z$
- orbitals centered on two F atoms.

**Figure 2.10**

- (d)
- H_2O
- : It is formed by overlap of two half-filled 2p orbitals centred on O – atom with 1s orbital of both the H – atom.

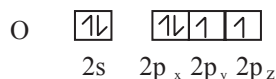
**Figure 2.11**

- (e)
- NH_3
- : It is formed by overlap of three half-filled 2p orbitals centred on N – atom with 1s orbital of H – atoms.

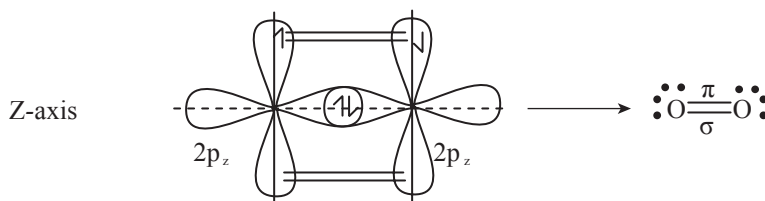
**Figure 2.12**

Molecules having σ and π bond both

- (a)
- O_2
- molecule: The O – atom has two half-filled 2p orbitals.

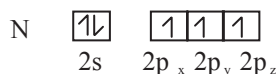


The 2p_z orbitals overlap axially to form a σ bond (z-axis is taken as bond axis). The 2p_y orbitals, which are perpendicular to the bond axis, overlap side by side to form a π bond.

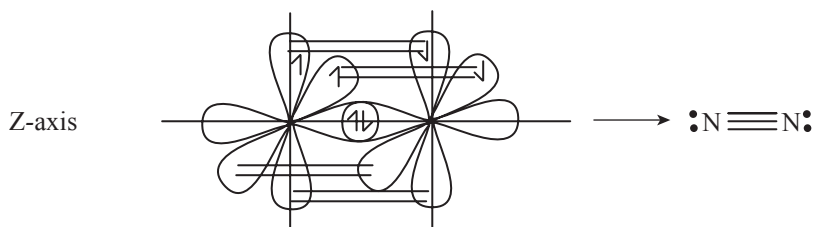
**Figure 2.13**

Thus O_2 has double bond between O – atoms, in which one is a σ bond and the other is a π bond. [The above structure of O_2 shows all electrons paired i.e., a diamagnetic molecule. But O_2 is found paramagnetic i.e., has unpaired electrons. It can be explained by molecular orbital model for covalent bonding not by valence bond model.]

- (b)
- N_2
- molecule: The N atom has three half-filled 2p orbitals.



The 2p_z orbitals overlap axially to form a σ -bond (Z-axis, bond axis). The remaining p-orbitals, 2p_x and 2p_y which are perpendicular on the bond axis overlap side ways to form two π bonds (2p_x-2p_x and 2p_y-2p_y).

**Figure 2.14**

Thus N_2 has a triple bond between N atoms, in which one is a σ – bond and the others are π -bonds (i.e., two π -bonds).

Electronegativity [χ (chi)]

Electronegativity is the property of a bonded atom. it is defined as: “ the tendency of an atom in a molecule to attract bond pair electrons towards itself is called electronegativity”. Elements differ in their electronegativity. Therefore, a covalent bond between two dissimilar atoms is always polar, e.g., HCl. In this molecule Cl is

more electronegative ($\chi_{\text{Cl}} = 3.0$) than H ($\chi_{\text{H}} = 2.1$). So, bond pair electrons are inclined towards Cl, making it partially negative and H partially positive,

As polarity is partial, δ is always less than unity (i.e., $\delta < 1$). On the other hand a covalent bond between two similar atoms is always non-polar because both the atoms have the same χ , e.g., H_2 , N_2 , O_2 , F_2 , Cl_2 etc. Hence covalent bonds can be of two types:

- Polar covalent bond:** It is always formed between two different non-metals, Example, the bonds $\text{O}-\text{H}$, $\text{N}-\text{H}$, $\text{F}-\text{H}$, $\text{S}-\text{O}$, $\text{N}-\text{O}$ are polar covalent.
- Non-polar covalent bond:** It is present in homonuclear diatomic molecules like, H_2 , F_2 , Cl_2 , O_2 , N_2 , Na_2 , B_2 etc.

Electronegativity of some elements

| | | | | | | | | |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Li | Be | B | H | C | N | O | F | Br |
| 1.0 | 1.5 | 2.0 | 2.1 | 2.5 | 3.0 | 3.5 | 4.0 | 2.8 |
| Na | Mg | Al | Si | P | S | Cl | I | |
| 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 | 2.5 | |

Electronegativity is a relative property of an element and not an absolute measure of the attraction for electrons. Degree of polarity in a bond depends on electronegativity difference. A rough estimate is:

- If $\Delta\chi = 1.8$, bond is 50% ionic and 50% covalent.
- If $\Delta\chi < 1.8$, bond is less ionic and more covalent.
- If $\Delta\chi > 1.8$ bond is more ionic and less covalent.

The per cent ionic nature can roughly be calculated by the equation,

$$\% \text{ Ionic nature} = 16 (\chi_{\text{A}} - \chi_{\text{B}}) + 3.5(\chi_{\text{A}} - \chi_{\text{B}})^2$$

(The polar nature is best-calculated using dipole moment data).

Some important points

- Electronegativity is relative property.
- Electronegativity of an element change with its oxidation state (It is because attraction for electrons increases with increase in oxidation state).

Electronegativity also changes with hybrid nature, e.g., an sp^3 carbon is less electronegative than sp^2 carbon, which in turn is less electronegative than sp carbon. It is due to change in s-characters of the hybrids,

Table 2.12

| Ion | χ | Ion | χ |
|------------------|--------|------------------|--------|
| Fe^{+2} | 1.83 | Sn^{+2} | 1.8 |
| Fe^{+3} | 1.96 | Sn^{+4} | 1.96 |

Table 2.13

| Hybrid | $\text{Csp}^3 < \text{Csp}^2 < \text{Csp}$ |
|---------------|--|
| S – character | 25% 33.3% 50% |
| χ | 2.5 2.7 3.3 |

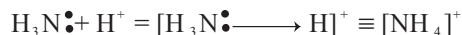
Coordinate covalent bond

A covalent bond in which both the shared electrons are provided by only one atom is called a coordinate covalent bond. It is also called electron donor–acceptor bond. It is denoted by an arrow extending from donor towards acceptor. (\longrightarrow)

Electron donors :NH_3 , $\text{H}_2\ddot{\text{O}}$, Cl_3P , R_2O etc.

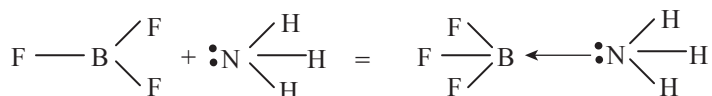
Electron acceptors H^+ , Cu^{2+} , Fe^{3+} , BF_3 etc.

Let us consider H^+ and NH_3 . The H^+ has vacant orbital and N of NH_3 has lone pair. The H^+ ion is, thus, an acceptor and NH_3 is a donor. They can combine due to formation of a coordinate bond.



Ammonium ion

The other example is formation of addition compound of BF_3 and NH_3 . BF_3 has vacant orbital (B is sp^2 in BF_3) and NH_3 has a lone pair (N is sp^3 in NH_3 and lone pair is in sp^3 orbital). These orbitals overlap resulting into the formation of addition compound.



Both BF_3 and NH_3 molecules get distorted due to the formation of addition compound. Due to this combination hybrid nature of B changes from sp^2 to sp^3 .

A coordinate bond has directional character because orbitals are involved in its formation.

Transition metals (or ions) form a vast number of compounds due to formation of coordinate bond. Such compounds are known as coordination compounds. For example, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{4-}$ etc.

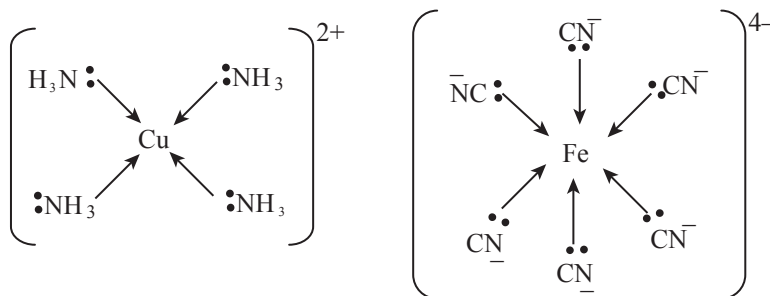


Figure 2.15

Electronegativity and Dipole moment

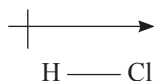
A covalent bond between two unlike atoms is always a polar covalent bond. It is due to the difference in the electronegativities of the two atoms. Example, HCl ($\chi_{\text{H}} = 2.1$ and $\chi_{\text{Cl}} = 3.0$). Thus HCl is represented as $\delta^+ \text{H} - \text{Cl} \delta^-$ i.e., polar centers in the molecule.

A polar bond has bond dipole moment, μ . It is given by,

$$\mu = q \times r$$

where r = bond length, q = charge on either end.

The bond dipole moment (μ) is a vector quantity and it is represented as,



Unit of μ

- (i) The CGS unit of bond moment is debye, D (in the honour of P. Debye who contributed much towards understanding of polar molecules).
 $1 \text{ D} = 10^{-18} \text{ esu.cm}$
- (ii) SI Unit: The SI unit is coulomb metre (cm).
 $1 \text{ D} = 3.33 \times 10^{-30} \text{ cm}$

For a heteronuclear diatomic molecule the bond moment is the molecular dipole moment. But for a polyatomic molecule the molecular dipole moment is the resultant of the bond moments. It is calculated using vector method.

Molecular dipole moment gives various informations:

1. μ and % ionic nature

$$\text{Per cent ionic nature} = \frac{\text{Expt. } \mu}{\text{Calculated } \mu} \times 100$$

Dipole moment is calculated using the concept of complete transfer of electron. For example, the % ionic nature in HCl.

$$\text{H} - \text{Cl bond length} = 1.3 \text{ \AA}$$

$$\text{Experimental } \mu = 1.03 \text{ \AA}$$

For complete transfer of electron (i.e., 100% ionic nature),

$$\mu = 4.8 \times 10^{-10} \times 1.3 \times 10^{-8} = 6.11 \text{ D}$$

$$\therefore \% \text{ ionic nature} = \frac{1.03}{6.11} \times 100 \approx 17\%$$

That is HCl has only 17% ionic nature. The covalent nature in HCl bond is, therefore, 83%.

2. μ and molecular structure

- (i) Atomicity, μ and structure are related.
- (ii) All unsymmetrical molecules (with respect to terminal atoms e.g., HCN, N_2O , CHCl_3 , CH_3Cl , SOF_4 etc.) have μ irrespective of atomicity and structure.
- (iii) The following table gives relation between μ and structure.

DIPOLE MOMENT (μ) AND STRUCTURE**Table 2.14**

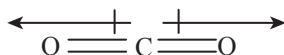
| Atomicity | μ | Structure | Example |
|-----------------|-------|--------------------|--|
| AB | Yes | Linear | H – F, CO, NO |
| AB ₂ | Yes | Angular | H ₂ O, SO ₂ , O ₃ |
| | No | Linear | CO ₂ |
| AB ₃ | Yes | Trigonal pyramid | NH ₃ , NF ₃ |
| | No | Trigonal planar | BF ₃ |
| AB ₄ | No | Tetrahedral | CCl ₄ |
| | No | Square planar | XeF ₄ |
| | Yes | Trigonal bipyramid | SF ₄ |

(Continued)

| Atomicity | μ | Structure | Example |
|-----------|-------|----------------------|---------|
| AB_5 | No | Trigonal bipyramic | PCl_5 |
| | Yes | Square pyramid | BrF_5 |
| AB_6 | No | Octahedral | SF_6 |
| | Yes | Pentagonal bipyramic | XeF_6 |

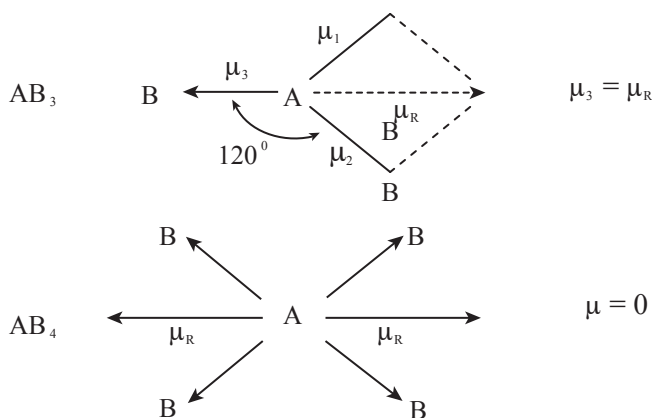
Note:

- (i) A molecule may have bond moment but may not possess dipole moment (due to structure) because of its linear structure.

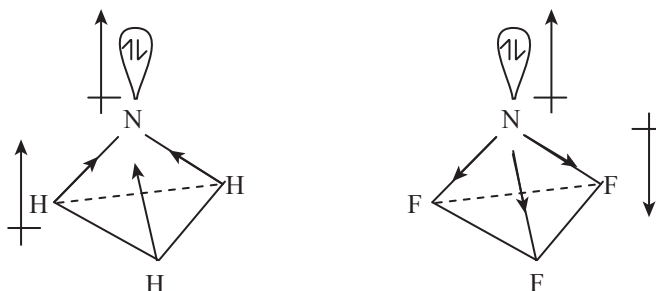


The two equal and oppositely oriented bond moments cancel each other.

- (ii) Tetraatomic with trigonal planar structure, pentatomic with tetrahedral structure and heptaatomic with octahedral structure also do not possess dipolment.

**Figure 2.16**

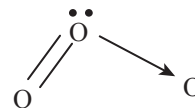
- (iii) NH_3 and NF_3 differ in μ , NH_3 (1.47D) NF_3 (0.2D)
Both have similar trigonal pyramid structure.

**Figure 2.17**

In NH_3 , N is more electronegative than H and N – H bond moments tend towards N atom. Therefore, bond moments and lone pair moment adds.

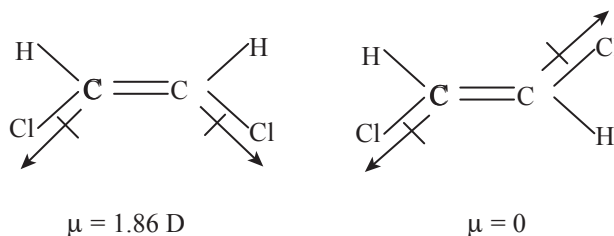
But in NF_3 , the N – F bond moments tends towards F atoms (F is more electronegative). The moment due to lone pair electron is opposite to it (i.e., a subtractive effect). Therefore, NH_3 has higher μ than NF_3 .

- (vi) A homonuclear triatomic molecule like O_3 has dipole moment (0.52 D). It is due to bent structure and a coordinate covalent bond.



3. μ and cis–trans isomers

The cis isomer has dipole moment but not the trans one.



The above fact is true for coordination compounds also, e.g., cis – $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has dipole moment but the trans – $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2]$ has no dipole moment.

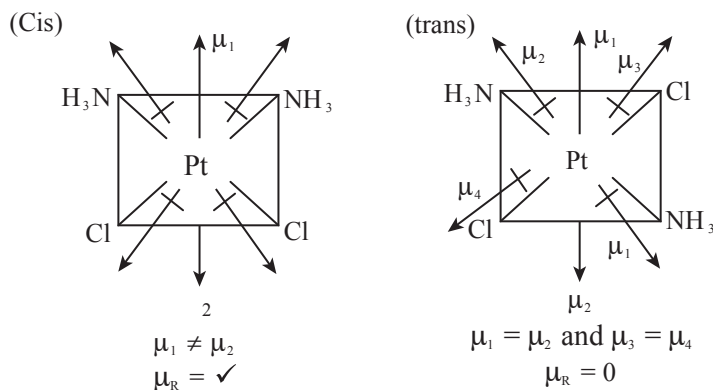


Figure 2.18

Some bond moments (D)

Table 2.15

| Bond | Bond moment | Bond | Bond moment |
|--------|-------------|-------------------|-------------|
| H – F | 1.9 | C – F | 1.4 |
| H – Cl | 1.0 | C – Cl | 1.5 |
| H – Br | 0.8 | C – Br | 1.4 |
| H – I | 0.4 | C – I | 1.2 |
| O – H | 1.6 | C – O | 0.9 |
| N – N | 1.3 | C – H | 0.4 |
| | | C = O | 2.3 |
| | | C – NO_2 | 3.5 |

Dipole moment of some molecules (D)**Table 2.16**

| Molecule | Dipolemoment | Molecule | Dipolemoment |
|------------------|--------------|------------------|--------------|
| HCN | 2.95 | H ₂ O | 1.8 |
| OCS | 0.71 | H ₂ S | 0.92 |
| N ₂ O | 0.16 | SO ₂ | 1.63 |
| NH ₃ | 1.47 | O ₃ | 0.52 |
| NF ₃ | 0.2 | NO ₂ | 0.39 |
| PF ₃ | 1.03 | | |

Lewis structure (or Dot structure)

Chemical species (molecules or ions) are stable when they have duet or octet electron configuration. It is strictly followed by second period elements. Presentation of species by showing their valence electrons by dots is called Lewis structure. This structure can be written following the rules:

- (i) Count total valence electrons:

Total Valence electrons = Valence electrons of atoms – charge

$$\text{NO}_2^+, \quad \text{V es} = 5 + 6 \times 2 - (+1) = 16$$

$$\text{N}_2\text{O}, \quad \text{V es} = 5 \times 2 + 6 = 16$$

$$\text{NO}_3^-, \quad \text{V es} = 5 + 6 \times 3 - (-1) = 24$$

- (ii) Find out
- π
- electrons (P)

$P = 6n + 2 - \text{Valence electrons}$, where, n = total number of atoms.

The π es in $\text{NO}_3^- = 6 \times 4 + 2 - 24 = 2 (\equiv 1\pi \text{ bond})$.

When the species contain H – atoms,

$P = 6X + 2 - \text{Valence electrons}$, where X = total atoms – number of H – atoms

 π – electrons in H containing species**Table 2.17**

| Species | Total valence electrons | π -electrons |
|------------------|---------------------------|--|
| HCN | $1 + 4 + 5 = 10$ | $6 \times 2 + 2 - 10 = 4 (\equiv 2\pi \text{ bond})$ |
| HNO ₃ | $1 + 5 + 6 \times 3 = 24$ | $6 \times 4 + 2 - 24 = 2 (\equiv 1\pi \text{ bond})$ |

- (iii) Fix central atom and make skeleton by joining terminal atoms with one electron pair, each atom (large atoms are generally central atoms).
- (iv) Place π bonds.
- (v) Distribute rest of the electrons among the atoms to complete octet.

In Lewis structures, there may develop, a charge on an atom due to limitation to provide octet to each atom. It is called formal charge which is calculated awarding equal electronegativity to each atom.

Formal charge = Valence electrons – $\frac{1}{2}$ bp electrons – lp electrons of the atom.

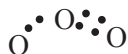
O_3 (Lewis structure)

Steps: O $2s^2 2p^4$ i.e., 6 Valence electrons.

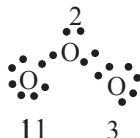
- (i) Total valence electrons = $6 \times 3 = 18$
- (ii) π – electrons = $6 \times 3 + 2 - 18 = 2$ ($\equiv 1 \pi$ bond)
- (iii) O is central atom.



- (v) One double bond is added to the above skeleton.



- (vi) Then electrons are distributed to the atoms to complete octet.

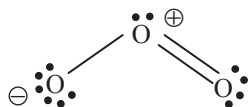


FC on O – atom single bonded. (i.e.1) = $6 - \frac{1}{2} \times 2 - 6 = -1$

FC on the central O – atom (i.e.2) = $6 - \frac{1}{2} \times 6 - 2 = +1$

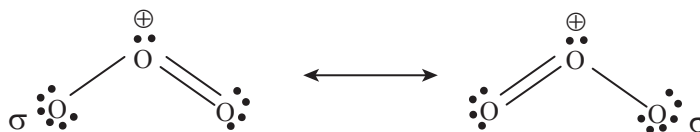
FC on the O – atom double bonded (i.e., 3) = $6 - \frac{1}{2} \times 4 - 4 = 0$

$\therefore O_3$ is



The π bond may also be between the other pair of O – atoms.

Thus, O_3 may have two perfect Lewis structures. It is called resonance and the structures are denoted by a doubled head arrow (\leftrightarrow), such as

**HCN molecule**

- (i) Total valence electrons = $1 + 4 + 5 = 10$
- (ii) π – electrons = $6 \times 2 + 2 - 10 = 4$ (2π bonds).
- (iii) C atom is central atom.
- (iv) Skeleton $H \cdot \cdot C \cdot \cdot N$
- (v) Since H – atom needs duet of electrons the two π – bonds are placed between C and N i.e., a triple bond between C and N.



- (vi) In the above structure N is two electrons short of octet. Therefore, two electrons are provided to it.



Some Lewis structures

Table 2.18

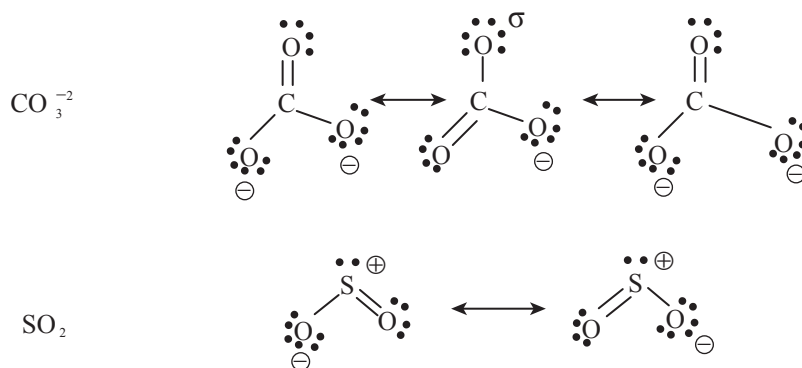
| | N_3^- | NCO^- | BF_3 | CO_3^{2-} | SO_2 |
|-------------------------|--|--|---------------|--------------------|---------------|
| Total valence electrons | 16 | 16 | 24 | 24 | 18 |
| π electrons | $4(2\pi)$ | $4(2\pi)$ | $2(1\pi)$ | $2(1\pi)$ | $2(1\pi)$ |
| Central atom | N | C | B | C | S |
| Skeleton | $\text{N} \cdot \cdot \text{N} \cdot \cdot \text{N}$ | $\text{N} \cdot \cdot \text{C} \cdot \cdot \text{O}$ | | | |
| π -bonds | $\text{N}=\text{N}=\text{N}$ | $\text{N}=\text{C}=\text{O}$ | | | |
| Octet | $\cdot \cdot \text{N}=\text{N}=\text{N} \cdot \cdot$ | $\cdot \cdot \text{N}=\text{C}=\text{O} \cdot \cdot$ | | | |

The species N_3^- , NCO^- , BF_3 , CO_3^{2-} and SO_2 all have more than one perfect Lewis structures. It is due to placing of π bonds at different sites in the structure. That is, all the above will show resonance.

Resonance structure

Table 2.19

| Species | Resonance structures |
|---------------------------------|---|
| N_3^- (Azide ion) | $\begin{array}{c} \ominus \quad \oplus \quad \ominus \\ \cdot \cdot \text{N}=\text{N}=\text{N} \cdot \cdot \end{array} \longleftrightarrow \begin{array}{c} \oplus \quad -2 \\ \cdot \cdot \text{N} \equiv \text{N}=\text{N} \cdot \cdot \end{array} \longleftrightarrow \begin{array}{c} -2 \quad \oplus \\ \cdot \cdot \text{N}^- - \text{N} \equiv \text{N} \cdot \cdot \end{array}$ |
| NCO^- (Cyanate ion) | $\begin{array}{c} \cdot \cdot \text{N}=\text{C}=\text{O} \cdot \cdot \\ \ominus \end{array} \longleftrightarrow \begin{array}{c} \cdot \cdot \text{N} \equiv \text{C}-\text{O} \cdot \cdot \\ \ominus \end{array} \longleftrightarrow \begin{array}{c} -2 \quad \oplus \\ \cdot \cdot \text{N}^- - \text{C} \equiv \text{O} \cdot \cdot \end{array}$ |
| BF_3 | |

**Note:**

- If the chemical species is triatomic or tetraatomic and has π bonds then it will have more than one Lewis structure i.e., it will show resonance.
- Formal charges are shown in the above structures.

Hybridization

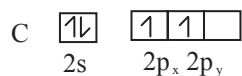
Half-filled orbitals take part in overlap and bond formation. However, there are many elements in which number of half filled orbitals and bonds formed by them differ.

Table 2.20

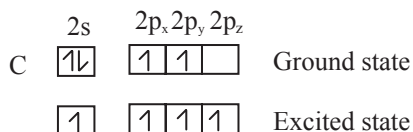
| Atom | Valence electron | No. of unpaired electrons | Bond formed | Examples |
|------|------------------|---------------------------|-------------|--|
| Be | $2s$ | 0 | 2 | BeH_2 , BeF_2 |
| B | $2s$ | 1 | 3 | BF_3 , BH_3 |
| C | $2s$ | 2 | 4 | CH_4 , C_2H_4 , C_2H_2 etc. |

The above anomaly is explained by promotion of electrons to higher energy orbital and then their mixing, i.e., hybridization.

Let us consider carbon which has valence shell configuration,



This configuration has two unpaired electrons. So, carbon should be divalent. Although species like CH_2 (carbene) is known, it is highly reactive reaction intermediate. In its stable compounds carbon is always tetravalent. Tetravalency requires four unpaired electrons. This, carbon achieves by promotion of its one of the two 2s electrons to high-energy 2p orbitals.



The excited state has four unpaired electrons. Thus, carbon can form four bonds. Now one question may be asked. Where from 2s electron gets energy for promotion to higher energy 2p orbital? It is explained as, in excited state C can form four bonds (instead of two) leading to greater energy lowering which compensates need of energy for electron promotion. However, the four bonds of C should not be identical as electrons are in different orbitals, 2s and 2p. But the four bonds of C (in CH_4 , CCl_4 etc.) are found quite similar and they are tetrahedral. Promotion of electron does not explain it. The similarity of four bonds is explained by the concept of hybridization.

The process of mixing of atomic orbitals at an atom to give equivalent (or non – equivalent) orbitals is called “Hybridization”. The new orbitals are known as hybrid orbitals.

Number of hybrid orbitals = Number of atomic orbitals mixed

Conditions for hybridization

Atomic orbitals taking part in the process of hybridization should:

- have comparable energy
- be of comparable size

Advantages of hybridization

- Hybrid orbitals are highly directional
Hybrid orbitals ensure greater overlap. Therefore, hybrid orbitals form much stronger bonds.

Table 2.21

| Molecules | Li_2 | F_2 | C_2 (in C_2H_6) |
|-----------------------|---------------|--------------|---|
| Orbitals for bonding | (s – s) | (p – p) | ($\text{sp}^3 - \text{sp}^3$) |
| Bond energy Kcal/mole | 25 | 36 | 83 |

The above data show that as the directional character of the orbitals increases bond energy increases. All types of atomic orbitals (s, p, d etc.) can form hybrid orbitals.

Important hybrids

Table 2.22

| Hybrid type | Atomic orbital | Orientation of Hybrid orbitals (structure) | Angular separation between hybrids |
|-------------------------|--|--|------------------------------------|
| sp | s + p | Linear | 180° |
| sp^2 | s + 2(p) | Triangular planar | 120° |
| sp^3 | s + 3(p) | Tetrahedral | $109^\circ 28'$ |
| sp^3d | s + 3(p) + d_{z^2} | Trigonal bipyramid | 90° and 120° |
| sp^3d^2 | s + 3(p) + $\text{d}_{x^2-y^2}^2 + \text{d}_{z^2}^2$ | Octahedral | 90° |
| d^2sp^3 | s + 3(p) + $\text{d}_{x^2-y^2}^2 + \text{d}_{z^2}^2$ | Octahedral | 90° |

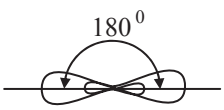
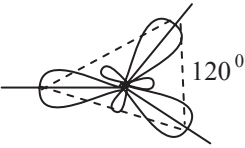
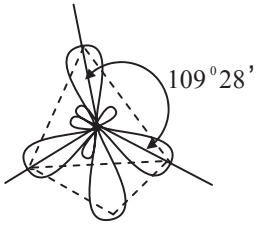
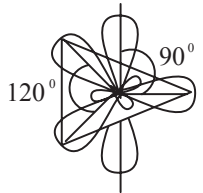
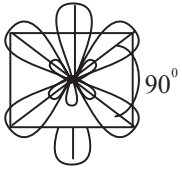
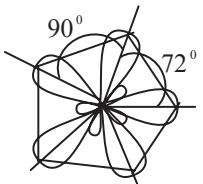
(Continued)

| Hybrid type | Atomic orbital | Orientation of Hybrid orbitals (structure) | Angular separation between hybrids |
|-------------|---------------------------------------|--|------------------------------------|
| dsp^2 | $s + 2(p) + d_{x^2-y^2}$ | Square planar | 90° |
| sp^3d^3 | $s + 3(p) + d_{xy} + d_{yz} + d_{xz}$ | Pentagonal bipyramid | 72° and 90° |
| sd^3 | $s + 3(d)$ | Tetrahedral | |

Note:

- (i) d^2sp^3 is found only in transition metals.
(ii) sd^3 is also found only in first transition series metal ions (MnO_4^- , CrO_4^{2-})
(iii) In sp^3d combination when $d_{x^2-y^2}$ is used the orientation of hybrid is square pyramid. It is rarely found.

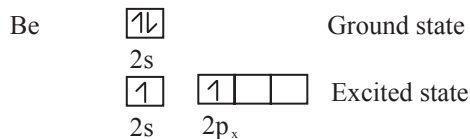
Table 2.23

| Structures | Diagram |
|--------------------------------|---|
| sp Linear |  |
| sp^2 Triangular |  |
| sp^3 Tetrahedral |  |
| sp^3d Trigonal bipyramid |  |
| sp^3d^2 Octahedral |  |
| sp^3d^3 Pentagonal bipyramid |  |

Structure of polyatomic molecules (or ions) can be explained using concept of hybrid orbitals. For example, formation and structure of BeF_2 , CH_4 , C_2H_4 , C_2H_2 etc.

BeF_2

The valence shell of Be is,



The 2s and 2p orbitals of Be in excited state, hybridise to form two sp hybrids having one electron in each. These hybrids are oriented at 180° i.e., linearly.

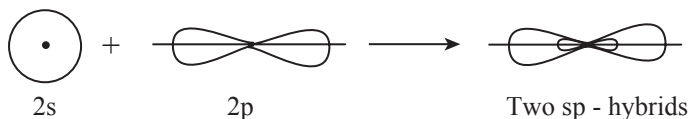


Figure 2.19

These hybrids linearly overlap with half-filled orbital centred at F atoms to form Be – F bonds.

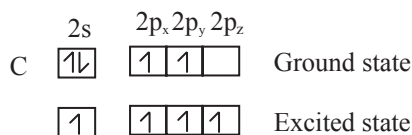


Figure 2.20

Thus, the BeF_2 molecule is linear.

CH_4 molecule

The valence shell of C is,



In the excited state, 2s and 2p orbitals hybridize to form four sp^3 hybrids. These hybrids are oriented along the four corners of a regular tetrahedron. The C – H σ bonds in CH_4 are formed by the linear overlap of sp^3 hybrid orbital of C with 1s of H. Methane, therefore, is a tetrahedral molecule.

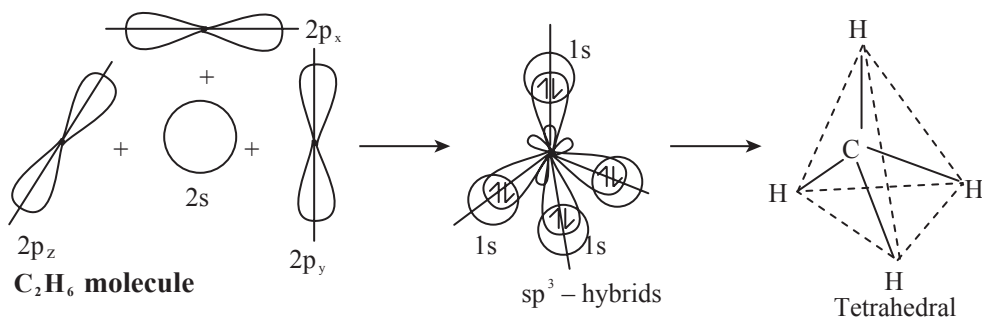


Figure 2.21

C_2H_6 molecule

In C_2H_6 , both C atoms are sp^3 hybridized. There is C – C and C – H σ bonds.

- (i) C – C σ – bond: It is formed by the linear overlap of sp^3 hybrid of one C with that of the other.
- (ii) C – H σ – bonds: It is formed by the linear overlap of sp^3 hybrids of C with 1s orbital of H.

Therefore, in C_2H_6 two tetrahedral are joined at a corner.

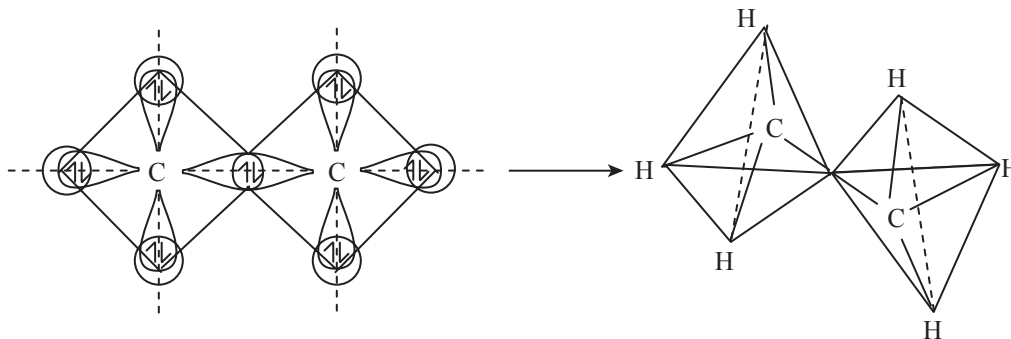


Figure 2.22

Ethylene C_2H_4 molecule

Ethylene is found triangular planar. It can be explained using sp^2 hybrid nature of C orbitals.

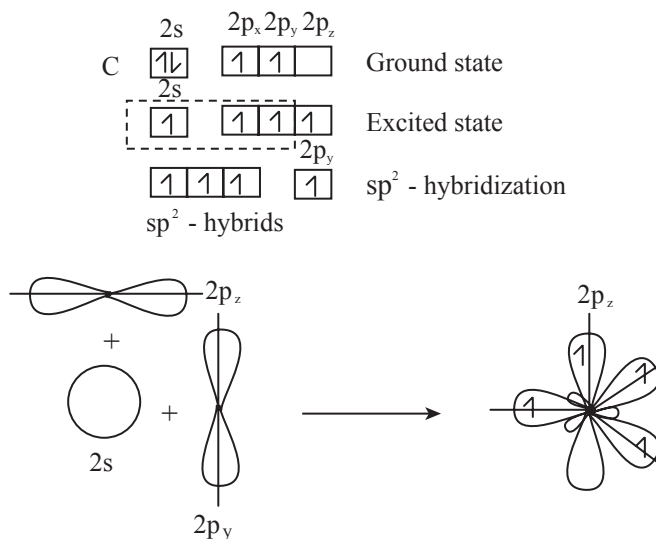


Figure 2.23

The sp^2 -hybridized C atom has three sp^2 -hybrids oriented along the corners of an equilateral triangle. The unhybridized $2p_y$ orbital is perpendicularly present at the plane of C and the three hybrids.

In C_2H_4 the bonds present are formed as:

- (i) C – H, σ – bonds (four) are formed by the linear overlap of sp^2 of C with 1s of H.
- (ii) C – C, σ – bond is formed by the linear overlap of sp^2 of one carbon with that of the other.
- (iii) C – C, π – bond: It is formed by side ways overlap of $2p_y$ orbitals present at carbon atoms.

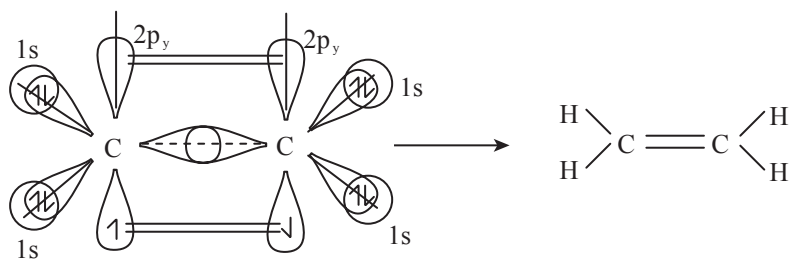
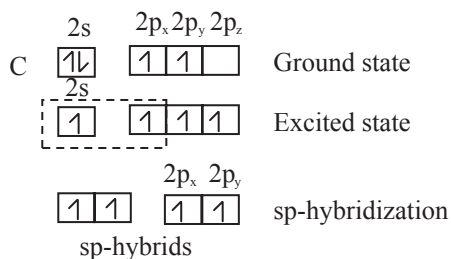


Figure 2.24

Acetylene, C_2H_2 molecule

This molecule is linear in structure. It is explained by using sp – hybrid orbitals of carbon.



The sp -hybridized C atom leaves two atomic p-orbitals ($2p_x$ and $2p_y$) which are mutually perpendicular. In C_2H_2 bonds are formed as:

- C – C, σ – bonds: It is formed by the linear overlap of sp -hybrid orbital of one carbon with that of the other.
- C – H, σ – bonds (two) are formed by the linear overlap of sp -hybrid of C with $1s$ of H.
- C – C, π – bonds: The two π -bonds are formed by side-by-side overlap of $2p_x - 2p_x$ and $2p_y - 2p_y$ orbitals.

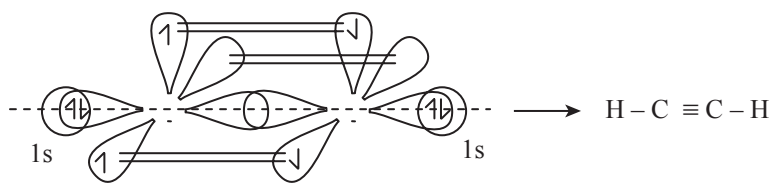


Figure 2.25

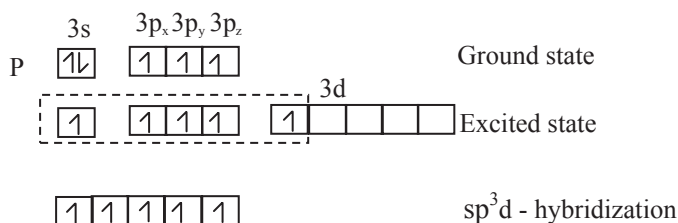
The two π – bonds are in planes at right angles to each other. Thus, C_2H_2 molecule is sheathed in a cylinder of negative charge.

Use of d – orbitals in hybrids

The higher covalencies of five, six etc., are found with third and higher period elements (P, S etc.). They are achieved by the use of low lying vacant d-orbitals ($3d$ in P, S etc.).

PCl_5 molecule

Phosphorus in PCl_5 uses $3d_z^2$ orbital to form sp^3d hybrids. The five hybrids are used by P to form five bonds with Cl.



As the size and energy of 3s, 3p and 3d orbitals are very comparable, this mixing becomes possible. The five bonds in PCl_5 are oriented along the corners of a trigonal bipyramid making PCl_5 a tpb molecule.

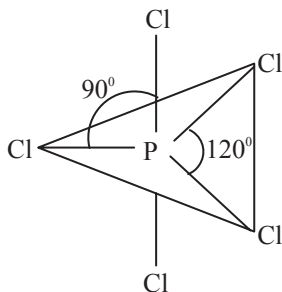
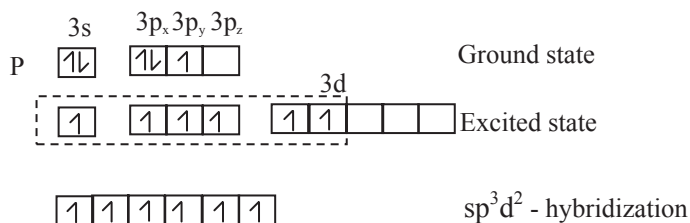


Figure 2.26

The bonds which lie in the triangular plane are known as equatorial bonds whereas bonds which are perpendicular on the triangular plane are called axial bonds. Thus there are three equatorial and two axial bonds in PCl_5 .

SF_6 : Sulphur hexafluoride

The S – atom uses sp^3d^2 hybrids for the formation of SF_6 .



The 3s and 3p electron are promoted to two of the d-orbitals ($d_{x^2-y^2}$ and d_z^2).

It becomes possible because 3d is comparable in energy to 3s and 3p. These orbitals are also of comparable size. Therefore, hybrid is formed easily. The six hybrids are oriented along the corners of an octahedron. They are used by S to form six S – F σ – bonds. The molecule is, therefore, octahedral.

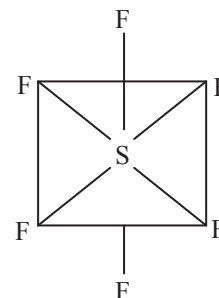
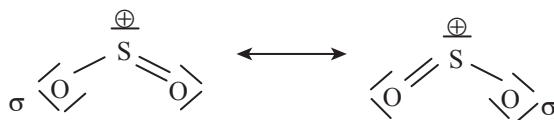


Figure 2.27

Resonance

Many chemical species may have more than one perfect Lewis structure (or valence bond structure). This phenomenon is called resonance and the structures are known as resonating structures or canonical forms. The structures are written putting double head arrow (\longleftrightarrow) between them.

The concept of resonance was introduced in valence bond model by L. Pauling, to explain molecular properties like bond energy, bond length, bond angle etc. For example, SO_2 .



These structures have S – O single and double bonds which should not be equal. However, both the S – O bonds are equal. It is because the actual molecule is represented by neither of the structures. It is actually a resonance hybrid of both the structures and so both S – O bonds are equal. The resonance structures have no physical reality i.e., they can not be synthesized or isolated.

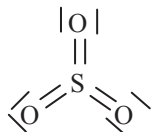
Rules of resonance

- The position of nuclei should remain fixed in all the structures.
- The molecule (or ion) should be planar (or nearly so).
- Number of lone pairs should be equal in all the structures.
- The structures should have comparable energy.

Table 2.24

| Molecule or ion | Resonance structures | Resonance hybrids |
|--------------------|----------------------|-------------------|
| CO_3^{-2} | | |
| O_3 | | |
| SO_3 | | |

In SO_3 , the S – atom, using valence shell $n = 3$, is not restricted to an octet. Additional bonds may be formed from the S vacant 3d orbitals and lone pairs at O – atoms to equalize charge. So the structure is



Bond order from resonance structures

Bond multiplicity (or bond order) can be calculated using resonance concept,

$$\text{Bond order} = \frac{\text{Total bonds in the molecule (or ion)}}{\text{Number of resonance structures}}$$

For example bond order in CO_3^{2-} ion,

$$\text{Bond order} = \frac{1 + 1 + 2}{3} = \frac{4}{3} = 1\frac{1}{3}$$

The one in bond order is σ bond and $1/3$ is π bond contribution.

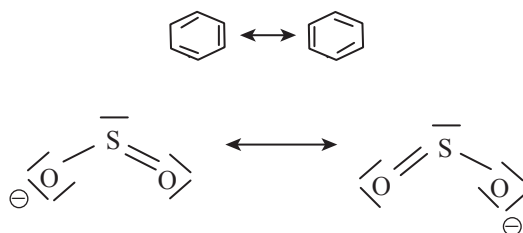
Bond order in SO_2

$$\text{B. O.} = (1 + 2)/2 = 3/2 = 1\frac{1}{2}$$

Resonance effect

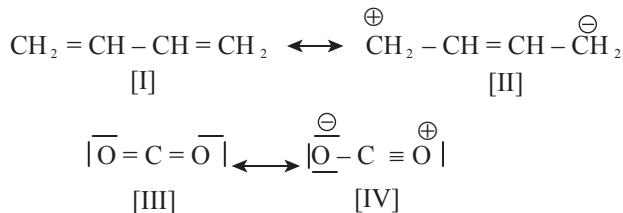
Resonance stabilizes a molecule (or ion). It is known as resonance effect. The following are important in this regard:

- (i) The more is the number of resonating structures the greater is the stability of the molecule (or ion).
- (ii) Equivalent structure are equally stable.



In both the above cases, structures are equivalent.

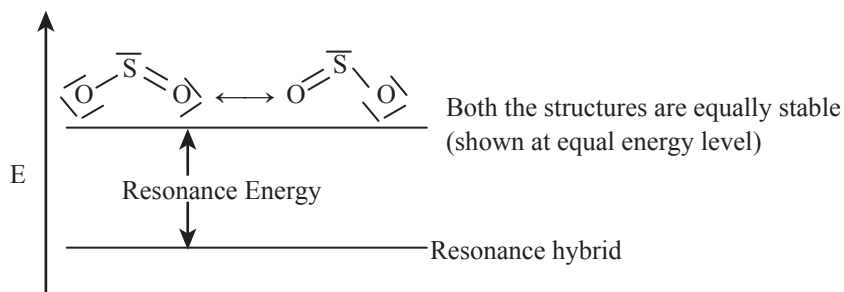
- (iii) Charge separated structures are less stable (or contributing).



The structure (II) and (IV) are charge separated. So, they are less contributing to the resonance hybrid.

Resonance Energy

Resonance stabilizes a molecule i.e., the resonance hybrid has lower energy compared even to the most stable resonating structure. The resonance energy is defined as: the difference in energy between the resonance hybrid and the most stable resonating structure is known as Resonance Energy.

**Figure 2.28**

The higher is the resonance energy more stable is the molecule (or the ion).

Bond length

In every molecule atoms are separated at an equilibrium distance. The bond length is defined as: “The separation between the centers of the two atoms bonded together”. If atoms are taken as hard spheres, then

$$r_{A-B} = r_A + r_B$$

Where r_{A-B} = bond length in the A – B molecule.

r_A = covalent radius of A

r_B = covalent radius of B

Thus bond length may also be defined as – “The sum of the covalent radii of two atoms is bond length”. However, the actual bond lengths are not the same as calculated by the above equation.

Some calculated and actual single bond lengths (Å)

Table 2.25

| Covalent radii (Å) | | Bonds | Calculated bond length (Å) | Actual bond length (Å) |
|--------------------|------|--------|----------------------------|------------------------|
| C | 0.77 | C – F | $0.77 + 0.64 = 1.41$ | 1.32 |
| F | 0.64 | Si – F | $1.17 + 0.64 = 1.81$ | 1.54 |
| Si | 1.17 | C – Cl | $0.77 + 0.99 = 1.76$ | 1.77 |
| P | 1.10 | P – Cl | $1.10 + 0.99 = 2.09$ | 2.04 |
| Cl | 0.99 | Si – C | $1.17 + 0.77 = 1.94$ | 1.87 |

It is seen in the above table that calculated and actual bond lengths compares well but the agreement is not perfect. It is expected as bond lengths vary somewhat with the chemical environment.

The main reasons for variation of bond lengths are:

- (i) Bond polarity, (i.e., $\Delta\chi$ large),
- (ii) Formation of π bonds,
- (iii) Hybrid nature of the atoms forming the bond.

Bond Polarity and Bond Length

When there is large difference in electronegativity of the two atoms the bond length is generally less than the sum of the covalent radii of the two atoms. For example the C – F bond length, calculated is 1.41 Å whereas actual bond length is only 1.32 Å. It is due to polarity in the C – F bond i.e., due to ionic – covalent resonance,

This effect strengthens the bond so there is decrease in bond length

Formation of π -bond and bond length

Formation of π -bond also causes a decrease in the bond length. It is important for C, N, O and F etc. which form π bonds, e.g., C = C, C = N, C \equiv N, C = O, B = F etc. The π -bond may involve p-orbitals i.e., a (p – p) π bond (as in C, N, O, F compounds) or a (d – p) π bond which involve vacant d – orbital and filled p – orbital. The (d – p) π bond is important in third period elements like Si, P, S etc.

Let us consider Si – F bond. The actual Si – F bond distance (1.54 Å) is much shorter than the calculated bond distance (1.81 Å). This large decrease (0.27 Å) is mainly due to π -bonding which involves vacant 3d orbital of Si and filled p – orbital at F.

A part of large decrease is also due to polarity of Si – F bond ($\Delta\chi = 2.2$ for Si and F).

Fractional π bonding may also shorten a single bond.

Table 2.26

| Atom | χ | $\Delta\chi$ |
|------|--------|--------------|
| C | 2.5 | 1.5 |
| F | 4.0 | |

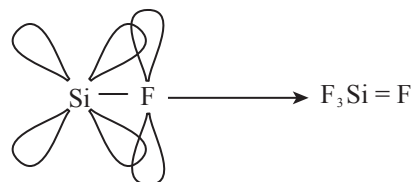


Figure 2.29

Hybrid Nature and Bond Length

The nature of hybrid orbitals involved in bond formation also affects bond length. It is because covalent radius changes with hybrid state.

Hybrid states and covalent radius of Carbon

The larger covalent radius of sp^3 carbon is due to greater projection of sp^3 hybrid from the carbon nucleus (75% p – nature). Thus, the C – C distance in ethane (sp^3 carbon) is 1.54 Å whereas it is only 1.51 Å in toluene ($C_6H_5 - CH_3$). It is because the C – C bond in toluene involves sp^2 carbon of the benzene ring and sp^3 carbon of the CH_3 group.

Multiple bonds are always smaller than the corresponding single bonds. Thus multiple bond radius of an atom is smaller than single bond radius.

Table 2.27

| Hybrid | Covalent radii (Å) |
|--------|--------------------|
| sp^3 | 0.77 |
| sp^2 | 0.73 |
| sp | 0.70 |

Table 2.28

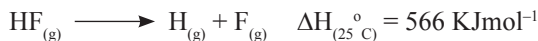
| Bonds | Bonds length (Å) | Radius (Å) | Bonds | Bonds length (Å) | Radius (Å) |
|--------------|------------------|------------|--------------|------------------|------------|
| C – C | 1.54 | 0.77 | N – N | 1.45 | 0.72 |
| C = C | 1.33 | 0.66 | N = N | 1.25 | 0.62 |
| C \equiv C | 1.20 | 0.60 | N \equiv N | 1.10 | 0.55 |

It is generally found that the double and triple-bond radii are only 0.87 and 0.78 times the single bond radii respectively.

Bond Energy

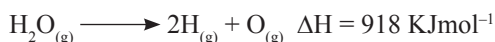
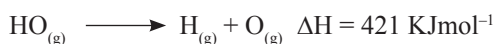
The energy required to break a bond is called the bond energy (or the energy released when a bond is formed is called the bond energy).

For diatomic molecules like H_2 , HF, HI etc. the bond energy is the dissociation energy of the molecule.



It is also found that when HF bond is formed 566 KJmol^{-1} is released.

For a polyatomic molecule H_2O , NH_3 , CH_4 etc. bond energy is the average of the dissociation energy of the molecule. For example,



Therefore, the average,

$$\text{O} - \text{H} \text{ bond energy} = 918/2 = 459 \text{ KJmol}^{-1}.$$

The energy required to break two O – H bonds, one after the other in H_2O is different. It is due to different chemical environment. Bond energy of covalent molecules can be calculated using Pauling's formula.

$$E_{\text{A-B}} = \frac{1}{2}(E_{\text{A-A}}) + \frac{1}{2}(E_{\text{B-B}}) + 23(\chi_{\text{A}} - \chi_{\text{B}})^2$$

Where $E_{\text{A-B}}$, $E_{\text{A-A}}$ and $E_{\text{B-B}}$ are the bond energies of the molecules A – B, A_2 and B_2 respectively and χ_{A} and χ_{B} are the electronegativities of A and B.

Bond energy of HCl

$$E_{\text{H-Cl}} = \frac{1}{2} E_{\text{H-H}} + \frac{1}{2} E_{\text{Cl-Cl}} + 23(\chi_{\text{Cl}} - \chi_{\text{H}})^2$$

$$= \frac{1}{2} \times 104 + \frac{1}{2} \times 58 + 23(3.0 - 2.1)^2$$

$$= 52 + 29 + 18.63 = 99.63 \text{ Kcal/mol}.$$

It compares well with the experimental value $103 \text{ Kcal mol}^{-1}$.

A more accurate value of bond energy is obtained when the geometric mean,

$$\sqrt{E_{\text{A-A}} \times E_{\text{B-B}}}$$

is used instead of the arithmetic mean .

$$\frac{E_{\text{A-A}} + E_{\text{B-B}}}{2}.$$

The term $23(\chi_{\text{A}} - \chi_{\text{B}})^2$ includes ionic contribution towards bond energy. Therefore, larger the ionic character in a covalent bond higher is the bond energy.

For a molecule like A – B (where $\chi_{\text{A}} > \chi_{\text{B}}$) the molecule is actually a resonance hybrid of the covalent and the ionic structures.

Thus the term $23(\chi_{\text{A}} - \chi_{\text{B}})^2$ is a measure of the resonance energy.

In addition to single bonds, there are double and triple bonds also. Such bonds are mainly formed by C, N, O, S, P etc.

The bond energy increases as the bond order increases.

*Some bond energies (KJmol⁻¹)***Table 2.29**

| Bond | Bond energy | Bond | Bond energy | Bond | Bond energy | Bond | Bond energy |
|---------|-------------|--------|-------------|--------|-------------|--------|-------------|
| H – H | 436 | H – F | 566 | C – F | 485 | C – H | 416 |
| C – C | 356 | H – Cl | 431 | C – Cl | 327 | P – F | 490 |
| F – F | 158 | H – Br | 366 | C – Br | 285 | P – Cl | 319 |
| Cl – Cl | 242 | H – I | 299 | C – I | 213 | P – Br | 264 |
| Br – Br | 193 | O – F | 190 | N – F | 272 | P – I | 184 |
| I – H | 151 | C – O | 336 | N – Cl | 193 | S – F | 326 |
| | | | | | | N – N | 160 |

*Multiple bond energies (KJmol⁻¹)***Table 2.30**

| Bond | Bond energy | Bond | Bond energy | Bond | Bond energy | Bond | Bond energy |
|-------|-------------|-------|-------------|-------|-------------|-------|-------------|
| C = C | 598 | N = N | 418 | C = N | 616 | C = O | 695 |
| C ≡ C | 813 | N ≡ N | 946 | C ≡ N | 866 | C ≡ O | 1073 |

The above discussions show that molecular parameters like bond length, bond order, bond energies are closely related. If bond order increases bond energy increases and bond length decreases.

Table 2.31

| Bond | Bond order | Bond energy (KJmol ⁻¹) | Bond length (Å) |
|-------|------------|------------------------------------|-----------------|
| C – C | 1 | 356 | 1.54 |
| C = C | 2 | 598 | 1.33 |
| C ≡ C | 3 | 813 | 1.20 |
| C – O | 1 | 336 | 1.42 |
| C = O | 2 | 695 | 1.21 |
| C ≡ O | 3 | 1073 | 1.128 |
| N – N | 1 | 160 | 1.45 |
| N = N | 2 | 418 | 1.25 |

Structure and shape of Molecules

VSEPR model

VSEPR stands for valence shell electron pair repulsion. In a molecule (or ion) the central atom is surrounded by electron pairs (bond pairs and lone pairs). The electron pairs repel each other. To minimize this repulsion electron pairs remain as far apart as possible. This results into a definite geometrical arrangement of electron pairs around the central atom leading to a definite structure. It is decided using VSEPR rules. They are:

1. Total electron pairs around the central atom remain at maximum angular separation to minimize repulsion. It results into a definite structure:

Table 2.32

| Total electrons pairs | Structure | Bond Angle |
|-----------------------|----------------------------|------------|
| 2 | Linear | 180° |
| 3 | Triangular planar | 120° |
| 4 | Tetrahedral (Td) | 109°28' |
| 5 | Trigonal bipyramid (tbp) | 90°, 120° |
| 6 | Octahedral (Oh) | 90° |
| 7 | Pentagonal bipyramid (pbp) | 72°, 90° |

2. Lone pair electrons occupy more space than bond pair electrons (lp is affected by only one nucleus whereas bp lies between two nuclei). The repulsion order is
 $lp - lp > lp - bp > bp - bp$
3. Increase in electronegativity of the terminal atom causes decrease in bond angle [HOH – 105°, FOF – 102°]
4. Double and triple bonds occupy more space than a single bond (bond angle is affected).
5. Double and triple bonds are taken as one pair in VSEPR. [H – C \equiv N, both C – H and C \equiv N are taken as one pair].


Structure and Shape

The arrangement of total electron pairs around the central atom determines structure. But shape is determined by bond pairs and lone pairs both. When

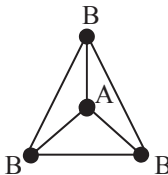
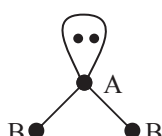
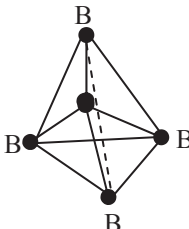
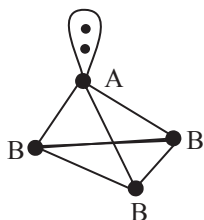
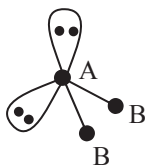
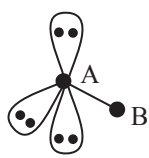
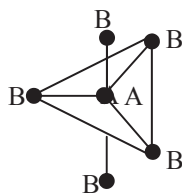
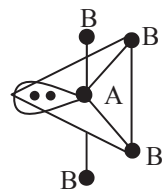
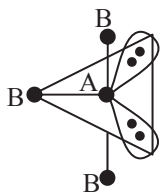
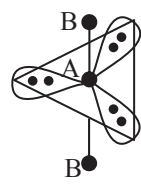
1. There is no lone pair at the central atom structure and the shape are similar (CH₄ is Td in structure and shape both as there is no lp at C).
2. There is lone pair at the central atom shape is different from the structure (NH₃ is Td in structure but triangular pyramid in shape as N has lp). It is because electrons are not located in the structure (only nuclei are located)

Shape of Molecules

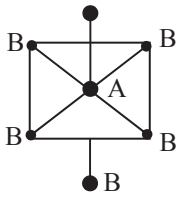
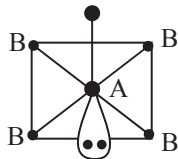
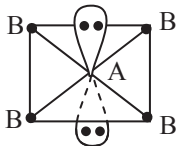
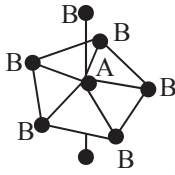
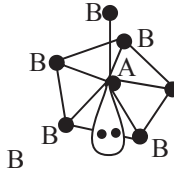
Table 2.33

| Electron pairs | Possible Molecules E = lone – pair | | Shape | |
|----------------|---------------------------------------|---|--------|------------------|
| 2 | AB ₂ |  | Linear | BeF ₂ |


(Continued)

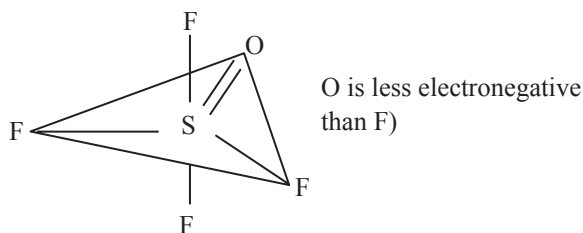
| Electron pairs | Possible Molecules E = lone – pair | Shape | |
|----------------|--|---|--|
| 3 | AB_3, AB_2E ($BF_3, SnCl_2$) |  (trigonal planar) |  (Angular) |
| | | | |
| 4 | AB_4, AB_3E (CH_4, NH_3) |  (Tetrahedral) |  (trigonal pyramid) |
| | | | |
| 5 | AB_2E_2, ABE_3 (H_2O, OCl^-) |  (Angular) |  (Linear) |
| | | | |
| 5 | AB_5, AB_4E (PCl_5, SF_4) |  (trigonal bipyramid) |  (distorted Td) |
| | | | |
| 5 | AB_3E_2, AB_2E_3 (ClF_3, I_3^-) |  (distorted T - shaped) |  (Linear) |
| | | | |

(Continued)

| Electron pairs | Possible Molecules E = lone – pair | Shape |
|----------------|---------------------------------------|---|
| 6 | AB_6, AB_5E (SF_6, BrF_5) |  (Octahedral)  (Slightly distorted square pyramid) |
| 7 | AB_4E_2 (XeF_4) |  (Square planar) |
| | AB_7, AB_6, E (IF_7, XeF_6) |  (Pentagonal biyramid)  (distorted Oh) |

Note

- (i) E represents lone-pair, denoted as: 
- (ii) Lone pairs in trigonal bipyramid always occupy equatorial positions. [Corners of the triangle are equatorial positions, bonds perpendicular on this trigonal plane are called axial bonds). Less electronegative atoms also occupy equatorial position. Thus SOF_4 has the structure:

**Figure 2.30**

- (iii) Lone pairs in octahedral structure occupy axial positions.

Calculation of Total electron pairs around the Central atom

Valence shell electron pair (VSEPR) model is used to determine molecular geometry. It needs to know the number of bond-pair and lone-pair (or non-bonded-pair) of electrons around the central atom.

Students generally find it difficult. A most simple and quick method to determine bond-pair and lone-pair electrons is described here.

Molecules (or ions) generally contain H, halogens and oxygen as terminal atoms. Nitrogen and S are rarely found as terminal atoms (e.g., N_3^- , CS_2 etc.).

Stable chemical species are those in which atoms achieve closed shell electron configuration like noble gases [i.e., either a duet configuration like other noble gases ($ns^2 np^6$)]. This basic concept has been used to find out bond-pair and lone-pair electrons around the central atom which ultimately determines molecular geometry. The central atoms belonging to third period onwards like Si, P, S etc. may have more than 8 electrons (hypervalent state) around them using their vacant d-orbitals. The method will apply in these cases also. The following steps are followed:

- Number of **bond-pairs** = Number of **terminal atoms** (It is because σ - bonds determine geometry).
- Halogens and H require only one electron of the central atom to make their electron configurations stable (i.e., octet and duet).
- Oxygen and sulphur require **two electrons** of the central atom to complete octet.
- Nitrogen atom uses **three electrons** of the central to complete octet.
- Charge on the ion is supposed to be due to loss or gain of electron by the central atom. For example, in NO_2^+ ion the effective number of valence electrons of nitrogen is 4 (i.e., $5 - 1$) and in NO_2^- the number of Valence electrons of N is 6 (i.e., $5 + 1$).
- Central atom achieves octet on its-own.
- The method, however, cannot explain how the bonding electron are used by the atoms. For, this one has to use method to write Lewis structure.

Some examples are given below:

NH_3 – Nitrogen has five valence electrons. Three of these electrons will be used by three H atoms to achieve duet configuration of He ($1s^2$). It will leave two electrons at N i.e., a lone pair. Thus, NH_3 has three bond pairs and one lone-pair which makes, ammonia trigonal pyramidal.

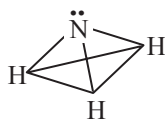


Figure 2.31

SF_6 – Sulphur atom has 6 valence electrons. All of the valence electrons are used by six fluorine atoms for bond formation, leaving no lone pair at S atom. It is, thus, a six electron-pair molecule and has octahedral geometry. The following table illustrate some more examples.

Table 2.34

| Molecule or Ion | Bond pairs = Terminal atoms | Valence electrons at central atom | Electron used by terminal atoms | *Lp at central atom (Ves of central atom – es used by terminal atoms) | Geometry |
|-----------------|-----------------------------|-----------------------------------|---------------------------------|---|--------------------|
| PCl_5 | 5 | (P) 5 | 5 Cl = 5 | 0 | Trigonal bipyramid |
| XeOF_4 | 5 | (Xe) 8 | 4 O = 2 F = 4 = 6 | 1 | Square pyramidal |
| ClF_3 | 3 | (Cl) 7 | 3 F = 3 | 2 | T – shaped |

(Continued)

| Molecule or Ion | Bond pairs = Terminal atoms | Valence electrons at central atom | Electron used by terminal atoms | | *Lp at central atom (Ves of central atom – es used by terminal atoms) | Geometry |
|--------------------------|-----------------------------|-----------------------------------|---------------------------------|----------------------------------|---|---------------------|
| ICl_4 | 4 | (I) 6 | 4 | $\text{Cl} = 4$ | 1 | Dist. Square planar |
| ICl_4^- | 4 | (I) 8 | 4 | $\text{Cl} = 4$ | 2 | Square planar |
| I_4^- | 2 | (I) 8 | 2 | $\text{I} = 2$ | 3 | Linear |
| XeO_2F_2 | 4 | (Xe) 8 | 2 | $\text{O} = 4$ $\text{F} = 2$ | 1 | Dist. Square planar |
| N_3^- | 2 | (N) 6 | 2 | $\text{N} = 6$ | 0 | Linear |
| CS_2 | 2 | (C) 4 | 2 | $\text{S} = 4$ | 0 | Linear |

Note:

- (i) Ves=Valence electrons,
- (ii) Lp = lone pairs,
- (iii) es=electrons

Odd electron species cannot obey the octet rule on every atom but their geometry may also be determined by the above discussed method. The odd electron is supposed to be present at the central atom to decide geometry. For example, Nitrogen dioxide, NO_2 has 17 valence electrons. It has two bond pairs (N is central atom), and the two O-atoms use only four of the five valence electrons of N leaving fifth electron as lone-pair (half lone-pair) at N. Thus, NO_2 is a bent molecule. Similarly, ClO_2 (19 valence electrons) is also a bent molecule. In this case, there are two bond pairs and one and half long-pair at chlorine atom.

Bond angle

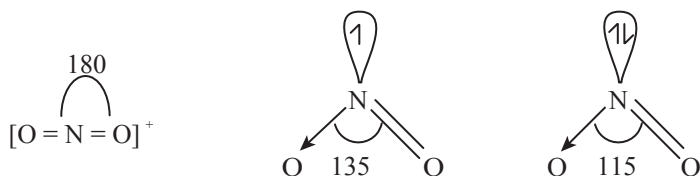
The bond angle is one of the fundamental properties of a molecule (or ion) various factors affect it. Some are discussed here.

Lone -pair at the central atom and bond angle

Presence of lp at the central atom causes a decrease in bond angle. It is due to repulsion between the lp and the bps. The larger the number of lps, the smaller is the bond angle.

Some bond angles**Table 2.35**

| Molecule or ion | Lone pairs at the central atom | Bond angle | |
|----------------------|------------------------------------|------------|------------------|
| CH_4 | 0 | HCH | $109^\circ 28'$ |
| NH_3 | 1 | HNH | $\sim 107^\circ$ |
| H_2O | 2 | HOH | $\sim 105^\circ$ |
| NO_2^+ | 0 | ONO | $\sim 180^\circ$ |
| NO_2 | $\frac{1}{2}$ (i.e., one electron) | ONO | $\sim 135^\circ$ |
| NO_2^- | 1 | ONO | $\sim 115^\circ$ |



However, if lps are symmetrically distributed around the central atom bond angle may not change. For example in I_3^- and XeF_4 .

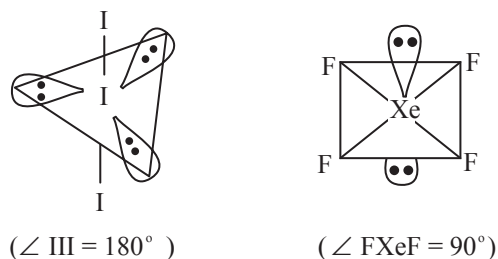


Figure 2.32

Electronegativity and Bond Angle

- (a) When electronegativity of the terminal atom increases, bond angle decreases. In H_2O , bond angle HOH is $\sim 105^\circ$ but in F_2O the bond angle is $\sim 102^\circ$. It is due to shift of bond pair electrons from the central atom towards the terminal atom. It decreases bp–bp repulsion so bond angle decreases.

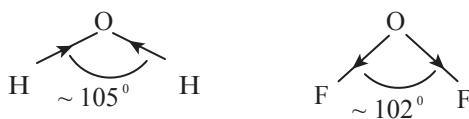
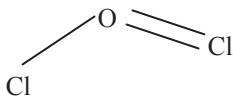


Figure 2.33

But if the terminal atom has vacant d – orbitals bond angle may not decrease rather it increases. It is due to $(d - p)\pi$ bonding. Example, in OCl_2 , the angle ClOCl is $\sim 111^\circ$.



The repulsion between double bond electrons and single bond electrons becomes large. It causes increase in bond angle.

- (b) When electronegativity of the central atom increases bond angle increases. Increase in electronegativity of the central atom cause concentration of bond pairs towards the central atom. It results into larger bp–bp repulsion and so bond angle increases. For example, bond angle in H_3O^+ is larger than NH_3 as O–atom is more electronegative.

Table 2.36

| Molecules | Bond angle | Molecule | Bond angle |
|------------------------------|------------|------------------|------------|
| H ₂ O | 105 | NH ₃ | 107° |
| H ₂ S | 92 | PH ₃ | 94° |
| NH ₃ | 107 | AsH ₃ | 92° |
| ⁺ OH ₃ | 115 | | |

Multiple bonds and bond angle

The two electron pairs of a double bond occupy more space than the one electron pair of a single bond. It causes increases in bond angle. Some examples are given below:

Table 2.37

| Molecules | Single Bond XMX (°) | Double bond /Single bond XM = O (°) |
|-----------------------|------------------------|--|
| F ₂ C = O | 108 | 126 |
| Cl ₂ C = O | 111 | 124 |
| F ₂ S = O | 93 | 107 |
| Br ₂ S = O | 96 | 108 |

Effects of vacant d-orbitals**1. Expansion of Valence:**

Vacant d – orbitals at the central atom may cause valance expansion. For example N is tri and tetravalent only whereas P is tri, tetra, penta and hexavalent. The penta and hexavalency of P is due to the presence of vacant 3d – orbitals in the valence shell of P (N has no d-orbitals in its valence shell). Therefore, third period (or higher period) elements like Si, P, S, Cl etc can use their d-orbitals to expand their valency i.e., coordination number.

Table 2.38

| Element | Species | Hybridization of the central atom | Coordination number |
|---------|--|--|------------------------|
| Si | SiF ₆ ²⁻ | Sp ³ d ² | 6 |
| P | PCl ₅ , PCl ₆ ⁻ | sp ³ d & sp ³ d ² | 5,6 |
| S | SF ₆ | sp ³ d ² | 6 |
| Cl | ClF ₃ | sp ³ d | 5 |

But higher coordination numbers are achieved only with more electronegative atoms (F, Cl etc). It is because more electronegative atoms can cause contraction of the valence shell of the central atom, hybrids involving d orbitals become possible, leading to increase in coordination number. Therefore, PF₅ SF₆ etc., are known but not PH₅.

2. (d – p) π bonding

Compounds containing third period (or higher period) elements (Si, P, S etc) and N or O or F (i.e., which has lone pairs) involve in (d – p) π bonding. It is due to vacant d – orbitals at Si, P etc and lone pairs at N or O or F. Thus,

P – O bond in POX_3 [X = F, Cl, Br]

S – O bond in SOX_2 [X = F, Cl, Br]

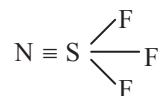
S – N bond in SNF_3

Si – N bond in $(\text{SiH}_3)_3\text{N}$ etc.

have (d – p) π bonding. Such a π -bonding has effect on

- (a) bond length
- (b) bond energy
- (c) molecular structure

Thionyl halides (OSX_2) thiazyl fluoride (NSF_3) are very good examples of the above discussed effect. Most electronegative F atom causes large contraction in the size of 3d orbitals of S. Very effective (d – p) π bonding takes place. Therefore, the N – S bond in NSF_3 is shortest (1.42Å) known between N and S. The structure is



The O – S bond order is highest in OSF_2 and lowest in OSBr_2 for the same reason.

Parameters in OSX_2

Table 2.39

| Properties O – S bond | O = SF ₂ | O = SCl ₂ | O = SBr ₂ |
|--------------------------|---------------------|----------------------|----------------------|
| Bond order | —————→ | | Decreases |
| Bond length | —————→ | | Increases |
| Bond energy | —————→ | | Decreases |

The (d–p) π bonding has effect on molecular structure also. Unlike trimethylamine, $(\text{CH}_3)_3\text{N}$ [trigonal pyramid] trisilylamine is trigonal planar. It is due to (d – p) π bonding in trisilylamine.

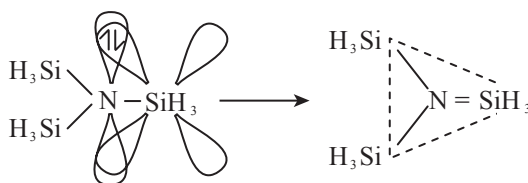
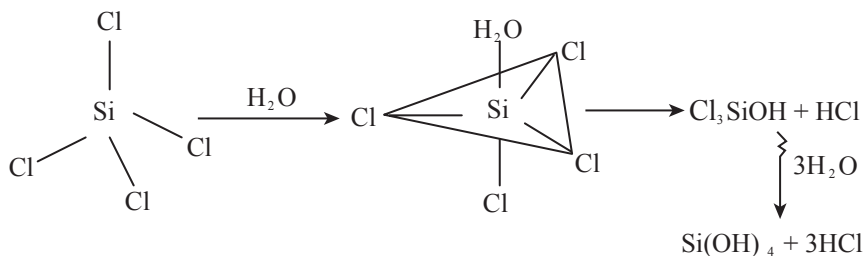


Figure 2.34

3. Vacant d – orbitals and reactivity

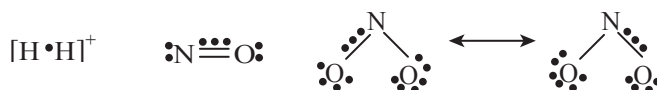
The presence of vacant d – orbitals at the central atom affect reactivity to a great extent. For example, CCl_4 is inert towards water whereas SiF_4 , SiCl_4 , PCl_3 , TiCl_4 etc are easily hydrolysed. It is because Si, P, Ti etc have vacant d – orbitals. The vacant d – orbitals act as electron pair acceptor, help attack by H_2O easy, leading to hydrolysis. The reactions can be summarized as:



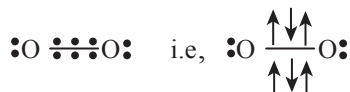
Odd electron molecules

Many molecules have odd number of valence electrons. They are called odd electron molecules. Such species contain unpaired electrons and so are paramagnetic.

Odd electron molecules have three-electron bond. A three-electron bond is equivalent to half bond. The H_2^+ has one-electron bond. It is also half-bond. Odd electron molecules have no octet of electrons to all atoms.



The above structures show that N – O bond order in nitric oxide (NO) is 2.5 and in NO_2 the N – O bond order is $1 + \frac{1}{2} = 1.5$. Dioxygen (O_2) has even number of valence electrons (*12) but the molecule is paramagnetic. It can be explained considering three electron bonds.



Molecular Orbital Model

It is one of the ways to explain bonding in molecules or ions. The method was developed by Hund and Mulliken. Important concepts are as follows:

1. As atoms have atomic orbitals for electrons molecules have molecular orbital.
2. Atomic orbitals are unicentric (i.e., influenced by only one nucleus) but molecular orbitals are polycentric (i.e., they are influenced by nuclei of all the atoms forming bond). Thus in this theory a molecule is regarded as a system of electrons and nuclei in which each electron moves in the field of all the nuclei.
3. Molecular orbitals are formed by linear combination of atomic orbitals (the LCAO method). It is adding and subtracting of suitable atomic orbitals. It may be represented in a very simple way as

Table 2.40

| Molecules | Valence Electrons |
|----------------|-----------------------|
| H_2^+ | 1 |
| NO | $5 + 6 = 11$ |
| NO_2 | $5 + 6 \times 2 = 17$ |
| ClO_2 | $7 + 6 \times 2 = 19$ |

$$\psi_1 = \psi_a + \psi_b \text{ and } \psi_2 = \psi_a - \psi_b$$

Where ψ_a and ψ_b are atomic orbitals at two atoms, ψ_1 and ψ_2 are resultants.
For such a combination the atomic orbitals should satisfy the following conditions.

- (a) The atomic orbitals should be of comparable energy.
 - (b) They should have the same symmetry relative to the bond axis.
 - (c) They should overlap as much as possible.
4. Number of molecular orbitals formed equals number of atomic orbitals combined.
 5. Half of the molecular orbitals have energy lower than the energy of the atomic orbitals. They favour bonding and are obtained by addition of wave functions (i.e., $\psi_a + \psi_b$). Such molecular orbitals are known as bonding MO. They are denoted by σ , π , δ etc.
 6. Rest half of the molecular orbitals have energy greater than the energy of the atomic orbitals. They do not favour bonding and result by the combination $\psi_a - \psi_b$. They are known as antibonding MO and are denoted by σ^* , π^* , δ^* etc.
 7. Filling of electrons in molecular orbitals follow Aufbau principle, Pauli's exclusion principle and Hund's rule.
 8. The stability of a molecule (or ion) is decided by a property known as Bond order (BO). It is defined as,

$$\text{Bond order} = \frac{n_b - n_a}{2}$$

where n_b = number of electrons in bonding MO, n_a = number of electrons in antibonding MO.

Bond order can be a whole number (1 or 2 or 3) or a fraction (0.5, 1.5, 2.5 etc) but can change by 0.5 only. The bond orders 1, 2 and 3 can roughly be compared with single bond, double bond and triple bond.

Bond order affects molecular parameters greatly. Some of these are

(a) Bond order and stability

Bond order and stability are directly related. Thus higher the bond order greater is the stability and vice versa.

Table 2.41

| Molecule | Bond order |
|----------|------------|
| N_2 | 3.0 |
| N_2^+ | 2.5 |

$\therefore N_2$ is more stable than N_2^+

(b) Bond order and Bond Energy

Bond order and bond energy are also directly related. Thus, higher the bond order greater is the Bond energy.

Thus bond energy in N_2 is greater than N_2^+ .

(c) Bond order and Bond Length

Bond order and bond length are inversely related.

Bond order $\propto 1 / \text{Bond length}$

Thus, higher the bond order smaller is the bond and vice versa.

Table 2.42

| Species | B. O. | Bond | Bond length (Å) |
|-----------------------------|-------|-------|-----------------|
| N ₂ | 3.0 | N – N | 1.097 |
| N ₂ ⁺ | 2.5 | N – N | 1.116 |

9. Magnetic properties of species can also be explained by MO model.

Molecular species having unpaired electrons are paramagnetic. It is represented in terms of paramagnetic moment, μ . It is given by

$$\mu = \sqrt{n(n+2)} \text{ BM, where } n = \text{number of unpaired electrons.}$$

However, substances having all their electrons paired are diamagnetic. There μ is zero.

The MO configuration of a molecule (or ion) shows presence or absence of unpaired electrons. Therefore, magnetic properties can be determined.

Formation of molecular orbitals can be represented in a qualitative way as

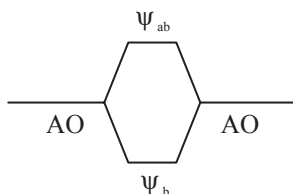


Figure 2.35

Where ψ_b = bonding MO, ψ_{ab} = antibonding MO

Shape and symmetry of molecular orbitals

Molecular orbitals formed by the linear combination of different atomic orbitals have different shape. It is given below

- (a) Combination of s and s orbitals

The combination of two s atomic orbitals centred at two atoms produces two molecular orbitals, one bonding σ and the other antibonding, σ^* . The bonding σ MO has cylindrical symmetry around the bond axis. The σ^* has a nodal plane perpendicular to the bond axis.

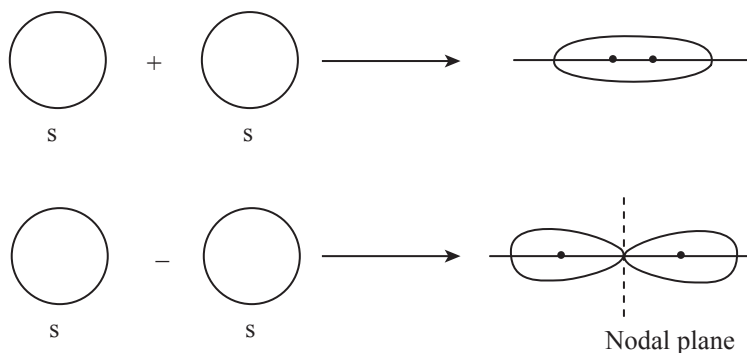


Figure 2.36

(b) Combination of s and p orbitals

The combination of s and p orbitals also produce one bonding σ MO and the other antibonding σ^* MO. The $\sigma_{(s-p)}$ is cylindrical around the bond axis. But the $\sigma^*_{(s-p)}$ orbital has no cylindrical symmetry and has a nodal plane perpendicular to the bond axis.

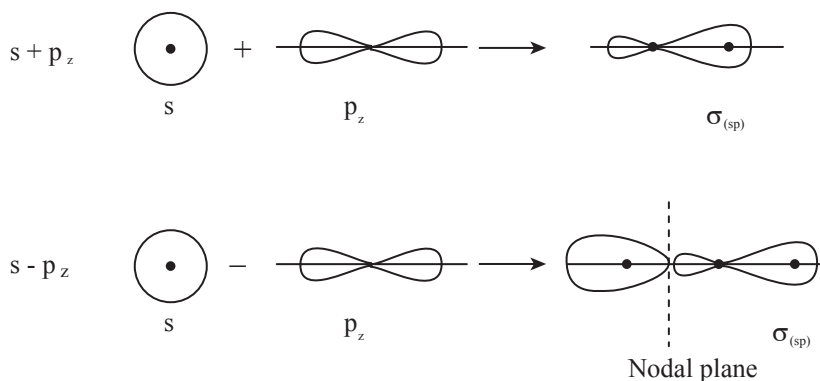


Figure 2.37

(c) Combination of p and p - orbitals

The p – orbitals can combine in two different ways

- (i) At an axis and (ii) At parallel axes which are perpendicular on the bond axis. It results into the formation of π bonds.

When two p orbitals combine at an axis (say on z – axis) two MOs are formed. One of these is bonding $\sigma_{(p-p)}$ MO which has cylindrical symmetry around the bond axis. The antibonding, $\sigma^*_{(p-p)}$ has no cylindrical symmetry around the bond axis. It has a nodal plane perpendicular to the bond axis.

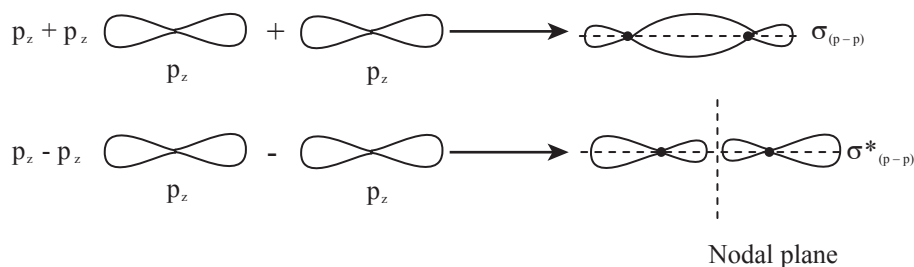


Figure 2.38

Formation of π bonds

When two p-orbitals (p_x and p_x or p_y and p_y) at parallel axes combine a π -bond is formed. The π bonds are always formed in pairs (i.e., π_{2p_x} and π_{2p_y}) because two set of p – orbitals ($p_x - p_x$ and $p_y - p_y$) always combine. Thus, two equivalent (degenerate) π bonding MOs and two equivalent π^* , anti-bonding MOs are formed.

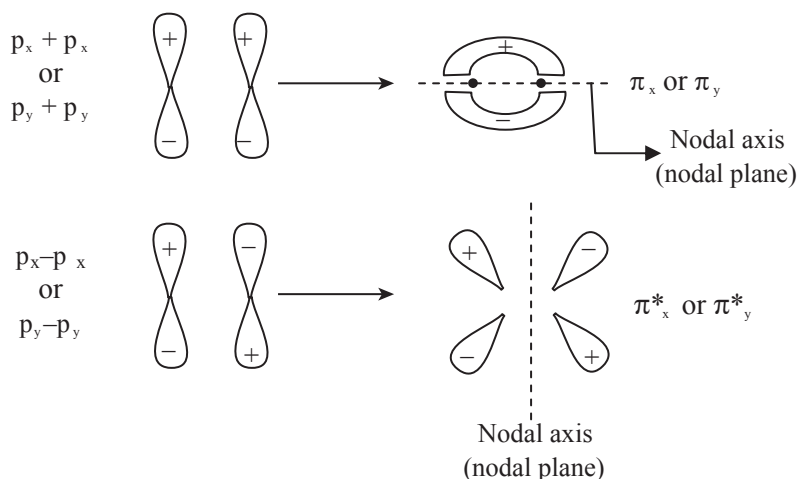


Figure 2.39

The π bonding MO has a nodal plane. This plane lies in the plane of the molecule dividing entire π MO in two parts i.e., above and below the nodal plane. For example, in C_2H_4 the nodal plane lies in the molecular plane and π MO is above and below this plane.

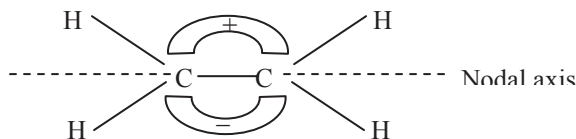


Figure 2.40

The π^* MO also has a nodal plane but it is perpendicular at the internuclear axis (or bond axis) indicated in the diagram of π^* MO.

Homonuclear Diatomic Molecules

Diatomic molecules of the same two atoms are homonuclear (Homo—'the same') diatomics. For example, H_2 , N_2 , C_2 , O_2 , F_2 etc.

Diatomics of the first period elements

The first period elements are H and He and their diatomics are H_2 , H_2^+ , He_2 , He_2^+ etc. The valence orbital for these elements is the 1s orbital only. Therefore, a diatomic molecule will involve only two 1s atomic orbitals for the formation of a diatomic molecule. The 1s atomic orbitals centred at two atoms combine to form one σ MO and the other σ^* MO.

H_2

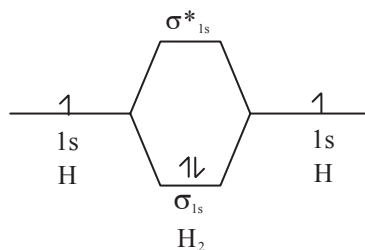
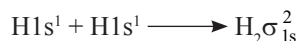


Figure 2.41

Figure 2.41 is the MO diagram of H_2 . The H_2 molecule can also be represented as



The σ_{1s}^2 presentation of H_2 is its molecular orbital configuration. Thus, bond order in H_2 ,

$$\text{B.O.} = \frac{2-0}{2} = 1$$

As there is no unpaired electron in H_2 , the molecule is diamagnetic.

Table 2.43 H_2 , H_2^+ , He_2 and He_2^+ molecules

| Property | | Molecules | | | |
|------------------------------------|-----------------|------------------------|-------------|-----------------------|--------|
| | | H_2^+ | H_2 | He_2^+ | He_2 |
| Molecular orbitals | σ_{1s}^* | — | — | — | — |
| | σ_{1s} | — | — | — | — |
| Bond order | | 0.5 | 1.0 | 0.5 | 0 |
| Bond length (Å) | | 1.06 | 0.74 | 1.08 | — |
| Bond energy (KJmol ⁻¹) | | 256 | 435 | 230 | — |
| Magnetic property, μ (BM) | | Paramag $\sqrt{3}$ | Diamag 0 | paramag $\sqrt{3}$ | — |
| Stability order | | $H_2 > H_2^+ > He_2^+$ | | | |

Note:

- The He_2 molecule is not possible because bond order is zero.
- Molecular cation is formed, like atom, by the loss of electron from the highest occupied molecular orbital (in He_2^+ from σ_{1s}^* MO).
- The diatomic system in the case of noble gas (e.g., He_2^+) is possible only in the excited state. Such species are often called exomomers.
- The bond energy in He_2^+ is smaller than H_2^+ due to the presence of electron in the anti-bonding (σ^*) molecular orbital in He_2^+ .

Homonuclear Diatomics of Second Period Elements

The second period elements are Li, Be, B, C, N, O, F and Ne. Their diatomics are Li_2 , Be_2 , B_2 etc.

The valence orbitals in second period elements is 2s and 2p i.e., a total of four orbitals, 2s, $2p_x$, $2p_y$ and $2p_z$. The 2s and 2p orbitals differ in energy but the three p-orbitals ($2p_x$, $2p_y$ and $2p_z$) are degenerate orbitals.

Let us first assume that z – axis is bond axis.

A combination of 2s atomic orbitals form two σ molecular orbitals, one bonding σ_{2s} and the other antibonding σ_{2s}^* . If z – axis is taken as bond axis then $2p_z$ orbitals will overlap to form two σ - type molecular orbitals, one bonding, σ_{2p_z} and the other anti-bonding $\sigma_{2p_z}^*$. Now the overlap of two $2p_x$ or two $2p_y$ will give π - type molecular orbitals.

A overlap of $2p_x$ and $2p_x$ will give π_{2p_x} bonding and $\pi_{2p_x}^*$ anti-bonding MOs. Similarly $2p_y$ and $2p_y$ overlap will form bonding π_{2p_y} and anti-bonding $\pi_{2p_y}^*$ MOs. As the type of overlap is similar and $2p_x$ and $2p_y$ orbitals are equal in energy, the π_{2p_x} and π_{2p_y} molecular orbitals are degenerate (i.e, of equal energy) so also the $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ MOs.

Spectroscopic data show that MO energy pattern is not similar for all the homonuclear diatomics of the second period. (This difference is due to difference in the energy gap between 2s and 2p atomic orbitals from elements to elements).

It is found that:

- (i) Energy sequence for diatomics from Li_2 to N_2 is,

$$\sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^* \text{ and}$$

- (ii) For diatomics from O_2 to F_2 the energy order is

$$\sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

The inner 1s orbitals overlap to form non – bonding MOs and so are not considered.

MO diagram for Li_2 to N_2

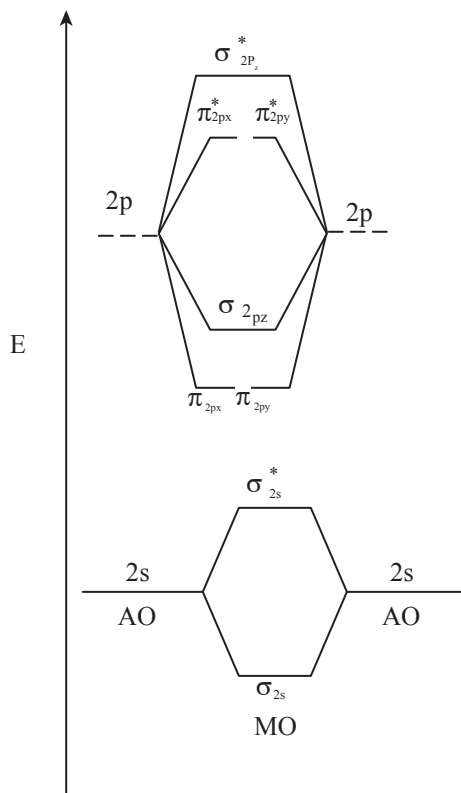


Figure 2.42

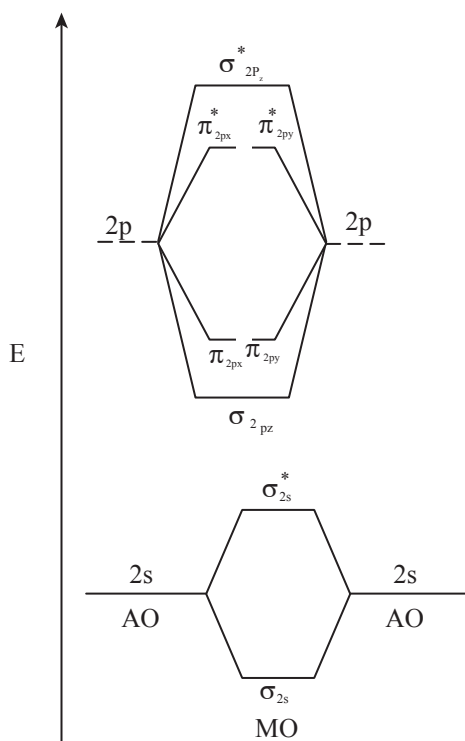
MO diagram for O_2 and F_2 

Figure 2.43

 Li_2 Molecule

Li has valence orbitals configuration $2s^1$. A Li_2 molecule will be formed by the combination of two $2s$ orbitals.

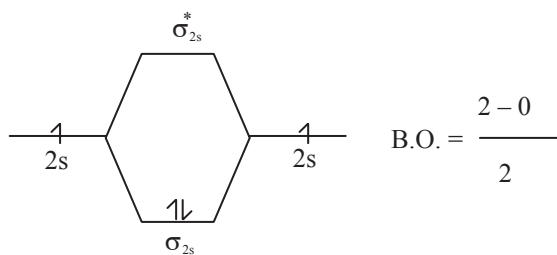
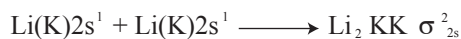
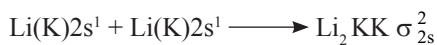


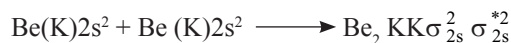
Figure 2.44

It has no unpaired electron. Li_2 is thus a diamagnetic molecule Li_2 is found in vapour state.

(The $1s$ orbitals will constitute non-bonding MOs. It is represented in the MO configuration of Li_2 as K and K).

Be₂ molecule

The valence orbital electron configuration of Be is $2s^2$.



$$\text{B.O.} = \frac{2-2}{2} = 0$$

Therefore, diatomic Be₂ is not possible. The MO diagram is

The σ_{2s} and σ_{2s}^* are non-bonding MOs.

The 1s orbitals will form non-bonding MOs (as in Li₂).

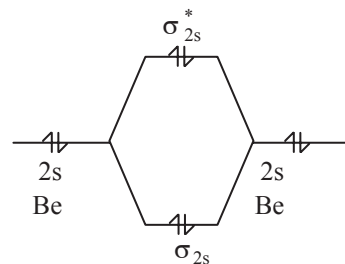


Figure 2.45

B₂, C₂, N₂ molecules

Table 2.44

| Property | B ₂ | C ₂ | N ₂ |
|------------------------------------|----------------|----------------|----------------|
| $\sigma_{2p_z}^*$ | _____ | _____ | _____ |
| $\pi_{2p_x}^* \pi_{2p_y}^*$ | _____ | _____ | _____ |
| $\pi_{2p_z}^*$ | _____ | _____ | |
| $\pi_{2p_x} \pi_{2p_y}$ | | | |
| σ_{2s}^* | | | |
| σ_{2s} | | | |
| Property | B ₂ | C ₂ | N ₂ |
| Bond order | 1 | 2 | 3 |
| Bond length (Å) | 1.59 | 1.31 | 1.1 |
| Bond energy (KJmol ⁻¹) | 288 | 627 | 940 |
| No. of unpaired electrons | 2 | — | — |
| Magnetism | Paramag | Diamag | diamag |
| $\mu(\text{BM})$ | $\sqrt{8}$ | 0 | 0 |

Note:

- Bond order increases (B₂ to C₂ to N₂) because number of electrons in bonding molecular increases.
- Bond energy increases when bond order increases.
- Bond length decreases when bond order increases.
- s and p mixing takes place as energy gap between 2s and 2p is small.

Molecular ions N₂⁺, N₂⁻, (N₂)

Molecular cations are formed when electrons are removed from highest energy occupied molecular orbitals (HOMO).

Molecular anions are formed when electrons are added in lowest energy unoccupied molecular orbitals.

Table 2.45

| Property | N_2 | N_2^+ | N_2^- |
|------------------------------------|---|---|---|
| $\sigma_{2p_z}^*$ | _____ | _____ | _____ |
| $\pi_{2p_x}^* \pi_{2p_y}^*$ | _____ | _____ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ _____ |
| $\pi_{2p_z}^*$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| $\pi_{2p_x} \pi_{2p_y}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| σ_{2s}^* | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| σ_{2s} | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| Bond order | 3 | 2.5 | 2.5 |
| Bond length (Å) | 1.1 | 1.12 | |
| Bond energy (KJmol ⁻¹) | 940 | 828 | |
| No. of unpaired electrons | 0 | 1 | 1 |
| Magnetism | Diamag | Paramag | Paramag |
| μ (BM) | 0 | $\sqrt{3}$ | $\sqrt{3}$ |
| Stability order | $N_2 > N_2^+ > N_2^-$ | | |

 O_2 , F_2 and Ne_2 Molecules**Table 2.46**

| Property | O_2 | F_2 | Ne_2 |
|-----------------------------|---|---|---|
| $\sigma_{2p_z}^*$ | _____ | _____ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| $\pi_{2p_x}^* \pi_{2p_y}^*$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| $\pi_{2p_x} \pi_{2p_y}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| σ_{2p_x} | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| σ_{2s}^* | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| σ_{2s} | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ | $\begin{array}{c} \diagup \diagdown \\ \end{array}$ |
| Bond order | 2 | 1 | — |





















(Continued)

| Property | O ₂ | F ₂ | Ne ₂ |
|------------------------------------|----------------|----------------|-----------------|
| Bond length (Å) | 1.21 | 1.42 | — |
| Bond energy (KJmol ⁻¹) | 494 | 159 | — |
| No. of unpaired electrons | 2 | 0 | — |
| Magnetism | Paramag | Diamag | — |
| μ(BM) | √8 | 0 | — |

Note

- Diatomic Neon is not possible as bond order is zero. Noble gases are monoatomic.
- bond energy sharply decreases from O₂ to F₂. It is because of the presence of more antibonding electrons in F₂.
- No s and p mixing takes place.

Table 2.47

| Property | O ₂ ⁺ | O ₂ | O ₂ ⁻ | O ₂ ⁼²⁻ |
|---|--|---|---|---|
| σ _{2p_z} [*] | — | — | — | — |
| π _{2p_x} [*] π _{2p_y} [*] |  |  |  |  |
| π _{2p_x} π _{2p_y} |  |  |  |  |
| 6 _{2p_z} |  |  |  |  |
| σ _{2s} [*] |  |  |  |  |
| σ _{2s} |  |  |  |  |
| Bond order | 2.5 | 2.0 | 1.5 | 1.0 |
| Bond length (Å) | 1.12 | 1.21 | 1.26 | 1.49 |
| Bond energy (KJmol ⁻¹) | 642 | 494 | 394 | 210 |
| No. of unpaired electrons | 1 | 2 | 1 | 0 |
| Magnetism | Paramag | Paramag | Paramag | Diamag |
| μ(BM) | √3 | √8 | √3 | 0 |
| Stability order | O ₂ ⁺ > O ₂ > O ₂ ⁻ > O ₂ ⁼²⁻ | | | |

Note

- For O₂⁺ electron is removed from π*.
- For O₂⁻ and O₂⁼²⁻ electrons are added in π*.

- The ion O_2^- is called superoxide ion (K, Rb and Cs form superoxides, MO_2 . They are paramagnetic and coloured.
- The $\text{O}_2^{=2}$ is known as peroxide ion.

Heteronuclear Diatomics

In a heteronuclear diatomic (Hetero—means different) two different atoms are bonded together (AB), e.g., HCl, CO, NO. Such species can be treated using LCAO – MO concept similar to homonuclear diatomics (A_2). But since the atoms are different –

- The energy of the atomic orbitals are different.
- Their relative contributions to the molecular orbitals are also different.
- The bonding MOs are closer in energy to the more electronegative atom.
- The antibonding MOs are closer in energy to the less electronegative atom.

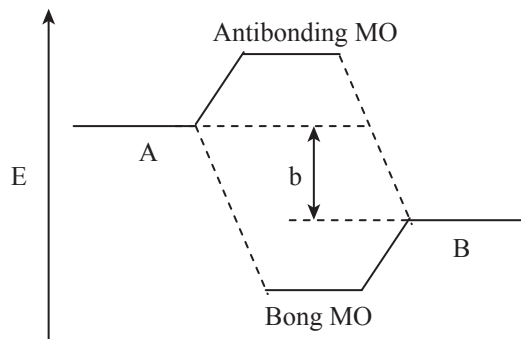


Figure 2.46

MO diagram

The orbitals of more electronegative atom are more stable. They are, therefore, kept at lower level when sketching MO diagram. The qualitative diagram may be represented as (where $\chi_B > \chi_A$).

The value of b , i.e., the difference in the electronegativity of A and B determines the polarity of the bond.

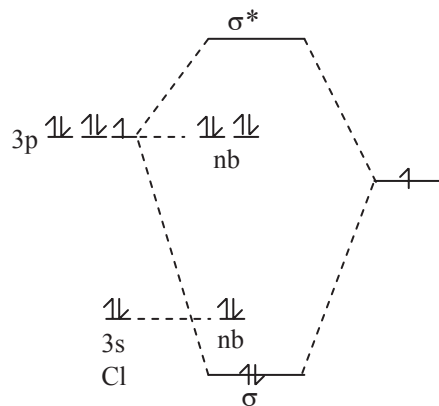


Figure 2.47

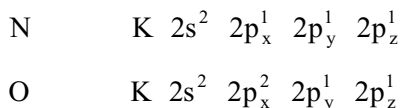
HCl Molecule

In HCl, the 1s orbital of H combines with $3p_z$ orbitals of Cl to form σ - type bonding and anti-bonding MOs. The Cl, 3s, $3p_x$ and $3p_y$ orbitals remain non-bonding (no orbital at H to combine with).

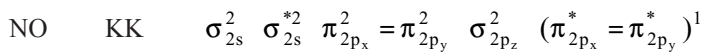
- The bonding MO is concentrated near Cl, so the bond is polar.
- The bond order is one, as there is no electron in σ^* MO.
- The HCl molecule is diamagnetic as there is no unpaired electron.

NO molecule

Nitrogen and Oxygen belong to the second period and do not differ widely in electronegativity. Therefore, MO energy levels may be taken either similar to N_2 (plus one electron) or O_2 (minus one electron).



Its MO configuration may be represented as



$$\text{Bond order} = \frac{8-3}{2} = 2.5$$

There is one unpaired in π^* MO. The NO molecule is paramagnetic, $\mu = \sqrt{3}\text{BM}$.

NO and NO⁺

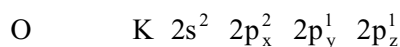
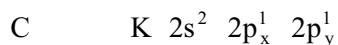
The cation, NO⁺ if formed when the π^* electrons of NO is removed.

Table 2.48

| Property | NO ⁺ | NO |
|------------------------------------|----------------------|------------|
| $\sigma_{2p_z}^*$ | — | — |
| $\pi_{2p_x}^* \pi_{2p_y}^*$ | — — | — — |
| $\pi_{2p_z}^*$ | — | — |
| $\pi_{2p_x} \pi_{2p_y}$ | — — | — — |
| σ_{2s}^* | — | — |
| σ_{2s} | — | — |
| Bond order | 3 | 2.5 |
| Bond length (Å) | 1.06 | 1.15 |
| Bond energy (KJmol ⁻¹) | 1046 | 678 |
| Magnetism | Diamag | Paramag |
| $\mu(\text{BM})$ | 0 | $\sqrt{3}$ |
| Stability order | NO ⁺ > NO | |

CO molecule

Carbon and Oxygen differ widely in electronegativity. Therefore, the molecular orbital energy level for CO is neither like C₂ nor like O₂. Oxygen is more electronegative and so its orbitals are kept at lower level.



The qualitative MO diagram of CO is:

Bond order = $(6 - 0) / 2 = 3$ (non-bonding electrons has no contribution towards bond order).

There are no unpaired electrons and CO is diamagnetic.

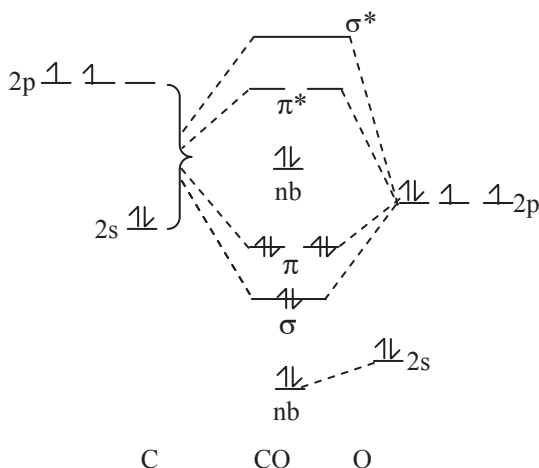












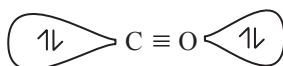
Figure 2.48

Table 2.49

| Property | CO | CO ⁺ |
|------------------------------------|---|---|
| σ^* | _____ | _____ |
| $\pi_x^* \pi_y^*$ | _____ | _____ |
| nb (MO) |  |  |
| $\pi_x \pi_y$ |   |   |
| σ |  |  |
| nb (MO) |  |  |
| Bond order | 3 | > 3 |
| Bond length (Å) | 1.128 | 1.115 |
| Bond energy (KJmol ⁻¹) | 1069 | – |
| Unpaired electrons | | 1 |
| Magnetism | Diamag | Paramag ($\mu = \sqrt{3}$) |
| Stability order | CO ⁺ > CO | |

Note

- Bond length in CO⁺ is smaller than CO. It shows stronger bond in CO⁺. It is explained by considering the fact that highest energy non-bonding MO in CO has some anti-bonding character. Therefore, loss of electron from that orbital increases bond order to some extent. It decreases bond length and increases bond energy in CO⁺.
- The CO molecule has two non-bonded electron pairs one each at C and O. The electron pair at C has more p – character (nb near p-orbital) and the electron pair at O has more s – character (lowest energy nb near s – orbital).



The C center has, thus more donor ability. It is seen in metal carbonyls where there is invariably M – C bond.

Secondary bonding**1. Hydrogen Bond**

When hydrogen is bonded to N, O, F or Cl (say Y), the H – Y bond is quite polar and H has partial positive charge,



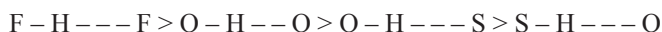
Such a H – atom has special ability to interact and form a bridge with another electron – rich centre. This weak interaction is called the H – bond.

It is represented by a perforated line (-----), $Y-H\cdots X$, where X = electron – rich centre.

Only H (or D) is able to form H – bond. It is because atomic radius of H (0.3\AA) is very small and second it has no core electrons. As a result, the e – rich centre can approach very closely to H without experiencing repulsive force.

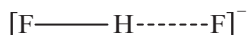
The H–bond is basically a weak bond and its bond–energy generally ranges from $5\text{--}50\text{ KJ mol}^{-1}$ (for a covalent bond, Bond energy $>100\text{ KJmol}^{-1}$).

A H – bond is mainly due to electrostatic attraction between H and X. Thus the greater the polarity in the $Y-H$ bond, stronger is the H – bond. Therefore, the following order for H – bond strength is found.



The H – bonding causes an increase in $Y-H$ distance but $H\cdots X$ distance is always longer than a normal covalent $H-X$ distance.

Some H – bonds are strong and the $Y-H$ and $H\cdots X$ distances are found quite similar, e.g., HF_2^- ion, i.e.,

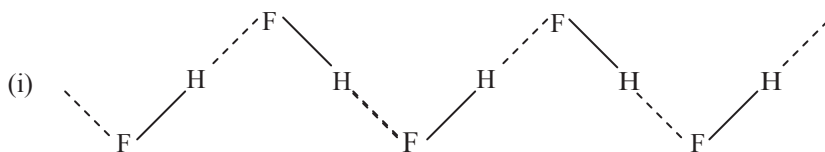


Types of H – bond

- (a) Intermolecular H – bond
- (b) Intramolecular H – bond

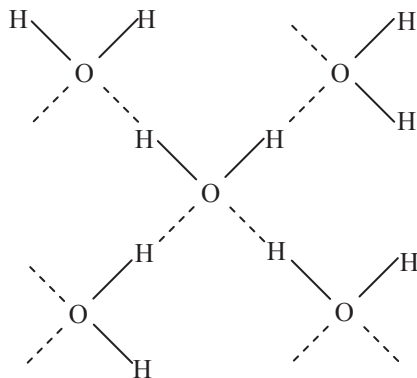
(a) Intermolecular H – bond

When a H – bond is formed between atoms of two separate molecules it is called intermolecular H – bond. Example are $(H-F)_x$, $(H_2O)_x$, $(HCOOH)_2$ etc.

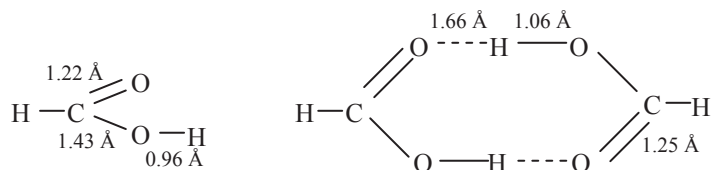


Zig-zag polymeric structure

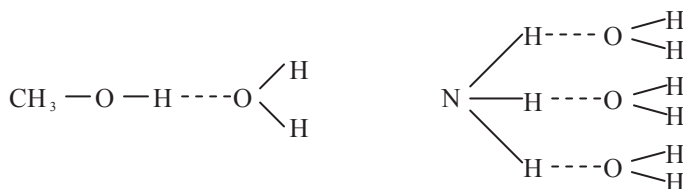
- (ii) In $(H_2O)_x$ a water molecule forms four H – bonds.



(iii) Formic acid forms a dimer



(iv) Two different molecules may also enter into intermolecular H – bond

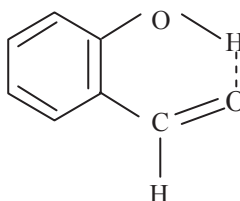


Intermolecular H-bond greatly affects mp, bp and solubility of a substance. Generally mp and bp increase due to intermolecular H – bond.

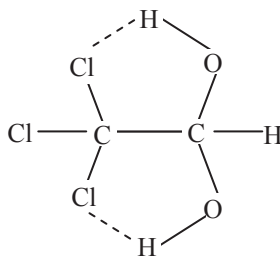
(b) Intramolecular H – bond

When a H – bond is formed between atoms in the same molecule, it is called intramolecular H – bond. It results in the formation of ring structure (i.e., chelate ring).

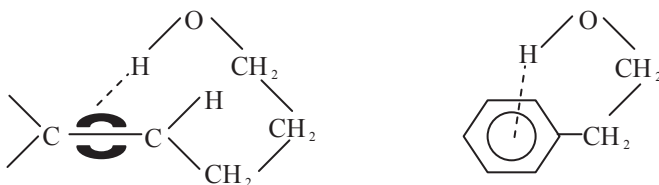
O – hydroxy benzaldehyde



Chloral hydrate $\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$



Intramolecular H – bond may also be possible between O – H and polarisable double bond or aromatic ring system, e.g.



Effects of H – bonding**(a) Liquid state of substances**

H_2O , HF, $\text{H}_2\text{N} - \text{NH}_2$ Liquid

H_2S , HCl, P_2H_4 Gaseous

Liquid state of the above substances is due to intermolecular H – bonding. H_2S , HCl etc., have larger molecular mass but are gaseous. It is because these cannot form H – bond (Cl, S, P less electronegative and so H – Y bonds are less polar).

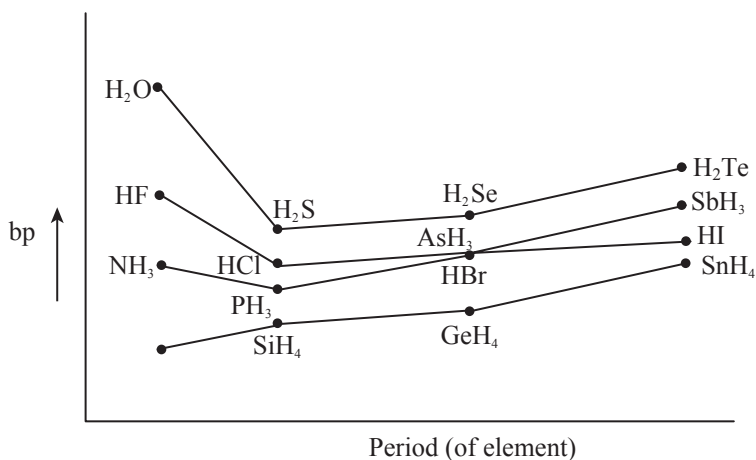
(b) High mp and bp

Substances having intermolecular H-bond have higher mp and bp, compared to those in which there is no H-bond. It is best seen in the hydrides of Gr 14, 15, 16 and 17.

Ammonia, H_2O and HF have abnormally high boiling points. It is due to extensive association of these molecules through, intermolecular H-bonding. The boiling points in the series CH_4 , SiH_4 , GeH_4 , and SnH_4 increases gradually from CH_4 to SnH_4 , i.e., with increasing molecular mass. It is because H-bonding is not present in any of them. Only van der Waals type force is present which increases with molecular mass (i.e., with increasing electrons).

Table 2.50

| Group | Hydrides |
|-------|---|
| 14 | CH_4 , SiH_4 , GeH_4 , SnH_4 |
| 15 | NH_3 , PH_3 , AsH_3 , SbH_3 |
| 16 | H_2O , H_2S , H_2Se , H_2Te |
| 17 | HF, HCl, HBr, HI |

**Figure 2.49**

Thus bp order of hydrides is

- (i) $\text{SnH}_4 > \text{GeH}_4 > \text{SiH}_4 > \text{CH}_4$
- (ii) $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
- (iii) $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$
- (iv) $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$

Table 2.51

| Compound | Molecular wt. | bp(°C) |
|---|---------------|--------|
| $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ | 44 | - 44 |
| $\text{CH}_3 - \text{O} - \text{CH}_3$ | 46 | - 25 |
| $\text{CH}_3 - \text{CH}_2 - \text{OH}$ | 46 | 78 |

Note:

Only $\text{CH}_3 - \text{CH}_2 - \text{OH}$ can have intermolecular H – bond.

However, intramolecular H-bonding has opposite effects, i.e., it causes decrease in mp.

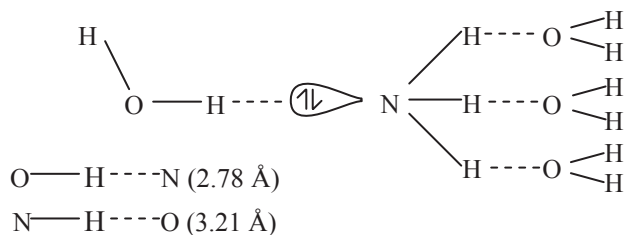
Table 2.52

| Ortho (Intramolecular H – bond) | | Para (Intramolecular H – bond) | |
|---------------------------------|--------|--------------------------------|--------|
| Compound | mp(°C) | Compound | mp(°C) |
| Salicylic acid | 158 | p – hydroxy benzoic acid | 214 |
| O – nitrophenol | 44 | p – nitrophenol | 114 |

(c) Water solubility

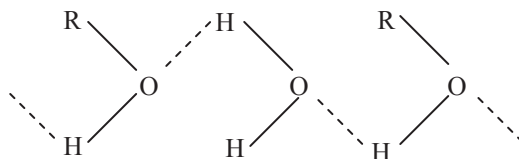
Intramolecular H – bonding, between the solute and the solvent molecules, promotes solubility. Therefore, covalent solutes which can enter into intermolecular H-bonding with water are water soluble. Examples include:

- (i) NH_3 is highly soluble in water through H-bonding



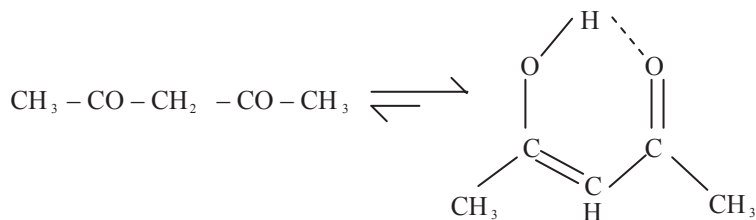
PH_3 can not form H – bond, so it is insoluble in water.

- (ii) Methanol and ethanol, are highly soluble due to H – bonding.



- (iii) The high solubility of sugars, polyhydric phenols in water is also due to H-bonding. It is because these substances have many – OH groups for H-bonding with water.

- (d) H – bonding can also explain
 (a) Acid – base strength
 (b) Greater stability of enols



- (c) Shape and reactivity of proteins the double stranded structure of DNA is due to strong H – bonds between the strands.
 (d) Reactivity of chemical species.
 (e) Unusual property of liquid water and ice (see Chapter on Hydrogen).

Van der Waals' forces

The weak force which arise between molecules (or atom or ions) is known as van der Waals' force. The energy required to break this type of bond is about 5 KJmol^{-1} . It may originate in different ways, such as:

1. **Attraction between polar species**

The positive end of one molecule attracts negative end of another molecule. It produces Van der Waals' force.

2. **Attraction between polar and non-polar species**

When a polar molecule approaches a non-polar molecule the electron cloud of the neutral molecule is distorted. It results into charge separation in the neutral molecule. Now it becomes a dipolar system.

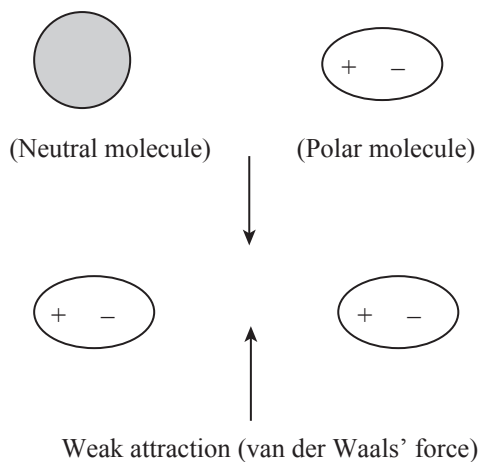


Figure 2.50

This attraction is similar to the attraction of a soft iron by a magnet.

3. Dispersion forces

Atoms (He, Ne or Ar) and molecules like H_2 , N_2 etc. are liquefied and naphthalene can crystallise. It shows that attractive forces exist even in such neutral species. In such species attractive force develop due to dispersion. The electron cloud surrounding the nucleus may suffer momentary imbalance in its distribution. It leads to temporary dipoles. This dipole interacts with nearby neutral species and cause an instantaneous induced dipole. This weak attractive force between the dipoles is called Dispersion or London force.

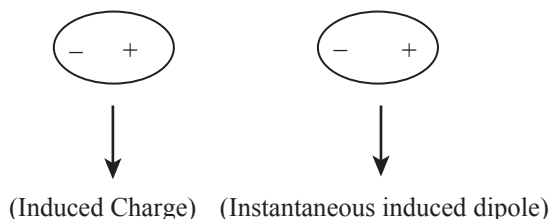


Figure 2.51

Characteristics of Van der Waal's forces

- Short range force
- Weak force
- Bond energy $\sim 5 \text{ KJmol}^{-1}$
- Increases as number of electrons in the species (atom or molecule or ion) increases.

Effect of Van der Waal's force

- Gases like He, Ne, H_2 , N_2 etc. liquefy due to van der Waal's force
- Iodine, naphthalene etc. are solid due to van der Waal's force.
- Van der Waal's force has contribution even in ionic crystals (the Van der Waal's energy in NaCl is found to be -13 KJmol^{-1}).

Metallic Bond

Metals: All metals except Hg are solids (Hg is liquid) and exist in lattice structure. They have some common properties which are different from other solids, e.g.,

- (i) Metals are good conductors of heat.
- (ii) They have high electrical conductance, decreasing with increasing temperature.
- (iii) They are strong but deformable (i.e., ductile and malleable).
- (iv) They have lustre etc.

All the above properties are related to the structure and electronic nature of the metals.

Metal Structures

There are three basic metal structures:

- (i) Body centred cubic (Bcc). In bcc packing each metal atom has 8 nearest neighbours (i.e., coordination number). Alkali metals have bcc structure.
- (ii) Hexagonal close packed (hcp). It has 12 nearest neighbours (i.e., CN). Magnesium, Zn, Tl etc. have hcp structure.
- (iii) Cubic close packed (ccp). It also has a coordination number of 12. The ccp structure has an atom at the face centre. So, it is face centred cubic also i.e., ccp and fcc are equivalent structure. Copper, Ag, Au etc., have ccp (or fcc) structures.

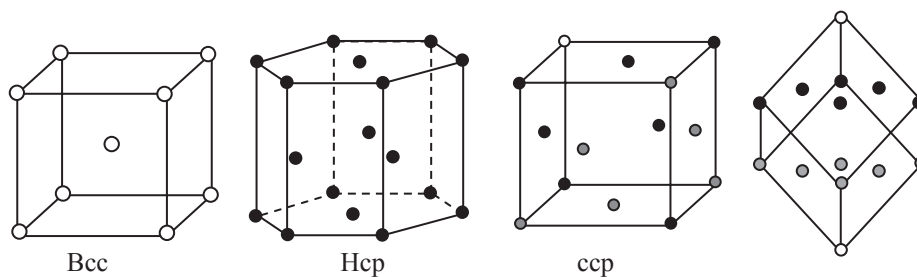


Figure 2.52

There is however, deviation from the ideal structure i.e., the same metal may have more than one structure type (see Fe). For example, Fe has both the structures bcc and ccp.

Metallic Bonding

The common physical properties of metals as well as the high coordination number (8 or 12) suggest that:

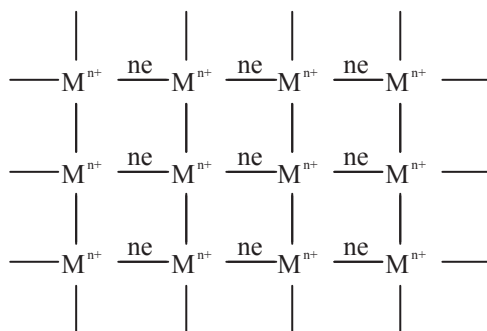
- (i) 2 – electron covalent bonds between all adjacent pairs are impossible as there are neither sufficient electrons nor the orbitals.
- (ii) Ionic bonding is also impossible as it requires at least two elements having very different electronegativities.

To account for common properties different bonding models have been proposed for metals, viz,

- (i) Electron gas model, and
- (ii) Band model

Electron Gas Model

This model assumes a metal as a collection of positive ions embedded in a sea of mobile electrons. The electro static attraction between M^{n+} and delocalised electrons gives stability to the structure. This attraction is metallic bond. It may be represent in a simple way as:



It is clear that as n i.e., charge on the metal ion (i.e., the number of mobile electrons) increases, metallic bond strength will increase. It is found true.

In the case of transition metal unpaired electrons are present in d orbitals. Those d orbitals can overlap and form covalent bonds, (i.e., electrostatic attraction + covalent force). This further stabilises lattice structure.

Therefore, transition metals are harder and have higher cohesive energy compared to non – transition metals.

The mobile electrons concept of metal structure explains:

- (i) Thermal and electrical conductivity
- (ii) Metallic lusture
- (iii) Property to deform i.e., ductility and malleability

Band Model

The molecular orbital model of metals is called the Band Model. It treats a metal as a single group of interacting particles.

A molecule is formed when atomic orbitals overlap and produce bonding and antibonding molecular orbitals.

Number of MOs = Number of atomic orbital combined.

Even a very small piece of metal contains around 10^{20} atoms. Therefore, very large number of MOs will exist even in a small piece of a metal. The energies of the molecular orbitals are very close, so much so, that they can be regarded as continuous. It is known as a Band. There is an energy gap between the bands.

The above concept for a linear array of metal atoms (say Li) can be shown as:

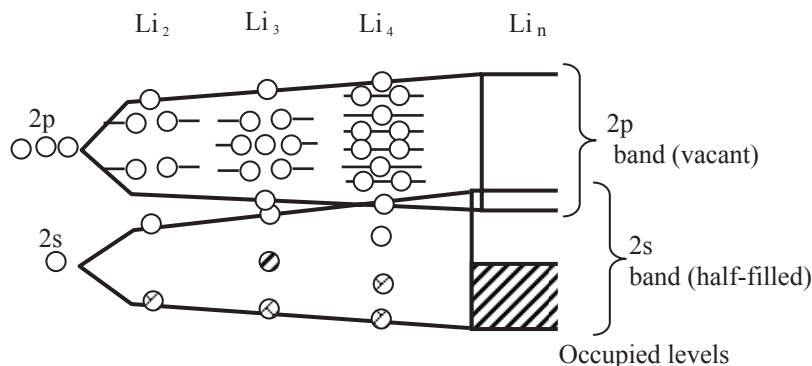


Figure 2.53

The following may be concluded from the figure above:

- (i) MOs are getting closer with increase in Li atoms
- (ii) s – band and p – band overlap
- (iii) s – band is half-filled (as there is only one electron in 2s orbital)

The above concept is valid for a three dimensional crystal also. The band occupied by electron is called the valence band while the vacant zone above it is called the conduction band. They may or may not overlap. When the bands do not overlap it is called Forbidden Band. In metals, valence and conduction bands overlap. Thus, electronic structure of a metal has large number of energy bands extending through out the crystal. The electrons in these bands are completely delocalized. It explains metallic properties.

(i) Metallic conduction

The MOs are spread over the whole crystal and electrons are delocalised in them. The valence and conduction bands overlap. Therefore, electrons can easily be excited. It happens when electric field is applied to a metal. The metal electrons receive energy and move in the direction of the field, i.e., electrical conduction.

The same two factors also explain thermal conductivity.

(ii) Metallic Lustre

The delocalised electrons absorb light energy and reemit light. This emitted radiation makes metal surface shiny and lustrous.

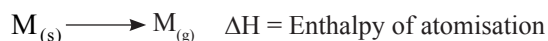
(iii) Property to deform

The bonding electrons in metals are not localized, rather delocalized. Therefore, on application of force, the lattice can easily be deformed. It explains malleable and ductile nature of metals.

Cohesive Energy

Metals have crystal structure. The crystals contain molecular orbitals which are spread over the entire crystal. The electrons are delocalized in these molecular orbitals. It gives stability to a metal crystal.

The strength of binding between atoms is measured in terms of cohesive energy. It may be defined as: enthalpy of atomization of one mole of metal i.e.,



Cohesive energy is found large when:

- There are more valence electrons in a metal.
- The lattice dimension is small.
- There are partially filled d orbitals (i.e., for transition metals).
- The coordination number is high (e.g., 12 i.e., for hcp and ccp structure).

Cohesive Energy in the Periodic Table

- It decreases in a group from top to bottom (Lattice dimension effect).
- It increases in a period (Valence electron effect).
- Maximum when more electrons are unpaired in the d – orbitals.
- W has highest cohesive energy ($\sim 837 \text{ KJmol}^{-1}$).

Table 2.53

| Element | Group | Cohesive Energy KJmol^{-1} | Element | Group | Cohesive Energy KJmol^{-1} |
|---------|-------|--|---------|-------|--|
| Li | 1 | 162 | Na | 1 | 108 |
| Na | do | 108 | Mg | 2 | 146 |
| K | do | 90 | Al | 3 | 326 |
| Rb | do | 82 | | | |
| Cs | do | 78 | | | |
| Be | 2 | 324 | Mn | 7 | 285 |
| Mg | do | 146 | Co | 9 | 428 |
| Ca | do | 178 | Ni | 10 | 430 |
| Sr | do | 163 | Cu | 11 | 329 |
| Ba | do | 178 | Zn | 12 | 130 |

Note:

- Ca and Ba have equal cohesive energies. It is because of involvement of 3d orbital in Ca and 4f orbital in Ba for bonding.
- Zn has lower cohesive energy than Cu, as Zn has full filled, $3d^{10}$ orbital.
- Low cohesive energy of Mn has no full proof explanation.

PRACTICE QUESTIONS

Explain the following in brief:

- (a) N_2 has triple bond and B_2 is paramagnetic using appropriate electrons configuration.
- (b) What is bond order? how it explains relative stability of O_2^- and O_2^{2-} .
- (c) The bond angle HOH in H_3O^+ is greater than HNH bond angle in NH_3 .
- (d) SF_4 has distorted tetrahedral shape.
- (e) First ionization energy of H_2 is greater than that of H – atom.
- (f) First ionization energy of O_2 is less than that of O – atom.
- (g) The Si – F bond length in SF_4 is much smaller than the sum of the covalent radii of Si and F.
- (h) CO_2 is linear but SO_2 is angular.
- (i) The length of the C – C single bonds differ in HCCCH_3 and H_2CCHCH_3 .
- (j) Valence electrons in N ($2s^2 2p^3$) and P ($3s^2 3p^3$) are five but N does not form NCl_5 like PCl_5 .
- (k) O_3 possesses dipole moment.
- (l) The species NO_2^+ and NO_2 differ in ONO bond angles.
- (m) When O_2 ionizes to O_2^+ the O – O bond length decreases but when N_2 ionizes to N_2^+ the N – N bond length increases.
- (n) The ion NO^+ has a stronger bond than NO.
- (o) The structures of BF_3 and BrF_3 differ (VSEPR).
- (p) BrF_5 has slightly distorted structure.
- (q) The triiodide ion (I_3^-) is linear but central iodine atom is not sp hybridized.
- (r) The dipolemoment of $\text{CH}_3 - \text{F}$ is lower than that of $\text{CH}_3 - \text{Cl}$.
- (s) O – hydroxybenzaldehyde is a liquid at room temperature but p – hydroxybenzaldehyde is a solid.
- (b) The shape of SF_4 is _____ because it contains _____ bonding pairs and _____ lone pair of electrons around s atom.
- (c) The shape of BrF_5 is _____ and the non-bonding pair at Br atom occupies _____.
- (d) There are _____ π bonds in tetracyanoethylene.
- (e) Solid KCl is a _____ conductor of electricity.
- (f) Gaseous HCl is a _____ conductor of electricity.
- (g) The dipolemoment of NF_3 IS _____ than that of NH_3 .
- (h) When N_2^+ goes to N_2 , the N – N bond length _____ and when O_2^+ goes to O_2 , the O – O bond length _____.
- (i) The angle between two covalent bonds is greater in _____ (NH_3 and H_3O^+).
- (j) The compound having both sp^2 and sp hybridized carbon atoms is _____. (Propene, Propyne, Propadiene)
- (k) The valence orbital of carbon in silver (or cuprous) acetylide is _____.
- (l) The much lower melting point of AlCl_3 over MgCl_2 is due to _____ in AlCl_3 .
- (m) The CO molecule is a _____ Lewis base for BF_3 .
- (n) In PH_3 the 3s and 3p orbitals form _____ hybrid orbitals.
- (o) The shape of SOF_4 is _____ and oxygen atom occupies _____ position.
- (p) The d-orbitals involved in sp^3d hybrid in trigonal bipyramid structure is _____.

Fill in the blanks

- (a) The shape of ClF_3 is not trigonal planar because it contains _____ than _____ electron pairs around the chlorine atom.

True or False

- (a) Anhydrous SnCl_2 is a linear molecule.
- (b) The dipolemoment of CH_3Cl is greater than CH_3F .
- (c) Intramolecular H – bonding increases water solubility of a compound.

- (d) The polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment.
- (e) CsI is more soluble than KI.
- (f) AgF is insoluble in water.
- (g) All FSF angle in SF_4 are equal.
- (h) The HCC and HCH angles in C_2H_4 are equal.
- (i) The AB_3 species (BF_3 , CO_3^{2-} , NO_2^+) has equal A – B bond orders.
- (j) The d – orbital involved in sp^3d , square pyramid, structure is dz^2 .
- (k) The single C – C bond energy is lower than N – N single bond energy.
- (l) For a molecule like SF_4 , a three-center bond model omits involvement of the d orbitals.
- (m) The isoelectronic species ICl_4 and I_3^- are isostructural.
- (n) The O_3 molecule has dipole moment.
- (o) The single bond C – C stronger than the single bond Si – Si but the single bond N – N is weaker than the single bond P – P.

OBJECTIVE-TYPE QUESTIONS

- Which is expected to be paramagnetic and has non-equivalent lone pair orbitals?
 - XeO_2F_2
 - XeOF_2
 - XeOF_3
 - XeOF_4
- The force present in a crystal of naphthalene is
 - Electrostatic force
 - Covalent force
 - Van der Waals force
 - dipole – dipole force
- The compound Mg_2C_3 contains the ion C_3^{4-} which has
 - two σ and two π bonds
 - three σ and one π bond
 - two σ and one π bond
 - two σ and three π bonds
- In the C – X bond (X = H, N, O, F) highest p-character present in the central atom sp^3 -hybrid orbital is
 - C – H
 - C – F
 - C – O
 - C – N
- The type of hybrid orbitals used by chlorine in hypochlorite ion is
 - dsp^2
 - sp
 - sp^2
 - sp^3
- The group of chemical species which are diamagnetic is
 - C_2 , O_2^{+2} , F_2
 - B_2 , N_2 , O_2^-
 - O_2 , N_2 , F_2
 - B_2 , C_2 , N_2
- Among BF_3 , NH_3 , NO_2^+ , NF_3 and H_3O^+ , identify the pair, which is not isostructural?
 - BF_3 and NO_2^+
 - NH_3 and H_3O^+
 - NH_3 and NF_3
 - BF_3 and NF_3
- How many equivalent perfect Lewis structures are possible for N_3^- ion?
 - One
 - Two
 - Three
 - Four
- Which of the following ion has $(18 + 2)$ e stable electron configuration?
 - Ca^{+2}
 - Fe^{2+}
 - Zn^{+2}
 - Sn^{+2}
- The angle between two covalent bonds is minimum is
 - NO_2^+
 - NO_2
 - NO_2^-
 - ClO_2^-
- Among the following cations, which one has an odd electron in σ -type molecular orbital?
 - O_2^+
 - N_2^+
 - C_2^+
 - B_2^+
- The hypochlorite ion disproportionates in basic medium as

$$3\text{ClO}^- \longrightarrow \text{ClO}_3^- + 2\text{Cl}^-$$
 The change in hybrid nature of chlorine is
 - sp to sp^2
 - sp^2 to sp^3
 - sp to sp^3
 - sp^3 to sp^3
- Carbon atoms in C_3O_2 are
 - sp^2 hybridized
 - sp^3 hybridized
 - sp hybridized
 - sp and sp^2 hybridized

14. The O – O bond energy decreases in the order
 (a) $O_2^+ > O_2 > O_2^- > O_2^{-2}$
 (b) $O_2 > O_2^- > O_2^+ > O_2^{-2}$
 (c) $O_2^{-2} > O_2^- > O_2^+ > O_2$
 (d) $O_2^+ > O_2^{-2} > O_2^- > O_2$
15. Ammonia and BF_3 form the addition compound, $H_3N \longrightarrow B_3$ which of the following statements is correct for the addition compound
 (a) Over all structure is distorted
 (b) Over all structure is regular Td with sp^3 , N and B
 (c) N surrounding regular Td and B surrounding distorted
 (d) B surrounding regular Td and N surrounding distorted
16. Which H – bond is expected to be weakest?
 (a) O – H – – – N (b) O – H – – – S
 (c) O – H – – – Cl (d) S – H – – – O
17. The correct N – N bond length is represented by
 (a) $N_2^- > N_2^{-2} > N_2^+ > N_2$
 (b) $N_2^{-2} > N_2^- > N_2^+ > N_2$
 (c) $N_2^+ > N_2 > N_2^- > N_2^{-2}$
 (d) $N_2 > N_2^{-2} > N_2^+ > N_2^-$
18. Carbon atoms in tetracyanoethene are
 (a) sp^2 hybridized
 (b) sp hybridized
 (c) sp^2 and sp hybridized
 (d) sp and sp^3 hybridized
19. If a molecule AB has zero dipole moment, the σ bonding orbitals used by A are
 (a) sp hybrids
 (b) sp^2 hybrids
 (c) sp^3 hybrids
 (d) p-orbitals
20. The geometry of O_3 (or H_2S) and its dipole moment are
 (a) Linear and zero
 (b) Angular and non-zero
 (c) Angular and zero
 (d) Linear and non-zero
21. The common features among the species CO , CN^- and NO^+ are
 (a) Bond order three and weak field ligands
 (b) Bond order three and strong field ligands
 (c) Bond order two and π -acceptors
 (d) Iso electronic and weak field ligands
22. The nodal plane in the π -bond of ethane is located in
 (a) A plane perpendicular to the molecular plane, which bisects the C – C, σ bond at right angle.
 (b) A plane perpendicular to the molecular plane which contains the C – C σ bonds.
 (c) The molecular plane
 (d) A plane parallel to molecular plane.
23. The correct order of increasing C – C length of CO , CO_2 and CO_3^{2-}
 (a) $CO_3^{2-} < CO_2 < CO$
 (b) $CO_3^{2-} < CO_2 < CO$
 (c) $CO < CO_3^{2-} < CO_2$
 (d) $CO < CO_3^{2-} < CO_2$
24. The correct order of decreasing N – O bond length of NO_2^+ , NO_2 and NO_2^- is
 (a) $NO_2^- > NO_2^+ > NO_2$
 (b) $NO_2^- > NO_2^+ > NO_2$
 (c) $NO_2^- > NO_2^+ > NO_2$
 (d) $NO_2^- > NO_2^+ > NO_2$
25. The octet rule is not strictly followed in
 (a) CO_2 (b) NO_2^+
 (c) NO_2 (d) SO_2

ANSWERS

1. (c) 2. (c) 3. (a) 4. (a) 5. (d) 6. (a) 7. (d) 8. (c) 9. (d) 10. (a)
 11. (d) 12. (d) 13. (c) 14. (a) 15. (a) 16. (d) 17. (b) 18. (c) 19. (b) 20. (b)
 21. (b) 22. (c) 23. (c) 24. (a) 25. (c)

3

Acids and Bases



BRONSTED-LOWRY THEORY (1923)

According to this theory, acids are proton (H^+) donors and bases are proton acceptors.



HCl donates a proton and H_2O accepts it. So HCl is acid and H_2O is base.

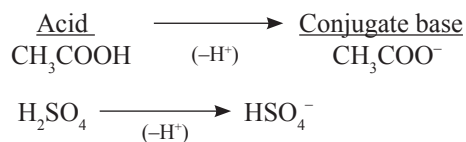
Bare proton (i.e., H^+ only) does not exist in H_2O . It is associated with water molecules i.e., is solvated,



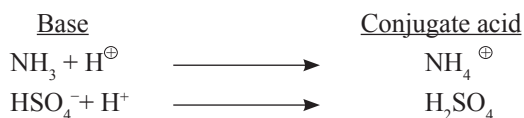
Solvated proton is simply denoted as H_3O^+ , which is called 'Hydronium ion'. However, hydration number of a proton may be 1, 2, 3, 4 etc., which may be represented as H_3O^+ , $H_5O_2^+$, $H_9O_4^+$ etc.

Conjugate acid-base pair

When a substance donates a proton it is converted to a base, the conjugate base of the parent acid.



When a base accepts a proton, it is converted to an acid, the conjugate acid



Thus, chemical species which differ in formula by a proton are called "A Conjugate Pair".

Bronsted-Lowry theory may, thus, be summarized as



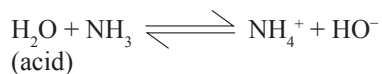
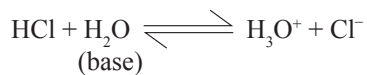
It is found that the conjugate base of a strong acid is a weak base and vice versa. Thus HSO_4^- is a weak base and CH_3COO^- is a strong base.

The conjugate acid of a weak base is a strong acid and vice versa.

Thus, NH_4^+ is a strong acid as NH_3 is a weak base and H_2O is a weak acid as HO^- is a strong base.

Some Important Points of B–L Theory

- (a) A substance is acidic only when another substance capable of accepting proton is present.
- (b) Proton in aq. solution is always solvated, $H^+_{(aq)}$, simply represented as H_3O^+ .
- (c) The same substance may act as an acid in one situation and as a base in another.



Such substances are called amphoteric. Thus H_2O is amphoteric.

- (d) Any compound that acts as an acid has its conjugate base and vice versa.
- (e) A strong acid (e.g., H_2SO_4) has a weak conjugate base (HSO_4^-) whereas a weak acid (e.g., CH_3COOH) has a strong conjugate base (CH_3CHOO^-).
- (f) In this theory, definition of acids and bases does not require any particular solvent.

Table 3.1 Some conjugate acids, bases and amphoteric species

| Species | Conjugate acid | Conjugate base | Amphoteric |
|--------------|----------------|----------------|--------------|
| H_2O | H_3O^+ | HO^- | Amphoteric |
| NH_3 | NH_4^+ | NH_2^- | — |
| HSO_4^- | H_2SO_4 | SO_4^{2-} | HSO_4^- |
| HCO_3^- | H_2CO_3 | CO_3^{2-} | HCO_3^- |
| $H_2PO_4^-$ | H_3PO_4 | HPO_4^{2-} | $H_2PO_4^-$ |
| HPO_4^{2-} | $H_2PO_4^-$ | PO_4^{3-} | HPO_4^{2-} |
| HF | H_2F^+ | F^- | HF |
| HNO_3 | $H_2NO_3^+$ | NO_3^- | HNO_3 |
| $H_2PO_3^-$ | H_3PO_3 | HPO_3^{2-} | $H_2PO_3^-$ |

Strength of Acids and Bases

According to B–L theory, ionization equilibrium of an acid may be represented as,



$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

The concentration of water, $[H_2O]$, = very large

∴ constant

$$\therefore K_{eq} = \frac{[H_3O^+][A^-]}{[HA]}$$

In this case, K_{eq} is called K_a , the dissociation constant of the acid HA .

The numerical value of K_a decides the strength of an acid.

It is found that if,

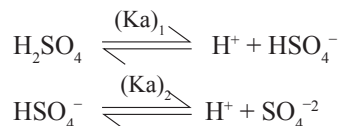
- (a) $K_a > 10$, the acid is strong (HCl , HNO_3 , HClO_4 etc.)
 (b) $K_a < 1$, the acid is weak (HCN , H_2S , HCOOH etc.)

Polyprotic Acid

Acids which contain more than one ionizable hydrogen are called “Polyprotic”.



Such acids ionize in successive steps,



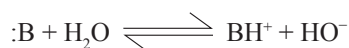
The quantities $(K_a)_1$ and $(K_a)_2$ are known as first and second ionization constants respectively. It is found that higher ionization constants are smaller than lower ionization constants. It is because in the second and higher ionization, protons are lost from negative ions.

Table 3.2

| Acids | $(K_a)_1$ | $(K_a)_2$ | $(K_a)_3$ |
|----------------------------------|----------------------|-----------------------|-----------------------|
| H_2SO_3 | 1.7×10^{-2} | 6.4×10^{-8} | |
| H_2SO_4 | very large | 1.2×10^{-2} | |
| H_2CO_3 | 4.3×10^{-7} | 5.6×10^{-11} | |
| $\text{H}_2\text{C}_2\text{O}_4$ | 5.9×10^{-2} | 6.4×10^{-5} | |
| Ascorbic acid | 7.4×10^{-4} | 1.6×10^{-12} | |
| H_3PO_4 | 7.5×10^{-3} | 6.2×10^{-8} | 4.2×10^{-13} |
| Citric acid | 7.4×10^{-4} | 1.7×10^{-5} | 4.0×10^{-7} |

Base Strength

The ionization equilibria for bases may be represented as

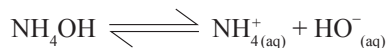


$$K_{\text{eq}} = \frac{[\text{BH}^+][\text{HO}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

As, $[\text{H}_2\text{O}] = \text{very large compared to B}$,
 $[\text{H}_2\text{O}] = \text{constant}$. In that case K_{eq} is denoted as K_b .

$$\therefore K_{\text{eq}} = \frac{[\text{BH}^+][\text{HO}^-]}{[\text{B}]}$$

For hydroxide bases, the equilibrium may be denoted as



$$K_b = \frac{[\text{NH}_4^+][\text{HO}^-]}{[\text{NH}_4\text{OH}]}$$

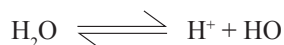
The numerical value of K_b decides base strength. If K_b is large the base is strong and vice versa.

Table 3.3

| Base | K_b | Comment on strength |
|--|-----------------------|---------------------|
| NaOH, KOH | ∞ | Very strong |
| Ca(OH)_2 | 3.7×10^{-3} | Weak |
| aq NH_3 or NH_4OH | 1.8×10^{-5} | Weak |
| $(\text{CH}_3)_2\text{NH}$ | 5.4×10^{-4} | Weak |
| $(\text{C}_2\text{H}_5)_3\text{N}$ | 6.5×10^{-5} | Weak |
| Pyridine, $\text{C}_5\text{H}_5\text{N}$ | 1.8×10^{-9} | Very weak |
| Aniline, $\text{C}_6\text{H}_5\text{NH}_2$ | 4.3×10^{-10} | Very weak |
| Urea, $\text{OC(NH}_2)_2$ | 1.3×10^{-13} | Very weak |

Ionization of water

Water self ionizes as,



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{HO}^-]}{[\text{H}_2\text{O}]}$$

As water is solvent medium, $[\text{H}_2\text{O}] = \text{large}$ and is taken constant

$$\therefore K [\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{HO}^-]$$

K_w is known as ionic product of water.

As K_w is equilibrium constant, it varies with temperature.

At 25°C , i.e., room temp., $K_w = 1.0 \times 10^{-14}$,

$$\therefore [\text{H}^+] = [\text{HO}^-] = 10^{-7} \text{ mol l}^{-1}.$$

The nature of an aqueous solution is determined by the relative concentrations of H^+ and HO^- .

If,

- (i) $[\text{H}^+] = [\text{HO}^-]$ Solution is neutral
- (ii) $[\text{H}^+] > [\text{HO}^-]$ Solution is acidic
- (iii) $[\text{HO}^-] > [\text{H}^+]$ Solution is basic

Table 3.4 K_w at various temperatures

| Temp. $^\circ\text{C}$ | K_w | Temp. | K_w |
|------------------------|------------------------|-------|------------------------|
| 0 | 1.14×10^{-15} | 40 | 2.71×10^{-14} |
| 10 | 2.95×10^{-15} | 50 | 5.3×10^{-14} |
| 25 | 1.0×10^{-14} | | |

pH

pH is a way of expressing H^+ ion concentration of a solution. It was introduced by Sorensen (1909). (pH stands for, French, puissance de hydrogen, meaning the hydrogen ion concentration).

The negative logarithm of the H^+ ion concentration in mol l^{-1} is defined as P^H ,

$$P^H = -\log_{10}[H^+]$$

Some other terms like P^H may also be defined as,

$$P^{OH} = -\log_{10}[HO^-]$$

$$P^{K_w} = -\log_{10}K_w$$

$$P^{K_a} = -\log_{10}K_a$$

$$P^{K_b} = -\log_{10}K_b$$

Where, K_w = ionic product of water, K_a = dissociation constant of acid, K_b = dissociation constant of a base.

pH and pOH of water

Water self ionizes, $H_2O \rightleftharpoons H^+ + HO^-$ and $[H^+] = [HO^-] = 10^{-7} \text{ mol l}^{-1}$ at 25°C .

$$pH = -\log_{10}[10^{-7}] = 7$$

$$pOH = -\log_{10}[10^{-7}] = 7$$

$$\text{i.e., } pH = pOH = 7$$

$$\therefore pOH + P^{OH} = 14$$

It is true for all aqueous solutions.

Buffer solution

A solution that maintains its pH constant on addition of a small amounts of acid or base is called 'Buffer Solution'. Such solutions are made by mixing

- (i) Weak acid + its salt ($CH_3COOH + CH_3COONa$), the acidic buffer solution.
- (ii) Weak base + its salt ($NH_4OH + NH_4Cl$), the basic buffer solution.

Henderson Equations

- (i) pH of acidic buffer solution,

$$pH = P^{K_a} + \log [\text{salt}] / [\text{acid}]$$

- (ii) pH of basic buffer solution

$$pH = P^{K_w} - P^{K_b} - \log [\text{salt}]/[\text{base}]$$

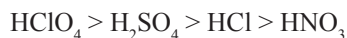
Leveling effect and differentiating solvents

The ability of an acid to donate proton (i.e., acid strength) depends upon the extent of the solvent to accept proton (i.e., basicity of the solvent). Thus an acid which is strong in one solvent may be weak in another. For example, HNO_3 and H_2SO_4 both are strong acids in H_2O (the solvent) but

Table 3.5 Some buffer solutions

| Buffer solution | pH at 25°C |
|---|--------------------------|
| 0.01M $CH_3COOH +$ 0.01M CH_3COONa | 4.7 |
| 0.01M $Na_2HPO_4 +$ 0.01M KH_2PO_4 | 6.85 |
| 0.05M Borax | 9.18 |
| 0.025M $NaHCO_3 +$ 0.025M Na_2CO_3 | 10.0 |

H_2SO_4 is found stronger acid than HNO_3 in acetic acid (the other solvent). Thus water cannot distinguish between the strength of HNO_3 and H_2SO_4 . It is known as “Leveling Effect”. That is water cannot level out acids with respect to their strength. However, if less basic (or more acidic) solvent than water is taken, distinction in acid strength can be made. It is because such a solvent will accept proton selectively and not freely. Such solvents are called “Differentiating Solvents”. One such solvent is acetic acid. In acetic acid the strength, of some common acids, found is



Amphoterism

Substances which behave as bases towards strong acids and acidically towards strong bases are called “Amphoteric”.

Water is the only non-metal oxide which is amphoteric.

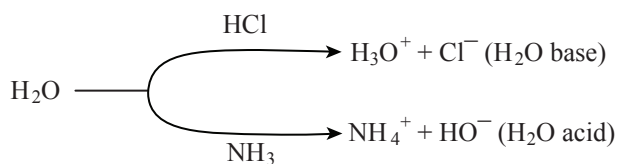


Figure 3.1

Metals in +1, +2 and +3 oxidation states generally form basic oxides and hydroxides, CaO , Na_2O , $\text{Fe}(\text{OH})_3$, NaOH , $\text{Ca}(\text{OH})_2$ etc., are basic. However, some metal oxides and hydroxides are amphoteric.

Table 3.6

| | | |
|--------------------------------|---------------------|------------|
| ZnO | Zn(OH) ₂ | AMPHOTERIC |
| SnO | Sn(OH) ₂ | |
| PbO | Pb(OH) ₂ | |
| Cr ₂ O ₃ | Cr(OH) ₃ | |
| Al ₂ O ₃ | Al(OH) ₃ | |

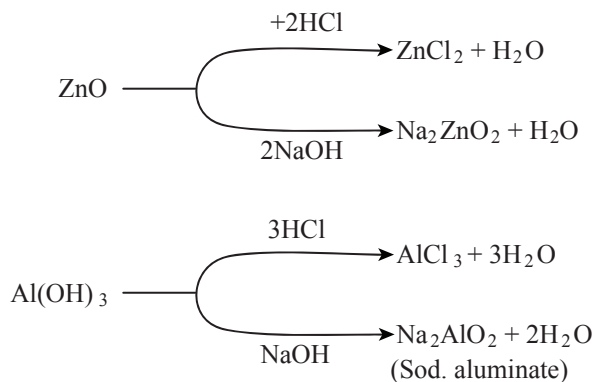


Figure 3.2

Similarly, Chromite (NaCrO_2), Stanite (Na_2SnO_2), Stannate (Na_4SnO_4), Plumbite (Na_2PbO_2) and Plumbate (Na_4PbO_4) are formed by reaction of the corresponding hydroxide (or oxide) with NaOH .





Salts of the above mentioned metals dissolve in excess NaOH (an alkali). It is due to the amphoteric nature of the hydroxides which are first formed.



Thus, salts of Zn^{+2} , Sn^{+2} , Pb^{+2} , Al^{+3} and Cr^{+3} dissolve in excess NaOH solution.

Amphoterism of Hydroxides

The hydroxides of the highly electropositive metals like Na, K, Ba etc. only contain discrete HO^- (hydroxides) ions. They dissolve in water and form aquated metal and OH^- ions:



Such substances are strong bases.

Amphoteric hydroxides are those in which M – O and O – H bonds break with almost equal ease.

(i) The M – O bond breaks by acid.



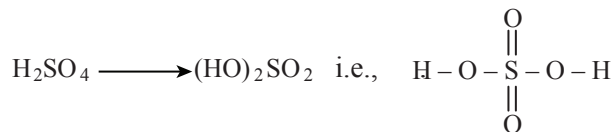
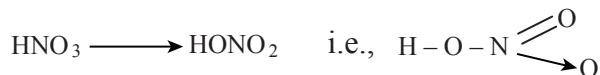
(ii) The O – H bond breaks by base.



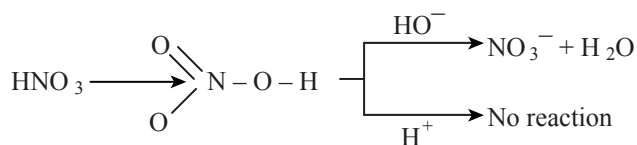
The above reactions are followed with formation of water, a highly favoured reaction.



In case of an extremely covalent M – O bond, (S – O, N – O, Cl – O etc.) only O – H bond reacts and the species is an acid.



Here, N – O, S – O, Cl – O bonds are much stronger than O – H bonds. The O – H only reacts and the substances are acids.



Strength of Acids and Bases (Prediction)

The following quantities may be used to predict strength of acids and bases:

Acids: (i) H^+ conc, (ii) K_a , (iii) P^{K_a} and (iv) P^H and P^{OH}

Base: (i) HO^- conc. (ii) K_b , (iii) P^{K_b} and (iv) P^{OH} and P^H

Acids**Table 3.6**

| H^+ conc | K_a | P^{K_a} | P^H | P^{OH} | Comments |
|------------|-------|-----------|-------|----------|-------------|
| High | Large | Small | Small | Large | Strong acid |
| Low | Small | Large | Large | Small | Weak acid |

Bases**Table 3.7**

| HO^- conc | K_b | P^{K_b} | P^H | P^{OH} | Comments |
|-------------|-------|-----------|-------|----------|-------------|
| High | Large | Small | Large | small | Strong base |
| Low | Small | Large | Small | Large | Weak base |

Acid strength

Proton acids can be classified as:

- (a) Hydra acids: HF, HCl, HBr, HI, H_2O , H_2O_2 , H_2S , H_2Se , H_2Te .
 (b) Oxy acids: HNO_2 , HNO_3 , H_3PO_2 , H_3PO_3 , H_3PO_4 , H_2CO_3 , H_2SO_3 , H_2SO_4 , HOX, HXO_2 , HXO_3 , HXO_4
 (X = Cl, Br, I), H_5IO_6 , H_6TeO_6 , H_3BO_3 , H_3AsO_3 , H_3AsO_4 , H_2SeO_4 .

Acid can also be classified as:

- (i) Monoprotic: which gives only one H^+ in solution HX , HNO_2 , HNO_3 , $HClO$, $HBrO$
 (ii) Diprotic: which gives two H^+ in solution H_2SO_4 , H_2SO_3 , $H_2C_2O_4$, H_2SeO_4
 (iii) Triprotic: which gives three H^+ in solution H_3PO_4

Strength of Hydra acids

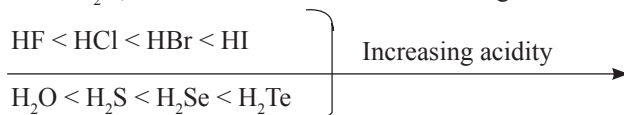
Hydrides (i.e., binary compounds) of Gr16 and Gr17 are acidic and known as hydra acids.



Strength of hydra acids depends on

- (i) Radius of the atom which forms the acid
 (ii) Oxidation state of the non-metal.

In HX or H_2X , as radius of X increases acid strength increases.



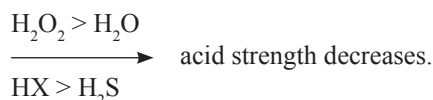
Radius of X and H – X bond energy are closely related. As radius of X increases H – X bond distance increases and so H – X bond energy decreases. The weak polar H – X bond breaks easily due to dipole – dipole interaction with water (polar molecule) easily. More H^+ ions are produced and acid strength increases.

Table 3.8

| Element (X) | O F | S Cl | Se Br | Te I |
|----------------------------|--------|---------|----------|-----------|
| Radii | —————→ | | | Increases |
| H – X bond distance | —————→ | | | Increases |
| H – X bond energy | —————→ | | | Decreases |
| Extent of H – X ionization | —————→ | | | Increases |
| Acid strength | —————→ | | | Increases |

Oxidation states of X and acid strength

When oxidation state of X is low, acid is strong and vice versa. Thus, H_2O_2 is stronger acid than H_2O and HX are stronger acids than H_2S .



Oxidation state of X decides affinity of X for proton (H^+). When the oxidation state of X is high, there is higher magnitude of negative charge on X. Therefore, proton is strongly attracted towards X. It leads to lesser ionizations and weak acid.

Table 3.9

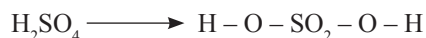
| Species | H_2O_2 | H_2O | H – X | H_2S |
|----------------------------|---|----------------------|--|----------------------|
| Oxidation state (X) | –1 | –2 | –1 | –2 |
| Charge of X | Low | High | Low | High |
| Attraction of X for proton | Less | More | Less | More |
| Acid strength | $\text{H}_2\text{O}_2 > \text{H}_2\text{O}$ | | $\text{H} - \text{X} > \text{H}_2\text{S}$ | |

Acid strength of HCl and H_2O_2

Oxidation state of both Cl and O is –1 in HCl and H_2O_2 . But HCl is stronger acid than H_2O_2 . It is due to radius effect. Radius of Cl^- is greater than O^- (in H_2O_2), so, charge density on Cl^- is lesser than O^- . Therefore, Cl^- attracts proton weakly than O^- and so HCl is stronger acid than H_2O_2 .

Strength of Oxy acids

Acids in which a central atom is surrounded by O atoms and OH groups are called oxy acids, HNO_3 , H_2SO_4 , H_3PO_4 etc.



Oxy acids in general can be formulated as $\text{XO}_n(\text{OH})_m$, Where ‘n’ are additional O – atoms which are not joined with H – atom, and $n = 0, 1, 2$, etc., and $m = 1, 2, 3$ etc.

Table 3.10

| | Comments |
|-----------------------|---|
| Acids strength | $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ Radius factor |
| | $\text{H}_2\text{O}_2 < \text{HCl}$ Radius factor |
| | $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ Radius factor |
| | $\text{H}_2\text{O} < \text{H}_2\text{O}_2$ Oxidation state effect |
| | $\text{H}_2\text{S} < \text{HCl}$ Oxidation state effect |

Different parameters are required to predict strength of oxy acids:

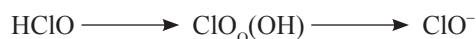
(A) The n in the general formula $\text{XO}_n(\text{OH})_m$ and acid strength.

Larger the value of n in the formula $\text{XOn}(\text{OH})_m$, stronger is the acid and vice versa.

n , dissociation constant (K_a) and acid strength

When an acid ionizes the conjugate base is produced. The negative charge is delocalized over all the O atoms. The more the O – atoms in the conjugate base, greater is the delocalization of the negative charge and thus the more stable is the anion. Hence, stronger is the acid.

For example,



There is no additional O-atoms for delocalization of negative charge. So HClO is a weak acid.



In this case delocalization is very effective as there are four O – atoms in the conjugate base. This makes dissociation highly favourable and HClO_4 is a very strong acid.

Table 3.11

| Acid | $\text{XO}_n(\text{OH})_m$ | n | m |
|-------------------------|----------------------------|-----|-----|
| HNO_3 | $\text{NO}_2(\text{OH})$ | 2 | 1 |
| H_2SO_4 | $\text{SO}_2(\text{OH})_2$ | 2 | 2 |
| H_3PO_4 | $\text{PO}(\text{OH})_3$ | 1 | 3 |

Table 3.12

| n | K_a | Acid strength |
|-----|-----------------------------|---------------|
| 0 | $\sim 10^{-7}$ to 10^{-9} | Weak |
| 1 | $\sim 10^{-2}$ to 10^{-3} | Mod strength |
| 2 | $\sim 10^2$ | Strong |
| 3 | very large | Very strong |

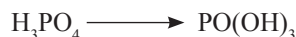
PROBLEM

Predict the strengths of the following acids –

- (a) HNO_2 and HNO_3
- (b) H_2SO_4 and H_2SO_3
- (c) HClO , HClO_2 , HClO_3 and HClO_4
- (d) H_3PO_2 , H_3PO_3 and H_3PO_4

Effective –ve charge per O-atom in the conjugate base and acid strength

The acid strength of H_3PO_2 , H_3PO_3 and H_3PO_4 can not be predicted using general formula $\text{XO}_n(\text{OH})_m$,



All have only one additional O-atom i.e., which is not joined with H-atom.

For such acids, negative charge per O-atom in the conjugate base can decide acid strength.

$$\text{Negative charge per O-atom} = \frac{\text{Charge}}{\text{Total no. of O-atoms}}$$

Smaller the negative charge per O-atom stronger the acid and vice versa.

Table 3.13

| Acid | Conjugate base | -ve charge per O-atom | Acid strength |
|-------------------------|---------------------------|-----------------------|---|
| H_3PO_2 | H_2PO_2^- | $-1/2 = -0.5$ | $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$ |
| H_3PO_3 | HPO_3^{2-} | $-2/3 = -0.66$ | 2.15 |
| H_3PO_4 | PO_4^{3-} | $-3/4 = -0.75$ | $\text{P}^{\text{Ka}} 1.2 \ 1.82$ |

Note:

In H_3PO_2 and H_3PO_3 , two H – atoms and one H – atom are directly attached to P atoms respectively.

Explanation for the above observation

It is found that when the negative charge per O – atom is smaller the acid is strong and vice versa. It is due to the fact that higher negative charge attracts proton strongly dissociation is depleted and acid is weak. When the negative charge on the O – atoms is lower, they attract proton weakly, dissociation becomes easy and acid is strong.

PROBLEM

Predict acid strength of

- (a) H_3PO_4 and H_2CO_3
 (b) H_2SO_4 and HNO_3

Electronegativity of the central atom and acid strength

Acid strength of HOCl , HOBr , HOI , H_2SO_4 , H_2SeO_4 and many likes can neither be predicted considering – $\text{XO}_n(\text{OH})_m$ formula nor taking into consideration negative charge per O – atom.

For such acids, electronegativity of the central atom (X) is used.

Lesser is the electronegativity of the central atom weaker is the acid and vice versa.

As the electronegativity of the central atom decreases, X – O bond gets more and more polar in which O atom is negative, $\text{X}^{\delta+} - \text{O}^{\delta-}$. The greater the accumulation of negative charge on O – atom stronger is its bond with proton. It results into lesser dissociation of O – H bond making the acid weak.

Table 3.14

| Acid | $\text{XOn}(\text{OH})_m$ | Negative charge per O – atom |
|--------------------------|-----------------------------|------------------------------|
| HOCl | $\text{ClO}_0(\text{OH})$ | –1 |
| HOBr | $\text{BrO}_0(\text{OH})$ | –1 |
| H_2SO_4 | $\text{SO}_2(\text{OH})_2$ | –2/4 |
| H_2SeO_4 | $\text{SeO}_2(\text{OH})_2$ | –2/4 |

Table 3.15

| Acids | Polarity order of X – O bond | Acid strength |
|--------------------------|---|--|
| HOCl | | |
| HOBr | $\text{I} - \text{O} > \text{Br} - \text{O} > \text{Cl} - \text{O}$ | $\text{HOCl} > \text{HOBr} . \text{HOI}$ |
| HOI | | |
| H_2SO_4 | | |
| H_2SeO_4 | $\text{Se} - \text{O} > \text{S} - \text{O}$ | $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4$ |

PROBLEM

Predict acid strength of –

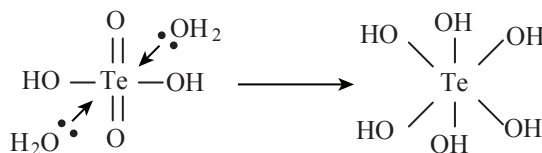
- (a) HO_3Cl , HO_3Br , HO_3I
- (b) HClO_4 , HBrO_4 , HIO_4
- (c) HClO_4 , HMnO_4
- (d) HClO_3 , HNO_3

Oxy acids of Te in +6 and iodine in +7 oxidation states

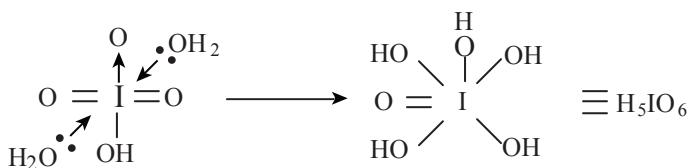
The oxy acids of Te in +6 and iodine in +7 are H_6TeO_6 and H_5IO_6 respectively. Oxy acids of S, Se and Te in +6 oxidation state are formulated as



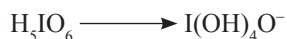
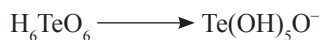
Tellurium is much larger atom compared to S and Se. Therefore, it can accommodate six O – atoms around it and so telluric acid is H_6TeO_6 .

**Figure 3.3**

Iodine is also very large. Therefore, it can also accommodate more O – atoms around it.

**Figure 3.4**

However, H_6TeO_6 and H_5IO_6 are very weak acids



As additional O – atoms in anions is one, the acids are weak.

Base strength

Two types of bases are found:

| 1. Hydra bases | 2. Hydroxide bases |
|--|---|
| NH_3 , PH_3 , AsH_3 , SbH_3 (MH_3) | LiOH , NaOH , KOH $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ $\text{Fe}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$ |

Strength of Hydra bases

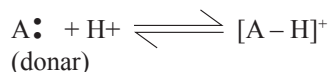
Hydrides of group 15 (N – family) are basic and are called hydra bases, NH_3 , PH_3 , AsH_3 , SbH_3 .

Base strength depends upon

- (i) Size of the central atom
- (ii) Oxidation state of the central atom

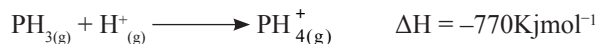
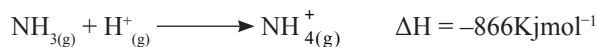
Size of the Central atom and Base strength

The tendency and ability of a chemical substance to donate electron pair to proton is called “basicity”. It is controlled by thermodynamic factor i.e., bond strength. In simple terms, it is proton affinity,



If A – H bond is strong, the base A is strong and vice versa.

When size of the donor atom (M) increases, bond distance $[\text{M} - \text{H}]^+$ increases and so bond with proton becomes weak. Therefore, the combination is not favoured energetically i.e., basic is weak.



Here N – H bond is stronger than P – H. So, NH_3 is a stronger base than PH_3 .

Table 3.16

| $\text{MH}_3 \rightarrow$ | NH_3 | PH_3 | AsH_3 | SbH_3 |
|---|---|---------------|----------------|----------------|
| Size of M | \longrightarrow | | | Increases |
| M – H bond strength in $\text{M} - \text{H}^+$ | \longrightarrow | | | Decreases |
| Base strength | \longrightarrow | | | Decreases |
| | $\text{HN}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$ | | | |

Oxidation state of the central atom and base strength

Oxidation state of the central atom decides bond strength with H^+ . When oxidation state of M is high bond with H^+ is strong and so the base is strong and vice versa. Thus HN_3 is stronger base than $\text{NH}_2 - \text{NH}_2$ as oxidation states of N in NH_3 and $\text{H}_2\text{N} - \text{NH}_2$ are –3 and –2 respectively.

**Table 3.17**

| Base | NH_3 | $\text{H}_2\text{N} - \text{NH}_2$ | $\text{H}_2\text{N} - \text{OH}$ |
|---------------------------------------|---|------------------------------------|----------------------------------|
| Oxidation state of N | –3 | –2 | –1 |
| Conc. of –ve charge on N | \longrightarrow | Decreases | \longrightarrow |
| $[\text{N} - \text{H}]^+$ bond energy | \longrightarrow | Decreases | \longrightarrow |
| Base strength | Decreases | | |
| | $\text{NH}_3 > \text{H}_2\text{N} - \text{NH}_2 > \text{H}_2\text{N} - \text{OH}$ | | |

Strength of Hydroxide bases

Hydroxide bases are NaOH, KOH, Ca(OH)_2 , Al(OH)_3 , Fe(OH)_2 , Cu(OH)_2 . That is, M(OH)_n , where M = metal. The overall base strength depends on M – O bond nature:

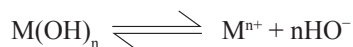
- (i) If M – O bond is more and more ionic, the hydroxide is stronger base.
- (ii) If M – O bond develops covalency base strength decreases.

The M – O bond nature depends on radius of M^{n+} , oxidation state of M i.e., value of n and core electrons in M^{n+} . Therefore, base strength depends on:

- (i) Radius of M^{n+}
- (ii) Oxidation state of M
- (iii) Core electrons in M^{n+}

Radius of M^{n+} and base strength

As radius of M^{n+} increases $\text{M}^{n+} \text{OH}^-$ bond becomes more and more ionic. Also attraction between M^{n+} and HO^- decreases. Therefore, the dissociation

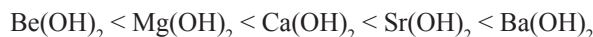


increase and base strength increases. Thus large metals form strong bases.

Table 3.18

| Base | LiOH | NaOH | KOH | RbOH | CsOH |
|--|---|-----------|-------|-------|-------|
| Radius M^{n+} | _____ | Increases | _____ | _____ | _____ |
| Electropositive Nature of M | _____ | Increases | _____ | _____ | _____ |
| Nature of $\text{M}^{n+} \text{OH}^-$ bond | Ionic nature increases | | | | |
| Attraction between M^{n+} and HO^- | _____ | Decreases | _____ | _____ | _____ |
| Base strength | Increases $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$ | | | | |

Similarly, for bases of group 2 i.e., M(OH)_2 , M = Be, Mg, Ca, Sr and Ba, the strength vary as:



Oxidation state of M (i.e., n) and base strength

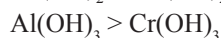
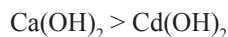
As charge on M increases, base strength decreases. It is due to the fact that, higher charge on M makes M^{n+} highly polarizing; M – O bond in M – OH develops covalency, ionization of M(OH)_n decreases and base strength decreases. Thus



Core electrons and Base strength

If two metal ions have the same oxidation state and the same ionic radii, the above two methods will fail to predict base strength. In such cases, core electrons decide base strength.

If core electrons are larger in number the metal hydroxide is a weaker base and vice versa.



It is due to the fact that M^{n+} having more core electrons is more polarising. It makes $M - O$ bond more covalent decreasing base strength.

PROBLEM

Arrange the following in decreasing order of base strength.

- (a) $Al(OH)_3$ $Cr(OH)_3$ $Fe(OH)_3$
 (b) $Ca(OH)_2$ $Cu(OH)_2$ $Fe(OH)_2$
 (c) $Ni(OH)_2$ $Ca(OH)_2$ $Ti(OH)_2$
 (d) $Al(OH)_3$ $La(OH)_3$ $Cr(OH)_3$

Lewis Acid–Base Theory

It is electronic theory of acids and bases proposed by G. N. Lewis (1923). According to this theory:

Acid is an electron pair acceptor and base is an electron pair donor. It can be represented as:



Here H^+ is electron pair acceptor and NH_3 is electron donor. Thus, H^+ is a Lewis acid and NH_3 is a Lewis base.

Some other examples include,

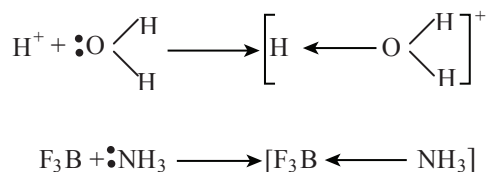
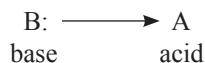


Figure 3.5

Therefore, a general acid – base situation can be represented as

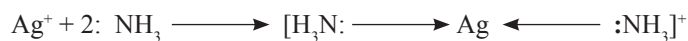


Lewis Acids

The following chemical species are Lewis acids:

(a) Cations (i.e., positive ions)

All positive ions are Lewis acids as they can accept electron pairs, Example, Na^+ , Ca^{+2} , Al^{+3} , Fe^{2+} , Zn^{+2} , Ag^+ etc



(b) Electron deficient species

Chemical species which lack octet of electrons at the central atom are called electron deficient. They can accept electron pairs (so Lewis acids), Example, BF_3 , $AlCl_3$, BeF_2 etc.

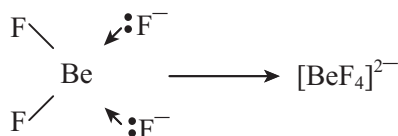
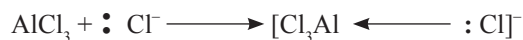


Figure 3.6

**(c) Molecules with multiple bonds**

Molecules having multiple bonds between atoms of different electronegativities have polar bonds. Positive centers in such species are Lewis acid centre, Example, CO_2 , SO_2 etc. In CO_2 , carbon atom is less electronegative and has positive polarity. Therefore, C centre is Lewis acid centre as it can accept electron pair.

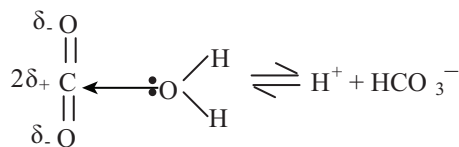


Figure 3.7

(d) Species in which the central atom has vacant d orbitals

The vacant d – orbitals can accept electron pairs. Hence, such species can act as Lewis acids. Example, SiF_4 , SnCl_4 , PCl_5 , TiCl_4 etc.

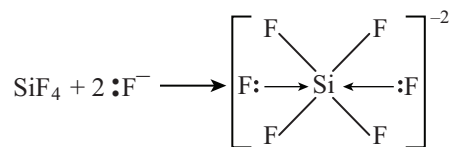


Figure 3.8

Lewis Bases**(a) Anions (or negative ions)**

All negative ions can donate electron pairs. Therefore, they are Lewis bases. Example, F^- , Cl^- , H^- , HO^- , CN^- , RO^- etc.

(b) Molecules which have lone pairs. Example,

NH_3 , H_2O , R-OH , R-NH_2 etc

(c) Multiple bonds can also act as a Lewis base. For example, $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$ etc.

Figure 3.9

(d) Aromatic systems may also behave as a Lewis base, for example, C_6H_6 , $C_5H_5^-$ etc.

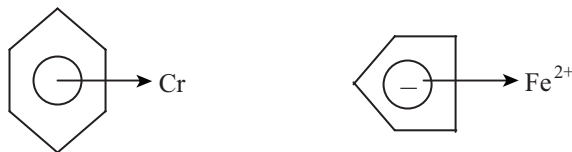
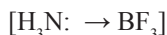


Figure 3.10

Lewis acid–base concept is of wide applicability. Formation of coordination compounds, charge transfer complexes, Ion–dipole interaction, dipole – dipole interaction, reactions of carbonium ions (Lewis acids), carbanions (Lewis bases) etc, may be viewed as Lewis acid–base reactions.

Strength of Lewis Acids and Bases

Acid and base strength in the Lewis sense are not fixed, but vary with the nature of the partner. For example, NH_3 is a good Lewis base for the Lewis acid BF_3 . The addition compound is formed easily,



But F_3N is not a Lewis base towards BF_3 and the compound $[F_3N \rightarrow BF_3]$ is not known. So is the case with CO, but it is a good Lewis base (Ligand) towards transition metals, Example $Fe(CO)_5$, $Ni(CO)_4$ etc.

The overall Lewis acid – base interaction depends on bond energy. Electronic as well as steric effect influence it. But complete discussion is beyond the scope of this text.

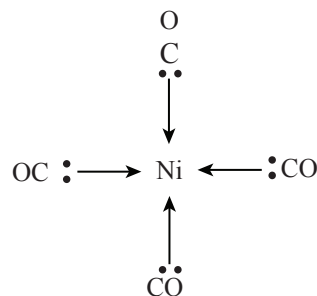


Figure 3.10

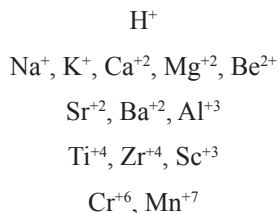
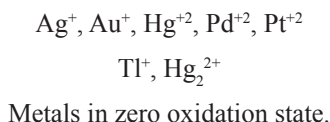
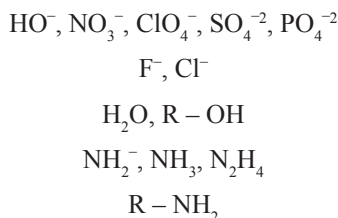
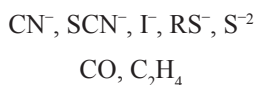
Hard and Soft Acids and Bases

Lewis acids and bases are classified as hard and soft. However, this classification is based on stability of metal complexes formed by different ligands. Metals are classified as:

- (i) Class 'a' metals and
- (ii) Class 'b' metals.
- (i) Class 'a' metals are the following
 - (a) Alkali metal ions, M^+
 - (b) Alkaline earth metal ions M^{+2}
 - (c) Lighter and highly charge metal ions, Ti^{+4} , Cr^{+6} , Mn^{+7} , Co^{+3} , Al^{+3} i.e., M^{n+} . Which have noble gas electron configuration or are small.

The above metal ions are small, compact and less polarizable. They form more stable complexes with ligands (Lewis bases) in which donor atoms are more electronegative, small and less polarisable (O, F, N etc.). The metal ions (M^{n+}) are Lewis acids and ligands are Lewis bases. Such acids and bases were called 'Hard' by Pearson.

- (ii) Class 'b' metals are larger and more polarizable. They include:
 - (i) Heavier transition metal ions.
Example, Cu^+ , Ag^+ , Pt^{+2} , Hg_2^{2+}
 - (ii) Metals in zero oxidation states. Example, metals in metal carbonyls, $Ni(CO)_4$, $Fe(CO)_5$ etc.
Such acids and bases were called soft.

Example of Hard and Soft acids and basesHard acidsSoft acidsHard basesSoft bases

On the basis of this concept, Pearson proposed that, “Hard acids prefer hard bases and soft acids prefer soft bases”. It is often called HSAB principle.

General concept of bonding shows that electrostatic attraction is responsible for hard – hard interaction where as covalent bonding is important in soft – soft interactions. It is, however, not the complete story and there is departure.

PRACTICE QUESTIONS

- Explain Bronsted–Lowry acids and bases.
- Why is acetic acid not an acid in H_2SO_4 ?
- State the Lewis definition of acids and bases including at least one example that involves a protonic acid.
- Rank the following acids in order of their strength giving reasons:
 - HOClO , HOClO_2 , HOClO_3
 - HMnO_4 , H_2SeO_4 , H_2AsO_4
 - H_2CrO_4 , HBrO_4 , HOSO_2F
 - H_2SO_4 , HClO_4 , HNO_3
- Why is B , Br_3 stronger acid than BF_3 ?
- Fill in the blanks:
 - H_2SO_4 is conjugate _____ of HSO_4^-
 - According to Lewis concept acids _____ base _____.
 - In pure water $[\text{H}^+]$ and $[\text{HO}^-]$ are _____.
 - In pure water $[\text{H}^+] = \text{_____}$ and $[\text{HO}^-] = \text{_____}$.
 - Cl^- is _____ of HCl and NH_4^+ is _____ of NH_3 .
 - In an aq. Solution $[\text{H}^+] = 10^{-2}$, $[\text{HO}^-]$ is _____.
 - $\text{pH} + \text{pOH}$ of a solution is _____.
 - pH of 10^{-8} M HCl is _____.
 - pH of 10^{-9} M NaOH is _____.
 - pK_b and K_b are related as _____.
 - The proticity of H_3PO_2 and H_3PO_3 respectively are _____ and _____.
 - Forms of proton in water are _____.
 - The bonding between hard acid with hard base is _____ in nature.
 - _____ concept of acids and bases includes redox reactions also.
 - pH of a buffer solution _____ by addition of a small amount of acid or base.

7. Why is H_3PO_2 is not a polyprotic acid?
8. Give conjugate acids of
 (a) HCO_3^- (b) N_2H_4
 (c) $\text{R}-\text{NH}_2$ (d) HNO_3
 (e) SO_3^{2-}
 (f) $[\text{Fe}(\text{H}_2\text{O})_5\text{HO}]^{2+}$ (g) H_2PO_4^-
9. Give conjugate bases of
 (a) HSO_4^- (b) NH_3
 (c) H_2O (d) H_2S
 (e) NH_4^+ (f) $\text{R}-\text{OH}$
 (g) H_3PO_2 (h) H_5IO_6
 (i) HOSO_2F
10. Rank the following bases in order of their strength.
 (a) NaOH , $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$
 (b) CH_3^- , HO^- , NH_2^- , H_3^-
- (c) SO_4^{2-} , PO_4^{3-} , SiO_4^{4-}
 (d) NH_3 , H_2H_4 , NH_2-OH
 (e) $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$
 (f) $\text{Ca}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$
11. Which of the following reactions are expected to proceed forward? Give reasons.
 (a) $\text{HS}^- + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{S} + \text{CH}_3\text{COO}^-$
 (b) $\text{HSO}_4^- + \text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + \text{NO}_3^-$
 (c) $\text{NO}_3^- + \text{HSO}_4^- \rightarrow \text{HNO}_3 + \text{SO}_4^{2-}$
 (d) $\text{CH}_3\text{COO}^- + \text{HNO}_2 \rightarrow \text{CH}_3\text{COOH} + \text{NO}_2^-$
 (e) $\text{NO}_2^- + \text{CH}_3\text{COOH} \rightarrow \text{HNO}_2 + \text{CH}_3\text{COO}^-$
- [A B-L acid-base reaction is favoured from stronger to weak acid – base direction. It is because conjugate base of a weak acid is a strong base and conjugate acid of a weak base is a strong acid]

OBJECTIVE-TYPE QUESTIONS

1. Conjugate base of HSO_4^- is
 (a) S^{2-} (b) SO_4^{2-}
 (c) H_2SO_4 (d) H_3SO_4^+
2. Conjugate acid of H_2PO_3^-
 (a) H_3PO_3 (b) HPO_3^{2-}
 (c) H_3PO_4 (d) H_3PO_2
3. Lewis base is
 (a) BF_3 (b) Al^{+3}
 (c) H_5 (d) AlCl_3
4. Which of the following is weakest base?
 (a) $\text{Ca}(\text{OH})_2$ (b) $\text{Zn}(\text{OH})_2$
 (c) KOH (d) NaOH
5. The compound that is not a Lewis acid
 (a) BF_3 (b) BaCl_2
 (c) SnCl_4 (d) AlCl_3
6. The H^+ concentration in a solution is 10^{-2}M , the HO^- concentration in the same solution is
 (a) 10^{-4}M (b) 10^{-2}M
 (c) 10^{-12}M (d) 10^{-10}M
7. Strongest acid is
 (a) $\text{K}_a = 10^4$ (b) $\text{K}_a = 10^{-4}$
 (c) $\text{K}_a = 1$ (d) $\text{K}_a = 0.01$
8. Strongest acid is
 (a) $\text{P}^{\text{H}} = 12$ (b) $\text{P}^{\text{H}} = 8$
 (c) $\text{P}^{\text{H}} = 4$ (d) $\text{P}^{\text{H}} = 3$
9. The correct order of acidity is
 (a) $\text{HOCl} > \text{HOBr} > \text{HOI}$
 (b) $\text{HOI} > \text{HOBr} > \text{HOCl}$
 (c) $\text{HOBr} > \text{HOCl} > \text{HOI}$
 (d) $\text{HOCl} > \text{HOI} > \text{HOBr}$
10. The correct order of base strength is
 (a) $\text{CH}_3^- > \text{NH}_2^- > \text{HO}^-$
 (b) $\text{HO}^- > \text{NH}_2^- > \text{CH}_3^-$
 (c) $\text{NH}_2^- > \text{CH}_3^- > \text{HO}^-$
 (d) $\text{CH}_3^- > \text{HO}^- > \text{NH}_2^-$
11. The P^{H} of 10^{-9}M NaOH solution is
 (a) 9 (b) < 5
 (c) > 5 (d) > 7
12. The P^{H} of 10^{-8}M HCl is
 (a) 8 (b) < 7
 (c) > 7 (d) < 6
13. Pair of amphoteric species is
 (a) H_2CO_3 and H_2O
 (b) HCO_3^- and H_2O

- (c) H_2CO_3 and HCO_3^-
 (d) CO_3^{2-} and H_3O^+
14. When HCl is dissolved in CHCl_3 , the equilibrium set up is

$$\text{CH}_3\text{COOH} + \text{HCl} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$$
 The set which represents conjugate acid–base pair is
 (a) $(\text{HCl}, \text{CH}_3\text{COOH}_2^+)$ and $(\text{CH}_3\text{COOH}, \text{HCl})$
 (b) $(\text{HCl}, \text{Cl}^-)$ and $(\text{CH}_3\text{COOH}_2^+, \text{CH}_3\text{COOH})$
 (c) $(\text{HCl}, \text{CH}_3\text{COOH})$ and $(\text{Cl}^-, \text{CH}_3\text{COOH}_2^+)$
 (d) $(\text{CH}_3\text{COOH}_2^+, \text{HCl})$ and $(\text{Cl}^-, \text{CH}_3\text{COOH})$
15. What is the decreasing order of strength of bases, HO^- , NH_2^- , C_2H_5^- , HC_2^- ?
 (a) $\text{HO}^- > \text{NH}_2^- > \text{C}_2\text{H}_5^- > \text{HC}_2^-$
 (b) $\text{C}_2\text{H}_5^- > \text{NH}_2^- > \text{HC}_2^- > \text{HO}^-$
 (c) $\text{HC}_2^- > \text{C}_2\text{H}_5^- > \text{NH}_2^- > \text{HO}^-$
 (d) $\text{NH}_2^- > \text{HC}_2^- > \text{HO}^- > \text{C}_2\text{H}_5^-$
16. The conjugate acid of NH_2^- is
 (a) NH_4^+ (b) NH_3
 (c) N_2H_4 (d) NH_2OH
17. Value of ionic product of water at 25°C is
 (a) $<10^{-14}$ (b) $>10^{-14}$
 (c) $=10^{-14}$ (d) 10^{-12}
18. Which of the following is a soft acid?
 (a) Na^+ (b) Ag^+
 (c) Ca^{+2} (d) Al^{+3}
19. Hg is found in nature as HgS because
 (a) Lattice energy of HgS is high
 (b) Hg^{+2} is soft acid and S^{2-} soft base
 (c) Hg and S are close in the periodic table
 (d) Ionization energy of Hg is very high

ANSWERS

1. (b) 2. (a) 3. (c) 4. (b) 5. (b) 6. (c) 7. (a) 8. (d) 9. (a) 10. (a)
 11. (d) 12. (b) 13. (b) 14. (b) 15. (b) 16. (b) 17. (c) 18. (b) 19. (b)

4

Chemical Reactions

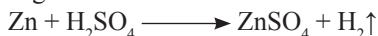


A chemical reaction produces products from suitable reactants.

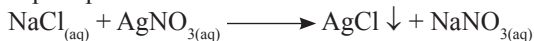


A reaction has taken place is shown by one or more of the following facts:

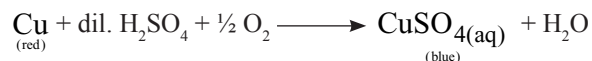
- (a) A gas is evolved.



- (b) A precipitate is formed.

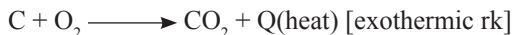


- (c) A colour change is observed.



- (d) A p^{H} change is detected (neutralization reactions follow with P^{H} change).

- (e) Heat change may take place.



Two physical factors control possibility of a reaction:

- (a) Enthalpy change, ΔH and
(b) Entropy change ΔS

The difference of these two quantities gives a third physical quantity G , known as free energy. These three are related as,

$$G = H - TS$$

For a reaction at constant temperature,

$$\Delta G = \Delta H - T\Delta S,$$

$$\text{Where } \Delta G = G_{\text{Prod}} - G_{\text{react}}, \Delta H = H_{\text{Prod}} - H_{\text{react}}, \Delta S = S_{\text{Prod}} - S_{\text{react}}.$$

The value of ΔG decides possibility of a reaction. The following are found:

- (a) When $\Delta G = -\text{ve}$, the reaction takes in the written direction i.e., from L to R. A $-\text{ve } \Delta G$ is possible when $\Delta H < 0$ i.e., $-\text{ve}$ (exothermic rk.) and $\Delta S > 0$ i.e., $+\text{ve}$.

- (b) When $\Delta G = +ve$, the reverse reaction is expected
 (c) When $\Delta G = 0$, it represents an equilibrium condition.

Entropy(s)

Entropy is a measure of disorder in a system. When the system is more ordered entropy is less and vice versa.

When Solid \longrightarrow Liquid

Liquid \longrightarrow Gas

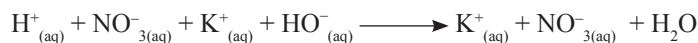
Solid \longrightarrow Gas

Disorder in the system increases. Therefore, entropy increases. Thus explosive reactions follow with large increase in entropy.

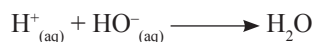
Types of Chemical Reactions

(a) Neutralization reactions

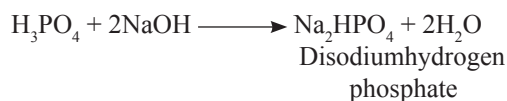
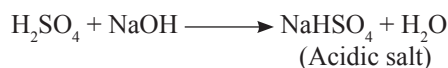
The reaction between an acid and a base is neutralization reaction. The products are a salt and water.



The actual reactions is thus between $\text{H}^+_{(\text{aq})}$ of acid with $\text{HO}^-_{(\text{aq})}$ of the base.



When polyprotic acid react with a base partial replacement of H^+ leads to the formation of an acidic salt.



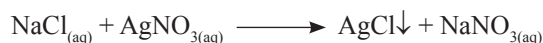
Basic oxides and carbonates can also neutralize an acid.



In neutralization reaction, there is no change in the oxidation number of any of the species, i.e., they are not redox reactions.

(b) Double decomposition or substitution or exchange of ions

In this group of reactions, a precipitate may be formed



For the precipitate to be formed,

Ionic product > solubility product of the compound.

Some times a gas is one of the products and separates from the medium

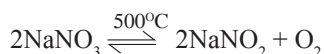


(c) Thermal decomposition

Action of heat can bring about chemical change. It is termed as “Thermal Decomposition”.



Some thermal decomposition is sensitive to temperature.



Some Important thermal decomposition

Ammonium salts

Many ammonium salts decompose around 300°C.



Two different modes of decompositions are observed:

- (i) When the salt contains oxidizing anion (NH_4^+ , NH_4^+ , CrO_7^{2-} , ClO_4^- etc) the NH_4^+ ion is oxidized to N_2O or N_2 .



- (ii) If the anion is not oxidizing (CO_3^{2-} , Cl^- , SO_4^{2-} , CH_3COO^-), then NH_3 is evolved.



Decomposition of oxosalts of metals (CO_3^{2-} , NO_3^- , SO_4^{2-} etc)

All oxosalts are not equally stable to temperature. Their thermal stability (i.e., decomposition temperature) depends on basicity of the metal ion.

- More basic is the metal ion, more stable is the oxo salt. Large metal ions are more basic and they have less polarizing power (Fajan's rule).
- Less basic is the metal ion, less stable is the oxo salt. Small metal ions are less basic and they have high polarizing power (Fajan's rule).

Carbonates and Nitrates (CO_3^{-2} , NO_3^{-})

These ions are trigonal planar and are resonance stabilized. They are best represented as a delocalized electronic system.

The electron screen surrounding the planar ion is easily distorted by a metal ion which is strongly polarizing. Therefore, the oxoanions easily decompose on heating.

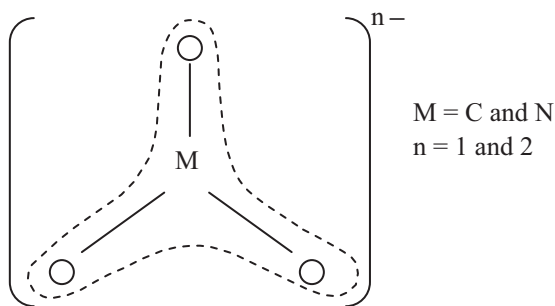


Figure 4.1

Conclusions

- (i) Alkalimetals are more basic (i.e., large in size) and have low polarizing power. Therefore, carbonates and nitrates of alkali metals are most stable (Li is exception as it is less basic, small in size and highly polarizing).



- (ii) Carbonate and nitrates of heavy metals (di and trivalent) decompose on heating.



In general,



(M = not an alkali metal).

The decomposition temperature, however, increases with increase in basic nature of the metal.

Sulphates

The SO_4^{-2} ion is tetrahedral. The three dimensional ion is not so easily distorted by even highly polarizing ions. Therefore, decomposition temperature of sulphates is higher than carbonates.



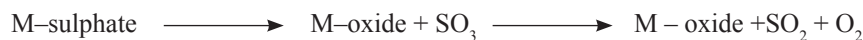
Size of M^{2+} increases \longrightarrow

Polarizing power decreases \longrightarrow

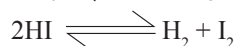
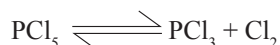
Basic nature increases \longrightarrow

Decomposition temperature increases \longrightarrow

The general reaction of decomposition of sulphate is

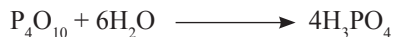


Some thermal decompositions are reversible

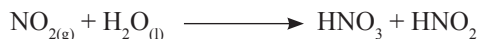


Hydration Reactions

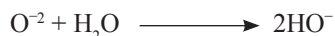
Many of the oxides add water to form products.



Such reactions actually involve bonding of water to another reactant. Some hydration reactions are redox e.g., disproportionation of NO_2 in water,

**Hydrolysis**

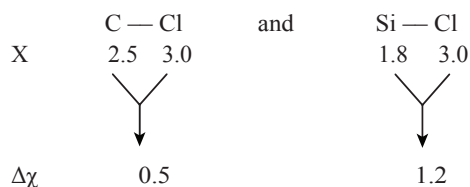
Splitting of water molecules by chemical species is termed as “Hydrolysis”.

**Hydrolysis of covalent compounds**

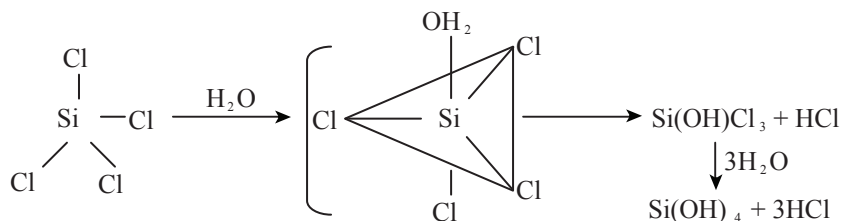
Hydrolysis of covalent compounds depends on:

- (i) Polarity of bond
- (ii) Presence of vacant d-orbitals at the central atom i.e., acceptor ability of the chemical species.
- (iii) Donor property of the chemical species.

CCl_4 and SiCl_4 ,

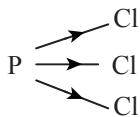


Therefore, Si is preferred more by the nucleophile (H_2O). In addition to this C is coordinatively saturated whereas Si can increase its coordination number by the use of vacant 3d orbitals. Thus, bond polarity and use of vacant d orbitals differentiate CCl_4 and SiCl_4 . The reaction of SiCl_4 goes as:

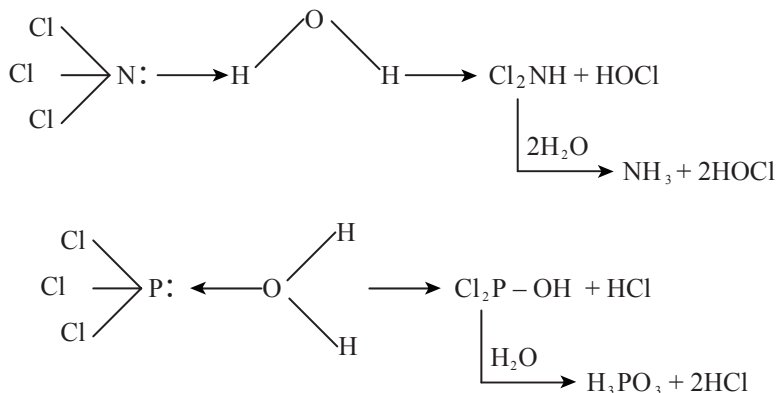


Hydrolysis of NCl_3 and PCl_3

The N – Cl bond is less polar than P – Cl bond. Therefore, lp at N has greater donor property than lp at P in PCl_3 .



Also P has vacant 3d orbitals. So it may act as an acceptor. Therefore, both hydrolyze but the nature of products differs, NCl_3 hydrolyzes to a base NH_3 and PCl_3 to an acid H_3PO_3 .

 **SF_4 and SF_6**

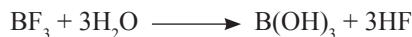
Among SF_4 and SF_6 , SF_6 is inert towards hydrolysis. This inertness is due to

- (i) High S – F bond strength
- (ii) Coordinative saturation of S in SF_6
- (iii) Steric hindrance

SF_4 is extremely reactive, instantly hydrolyzed by water to SO_2 and HF.



In general, non-metal halides are hydrolyzed to acids (with no change in the oxidation number of the non-metal). Among boronhalides, BF_3 is hydrolyzed partially whereas others hydrolyze to boric acid.



The partial hydrolysis may be due to greater stability of BF_4^- ion.



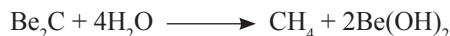
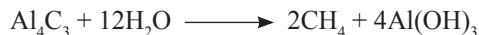
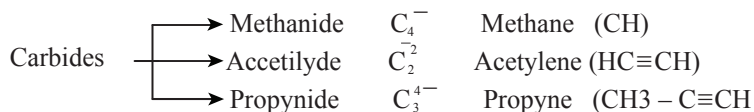
The species BX_4^- , not stable with increasing size of halogens.

Hydrolysis of Ionic Species of Non-metals

Common ionic species found are, Carbides, Nitrides, Oxides, Sulphides, Phosphides, Arsenides, Halides etc. All these compounds hydrolyze in water.

Carbides

Three types are found. The classification is based on the basis of the hydrolyze products produced.



Actually, the ionic units hydrolyze.



Nitrides hydrolyze to NH_3 .



Oxides hydrolyze to hydroxide, (insoluble oxides do not give this reaction).



Peroxides

Hydrolyze to H_2O_2



Superoxides (O_2^-)

Superoxides are strong oxidizing agents also. They produce H_2O_2 and O_2 on hydrolysis i.e., hydrolysis is oxidative.



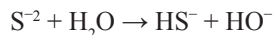
Phosphides (P^{3-}) and Arsenides (As^{3-})

These are hydrolyzed to PH_3 and AsH_3 (arsine)



Sulphides (S^{2-})

They hydrolyze to form hydrosulphide (SH^-)

**Halide ions**

(X^- , $X = F, Cl, Br, I$) do not hydrolyze. It is because the hydrolysis products HX being acids further ionize.

Conclusion

- (a) Anions of less electronegative non-metals (except oxygen) hydrolyse. It is because their hydrolysis products are stable (They are conjugate bases of the very weak acids).
- (b) Anions of halogens do not hydrolyze because the hydrolysis products are strong acids, and ionize in water (conjugate bases of strong acids are weak bases)

Oxidation–Reduction Reactions

One of the most important class of inorganic reactions is oxidation and reduction reaction. It occurs all around us in the environment, in the human body etc.

Oxidation

Loss of electron from a species is oxidation.



Oxidation is also defined as an increase in the oxidation number of a substance.

Reduction

Gain of electron by a species is reduction.

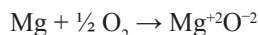


Reduction is also defined as a decrease in the oxidation number of a substance.

Oxidation and reduction reactions always take place together. Therefore, the overall reaction is termed as redox reaction.



In this reaction, Mg loses two electrons and these electrons are gained by oxygen



Thus Mg is oxidized and oxygen is reduced.

Oxidation Number

The charge which an atom appears to have in a molecule (or ion) is known as its "Oxidation Number". It is calculated using accepted rules of valency, viz.,

- (i) Bond pair electrons are equally divided between two like atoms.



Neither of the H atoms loses or gains electron. Therefore, oxidation number (ON) of H in H_2 is zero.

- (ii) Bond pair electrons between unlike atoms is counted with more electronegative atom.



Here H appears to lose one electron and Cl appears to gain one electron. Therefore, ON of H in HCl is +1 and that of Cl is -1.

Rules to calculate Oxidation Number (ON)

- (a) The ON of an element in uncombined state is zero. Example, Na, Fe, H, Cl etc., have oxidation number zero.
 (b) In mononuclear ions, the charge on it is its oxidation number

| <u>Ion</u> | <u>ON</u> |
|------------------|-----------|
| Na^+ | +1 |
| Fe^{3+} | +3 |
| S^{-2} | -2 |

- (c) Common ON of H is +1, except in the metal hydrides (Gr1 and Gr2), when it is -1

| <u>Compound</u> | <u>ON of H</u> |
|------------------------|----------------|
| HF | +1 |
| H_2O | +1 |
| H_2O_2 | +1 |
| NaH | -1 |
| CaH_2 | -1 |

- (d) Common ON of oxygen is -2, except in peroxides when it is -1, superoxides $-\frac{1}{2}$,
 Fluorine is more electronegative than oxygen, so oxygen has positive ON in fluorine oxides,

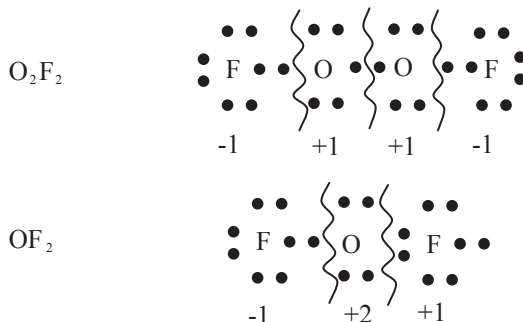
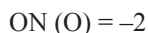


Figure 4.2

(e) The sum of the oxidation numbers of all the atoms in a compound is zero.



$$\text{Sum of ONs} = 2 \times 1 + (-2) = 0$$

(f) The sum of the oxidation numbers of all the atoms in a complex ion (polynuclear) is equal to the charge on the ion.



$$\therefore x + (-2 \times 4) = -1$$

$$\therefore x = +7 \text{ i.e.,}$$



PROBLEMS

Calculate the ONs of

- (i) Cr in Cr_2O_3 and CrO_5
- (ii) P in H_3PO_4 and H_3PO_3
- (iii) N in HNO_3 and NH_2OH
- (iv) Cr in CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_2Cl_2
- (v) Cl in ClO_2^- , ClO_3^- and ClO_4^-
- (vi) Cl in Ca(OC)Cl
- (vii) B in $\text{Na}_2\text{B}_4\text{O}_7$

Maximum and Minimum ONs

Maximum $\text{ON} = N$

Minimum $\text{ON} = N - 8$

Where N = valence electrons of the atom.

Table 4.1

| Elements | Valence shell e – configuration | Ves | Maximum ON | Minimum ON (N – 8) |
|-------------------|---------------------------------|-----|------------|--------------------|
| Na | $3s^1$ | 1 | +1 | – |
| Mg | $3s^2$ | 2 | +2 | – |
| Al | $3s^2 3p^1$ | 3 | +3 | – |
| S | $2s^2 2p^4$ | 6 | +6 | –2 |
| N | $2s^2 2p^3$ | 5 | +5 | –3 |
| X (X = Cl, Br, I) | $3s^2 3p^5$ | 7 | +7 | –1 |
| Si | $3s^2 3p^2$ | 4 | +4 | –4 |

Note:

- Metals have positive ON only. Some metals may adopt negative ON in special cases.
- Some metals may have more than one ONs (transition elements and some p – block metals)

| | |
|----|-------------------------------------|
| Fe | Fe ²⁺ , Fe ³⁺ |
| Pb | Pb ⁺² , Pb ⁺⁴ |
| Tl | Tl ⁺¹ , Tl ⁺³ |

Oxidizing agents

The substance which does oxidation is oxidizing agent. The ON of an oxidizing agent decreases in a redox reaction i.e., the substance which is reduced is oxidizing agent.

Reducing agents

The substance which does reduction is reducing agent. The ON of a reducing agent increases in a redox reaction, i.e., the substance which is oxidized is reducing agent.

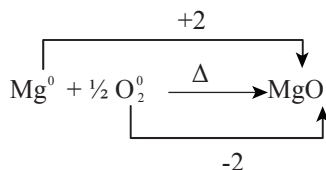
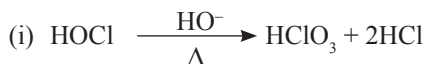


Figure 4.3

Here ON of oxygen is decreased (from zero to -2). So, oxygen is oxidizing agent. The ON of Mg is increased (from zero to +2), therefore, Mg is reducing agent.

Self Oxidation–Reduction Reaction or Disproportionation Reaction

There are many reactions in which the same substance is oxidized and reduced both. Such reactions are known as “Disproportionation Reaction”. In these reactions the same substance is the oxidizing agent as well as the reducing agent.

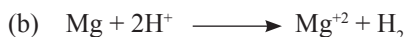


In this reactions ONs of Cl in HOCl is +1, in HCl -1 and in HClO₃ +5. Hence, Cl is oxidized (to HClO₃) and reduced (to HCl) both. It is thus, a disproportionation reaction.



PROBLEMS

Explain the following reaction w.r.t. oxidation – reductions:



Reactions followed with change in ON are redox. In



S^{-2} in H_2S is oxidized to S and S in SO_2 (S^{+4}) is reduced to S also. So, H_2S is reducing agent and SO_2 is oxidizing agent.

All the redox processes can be summarized as:

Table 4.2

| Substance oxidized | Substance reduced | Oxidizing agent | Reducing agent |
|--------------------|-------------------|-----------------|----------------|
| H_2S | SO_2 | SO_2 | H_2S |
| Mg | H^+ | H^+ | Mg |
| NH_4^+ | $Cr_2O_7^{-2}$ | $Cr_2O_7^{-2}$ | NH_4^+ |
| Cl | Cl | Cl | Cl |

The terms involved in a redox process may be summerized as:

Table 4.3

| Term | Change in electrons | Change in oxidation number |
|--------------------|--|--|
| Oxidation | Loss of electrons | Increases |
| Reduction | Gains of electrons | Decreases |
| Oxidizing agent | Accepts electrons | Decreases |
| Reducing agent | Gains electrons | Increases |
| Substance oxidized | Loses electrons | Increases |
| Substance reduced | Gains electrons | Decreases |
| Disproportionation | The same substance gains and loses electrons | Decreases and increases of the same atom |

Oxidizing and Reducing Agents

Oxidizing agent

$KMnO_4$, $K_2Cr_2O_7$, HNO_3 , H_2SO_4 , $HClO_4$, Cl_2 , O_2 , O_3 are common oxidizing agents.

The ON of an oxidizing agent decreases in a reaction. Therefore, when the ON of the active element is maximum, it can decrease only and the substance is oxidizing agent only.

For example, the oxidation number of Mn in MnO_4^- is +7 which is maximum for Mn. So, MnO_4^- is oxidizing agent only.

Reducing agents

H_2S , HI , HBr , $H_2C_2O_4$, $SnCl_2$, $FeSO_4$ etc., are reducing agents.

The ON of a reducing agent increases in a reaction. Therefore, when the ON of the active element is minimum, it can increase only and the substance is then only a reducing agent.

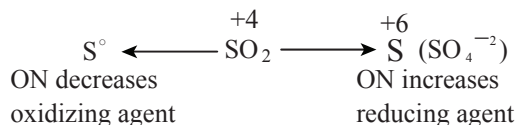
The ON of S in H_2S is -2 . It is minimum for S. therefore, H_2S is reducing agent only.

Oxidizing and Reducing Agent Both

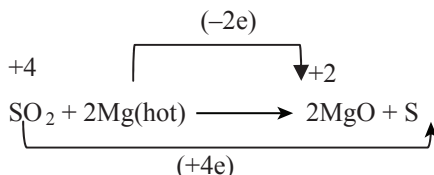
Common such agents are H_2O_2 , SO_2 (H_2SO_3), HNO_2 , etc.

When the ON of the active element is intermediate i.e., neither maximum nor minimum, it can decrease and increase both. Therefore, such substances are oxidizing and reducing agents both.

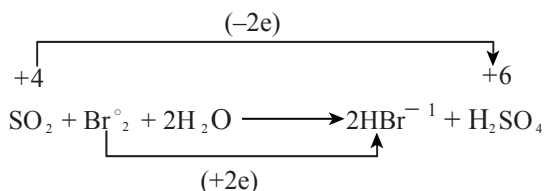
The ON of oxygen in H_2O_2 is -1 . It is intermediate (minimum -2 , maximum ON zero) for oxygen. Therefore, H_2O_2 is oxidizing and reducing agents both.



SO₂ oxidising agent



SO₂ reducing agent



The red colour of bromine water is discharged when SO₂ is passed in it.

Strength of Oxidants and Reductants

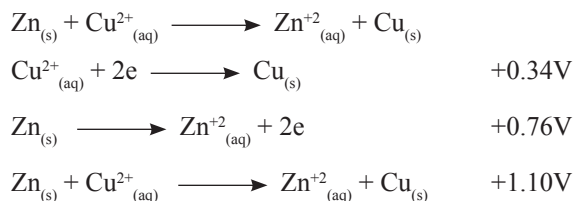
Standard electrode potential (E°) provides a direct measure of the relative oxidizing and reducing power of different species. The following are most common observations:

- (i) The more positive is the E°, the more powerful is the oxidizing agent.
- (ii) The more negative is the E°, the more powerful is the reducing agent.

Conclusions on table

- (i) The more positive the E°, the more energetically favourable the reaction.
- (ii) The stronger the oxidizing agent, the weaker is its corresponding reducing agent and vice versa.
- (iii) When E° of a cell is positive, the reaction is energetically possible, when E°, negative, it is not possible in the written direction.

For the reaction

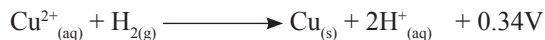
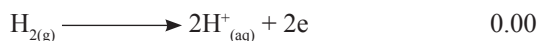
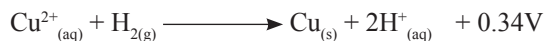


Therefore, this reaction is possible, but for the reverse reaction, E° = -1.10V

Table of E° for Common Species

| Strongest oxidizing agent | Reaction | E° (in volt) | Weakest reducing agent |
|---|--|---------------------|---|
| ↑ Increasing strength of oxidizing agent | $F_2 + 2e \rightarrow 2F^-$ | + 2.87 | ↓ Increasing strength of oxidizing agent |
| | $O_3 + 2H^+ + 2e \rightarrow O_2 + H_2O$ | + 2.07 | |
| | $S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-}$ | + 2.05 | |
| | $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ | + 1.77 | |
| | $MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$ | + 1.70 | |
| | $Ce^{+4} + e \rightarrow Ce^{+3}$ | + 1.61 | |
| | $2HClO + 2H^+ + 2e \rightarrow Cl_2 + 2H_2O$ | + 1.59 | |
| | $MnO_4^- + 8H^+ + 2e \rightarrow Mn^{+2} + 4H_2O$ | + 1.52 | |
| | $Cr_2O_7^{2-} + 6e + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$ | + 1.36 | |
| | $Cl_2 + 2e \rightarrow 2Cl^-$ | + 1.36 | |
| | $MnO_2 + 4H^+ + 2e \rightarrow Mn^{+2} + 2H_2O$ | + 1.23 | |
| | $IO_3^- + 6H^+ + 5e \rightarrow \frac{1}{2} I_2 + 3H_2O$ | + 1.20 | |
| | $Br_2 + 2e \rightarrow 2Br^-$ | + 1.09 | |
| | $IO_3^- + 6H^+ + 6e \rightarrow I^- + 3H_2O$ | + 0.8 | |
| | $NO_3^- + 2H^+ + e \rightarrow NO_2 + H_2O$ | + 0.8 | |
| | $Ag^+ + e \rightarrow Ag$ | + 0.77 | |
| | $Fe^{3+} + e \rightarrow Fe^{2+}$ | + 0.54 | |
| | $I_2 + 2e \rightarrow 2I^-$ | + 0.52 | |
| | $Cu^+ + e \rightarrow Cu$ | + 0.34 | |
| | $Cu^{2+} + 2e \rightarrow Cu$ | + 0.17 | |
| | $S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$ | + 0.15 | |
| | $Cu^{2+} + e \rightarrow Cu^+$ | + 0.15 | |
| | $Sn^{+4} + 2e \rightarrow Sn^{+2}$ | 0.00 | |
| | $2H^+ + 2e \rightarrow H_2$ | | |
| | $Cr^{+3} + e \rightarrow Cr^{+2}$ | -0.41 | |
| | $Fe^{2+} + 2e \rightarrow Fe$ | -0.44 | |
| | $Zn^{+2} + 2e \rightarrow Zn$ | -0.76 | |
| | $Al^{+3} + 3e \rightarrow Al$ | -1.76 | |
| | $Be^{2+} + 2e \rightarrow Be$ | -1.85 | |
| | $Mg^{2+} + 2e \rightarrow Mg$ | -2.34 | |
| | $Na^+ + e \rightarrow Na$ | -2.71 | |
| | $Ca^{+2} + 2e \rightarrow Ca$ | -2.87 | |
| | $Sr^{+2} + 2e \rightarrow Sr$ | -2.89 | |
| | $Ba^{+2} + 2e \rightarrow Ba$ | -2.90 | |
| | $K^+ + e \rightarrow K$ | -2.92 | |
| Weakest oxidizing agent | $Rb^+ + e \rightarrow Rb$ | -2.99 | Strongest reducing agent |
| | $Cs^+ + e \rightarrow Cs$ | -3.02 | |
| | $Li^+ + e \rightarrow Li$ | -3.04 | |

- (iv) The E° predicts possibility of a reaction only. Many reactions having +ive E° , may be too slow to occur (i.e., kinetic factor), Example, E° suggest that Cu^{2+} should oxidize H_2 to H^+ .



But nothing happens when H_2 is passed in CuSO_4 solution, because reaction rate practically is zero.

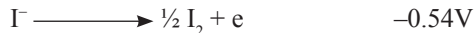
- (v) E° relates only to the standard condition (1M sol, 25°C temp., 1atm pressure).

Change in temperature, concentration, medium affects electrode potential.

The effect of non-standard condition is shown by,

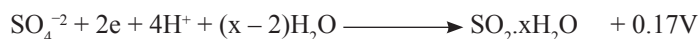


As E° is negative, this reaction should not occur. However, when MnO_2 is warmed with conc HCl , Cl_2 is produced (E° for both half cells becomes more positive, so, overall E° becomes positive). Other example of this E° anomaly is found in the reaction,



That is, the reaction should not occur as E° is negative. This reaction occurs because Cu^+ is precipitated as CuI ($\text{SP} \approx 10^{-12}$). This greatly reduces the concentration of Cu^+ . Therefore, the potential of $\text{Cu}^{2+}/\text{Cu}^+$ couple is increased greatly than that of $\text{I}_2/2\text{I}^-$, making overall E° positive.

The medium has effect on reducing power. SO_2 is stronger reducing agent in basic medium than in aq. medium, is shown by the E° s.



Equivalent Weights of Oxidizing and Reducing Agents

The equivalent weights of oxidizing and reducing agents are calculated by change in oxidation number.

$$\text{Eq. wt. of oxidant} = \frac{\text{Formula mass of oxidant}}{\text{Change in ON per mol}}$$

$$\text{Eq. wt. of reductant} = \frac{\text{Formula mass of reductant}}{\text{Change in ON per mol}}$$

(a) KMnO_4

Action of KMnO_4 as oxidizing agent depends upon medium:

- (i) Acid medium, the reaction is



Change in ON = $7 - 2 = 5$

\therefore Eq. wt. in acid medium = mass of $\text{K}^+\text{MnO}_4^-/5$

(ii) In the aq. or alkaline medium, it reacts as



Change in ON = $7 - 4 = 3$

\therefore Eq. wt. = mass of $\text{K}^+\text{MnO}_4^-/3$

(b) $\text{K}_2\text{Cr}_2\text{O}_7$

It reacts in acid medium as



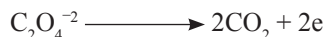
Change in ON = $2 \times 6 - 2 \times 3 = 6$

\therefore Eq. wt. = mass of $\text{K}_2\text{Cr}_2\text{O}_7/6$

(c) Oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$

(The acid always crystallize as a dihydrate)

It reacts in its reduction reactions as



Change in ON = $4 \times 2 - 3 \times 2 = 2$

\therefore Eq. wt. = mass of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/2$

(d) Sodium thiosulphate $(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O})$

The thiosulphate ion reacts as,



As one electron per mole of $\text{S}_2\text{O}_3^{2-}$ is lost,

Eq. wt. = formula mass of thiosulphate (248,19) including $5\text{H}_2\text{O}$.

Balancing of Redox Reactions

Two methods are in common use –

(i) Oxidation number method It can be used for molecular and ionic reactions both

(ii) Ion–electron method It can be used only for ionic reaction.

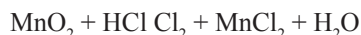
Oxidation Number Method

(a) Molecular reaction

The following steps are followed:

- (i) Change in the ON of the substance oxidized and reduced is determined.
- (ii) Electron balance is done. For this, change in ON of the substance oxidized is multiplied by substance reduced and vice versa.
- (iii) Atom balance is done by adding required coefficients where needed (i.e., L.H.S. or R.H.S.).

Example



Change in ON of Mn = $4 - 2 = 2$

Change in ON of Cl = $0 - (-1) = 1$



- (i) Change in ON of Mn = $4 - 2 = 2$
 Change in ON of Cl = $0 - (-1) = 1$

 Multiplied

- (ii) Electron balance



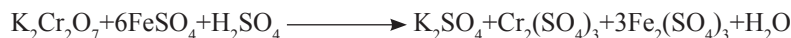
- (iii) Four Cl atoms are in the R.H.S. Therefore, two more HCl are added in L.H.S.



- (i) Change in ON of Cr = $6 \times 2 - 3 \times 2 = 6$
 Change in ON of Fe = $3 - 2 = 1$

 Multiplied

- (ii) Electron balance equation



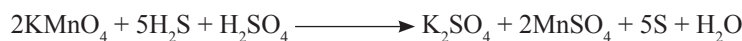
As there are 6 Fe atoms, L.H.S., So $3\text{Fe}_2(\text{SO}_4)_3$ written in R.H.S. to balance Fe atoms. There are 13 sulphate radicals in the R.H.S. and only seven in the L.H.S. So, 6 more H_2SO_4 are added in the L.H.S.



- (i) Change in ON of Mn = $7 - 2 = 5$
 Change in ON of S = $0 - (-2) = 2$



- (ii) Electron balance equation



There are 3 sulphate radicals in RHS and only one in LHS. So, two more H_2SO_4 molecules are added in LHS (reaction is taking place in H_2SO_4 medium). It will balance O – atoms and H – atoms also.

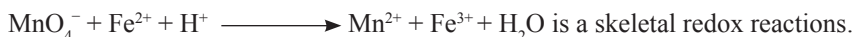
- (iv) Balance equation



($8\text{H}_2\text{O}$, as there are 16H atoms in LHS)

Balancing of Ionic Redox Reaction

In ionic redox reactions, species involved bears positive and negative charge. Therefore, charge and atoms both are balanced,

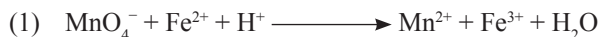



Rules for Balancing Ionic Redox Reactions

- Change in ONs of the substance oxidized and reduced are determined.
- Electron is balanced.** For this, change in ON of the substance oxidized is multiplied by substance reduced and vice versa.

- (c) **Net charge is balanced.** It is done by adding H^+ for reactions taking place in acid medium and OH^- . When reactions takes place in basic medium (either to LHS or RHS).
- (d) **Oxygen balance:** It is done by adding H_2O , in which side oxygen atoms are less.

Let us consider the redox reactions,



- (i) Change in ON of Mn = $7 - 2 = 5$
 Change in ON of Fe = $3 - 2 = 1$
- 
- Multiplication to balance electron

- (ii) Electron balance equation,



$$-1 + (+2 \times 5) + (+1 \times 1) + 2 + (+3 \times 5)$$

$$\text{Net Charge} = +10 = +17$$

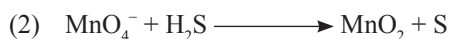
Here, 7 units positive charge is less towards LHS and reaction is taking place in acid medium. So, 7 H^+ are added in LHS to balance net charge (net charge balance equation must have similar equal charge, either +ive or -ive, both sides).

- (iii) Net charge balance equation




There are 4 O – atoms in LHS and only one in RHS. Therefore, three more H_2O are added in RHS to balance O – atoms.

- (iv) Balance equation



Step I (change in ON)

- Change in ON of Mn = $7 - 4 = 3$
 Change in ON of S = $0 - (-2) = 2$
- 
- Multiplication to balance electron

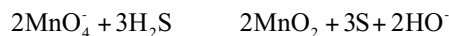
Step II (electron balance)



Step III (net charge balance)

Net charge $(-1 \times 2) = -2$ zero

So, to balance net charge, two HO^- are added in the RHS.

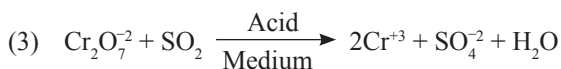


Step IV (Oxygen balance)

There are 8 O – atoms in the LHS and 6 in the RHS. So, two water molecules are added in the RHS.

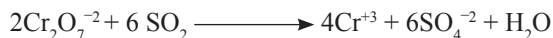
Balance Equation



Step I

$$\text{Change in ON of Cr} = +6 \times 2 - (+3 \times 2) = 6$$

$$\text{Change in ON of S} = 6 - 4 = 2$$

Step II (electron balance)Step III

$$\text{Net Charge } (-2 \times 2) + 0 = -4 \quad (+3 \times 4) + (-2 \times 6) = 0$$

Therefore, to balance net charge 4 H⁺ are added in the LHS (to make charges both sides similar and equal).

Step IV (O – balance)

There are 26 O – atoms in the LHS and only 25 in the RHS. Hence one H₂O is added in the RHS to balance O – atoms.



As 2 is common on both sides, the reactions may also be represented as,

**PROBLEM**

Balance the following equation

- $\text{MnO}_4^- + \text{SO}_3^{2-} \longrightarrow \text{MnO}_2 + \text{SO}_4^{2-}$
- $\text{MnO}_4^- + \text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{Mn}^{+2} + \text{O}_2 + \text{H}_2\text{O}$
- $\text{BrO}_3^- + \text{I}^- + \text{H}^+ \longrightarrow \text{I}_2 + \text{Br}^- + \text{H}_2\text{O}$
- $\text{H}_2\text{O}_2 + \text{Cr}(\text{OH})_3 \longrightarrow \text{CrO}_4^{2-} + \text{H}_2\text{O}$
- $\text{Cr}_2\text{O}_7^{2-} + \text{N}_2\text{H}_4 \longrightarrow \text{N}_2 + \text{Cr}^{+3}$

Ion Electron Method

This method is used for ionic equations only.

Rules

- Redox reaction is separated into two reactions, oxidation and reduction half-reactions.
- Each half-reaction is balance separately using ON method.
- Each half-reaction is multiplied by appropriate number to balance electron loss and gain.
- Add both equations.
- Common species on the left and right are subtracted.

ExampleStep I (separated oxd. and red. reaction)Step II (oxd. balance equation)Reduction balance equation

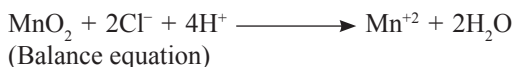
Net charge $-2 + 2$



O – balance



The oxidation half reaction loses one electron and reduction half reaction requires 2 electrons. So, oxidation half reaction is multiplied by 2 and the reactions are added.



ON of Cl in LHS = +1

ON of Cl in RHS = -1 and +5

∴ oxidation half reaction is



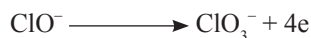
Reduction half reaction is



Oxidation half-reaction



Change in ON of Cl = 5 - 1 = 4, i.e., 4 electrons are lost



Net charge -1 -5



O - balance



Reduction half-reaction



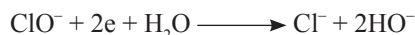
Change in ON of Cl = -1 - (+1) = -2, i.e., reduction requires addition of 2 electrons.



Net charge -3 -1



O - balance



The oxidation half reaction loses 4 electrons and the reduction half reaction requires 2 electrons. So, reduction half reaction is multiplied by 2 to balance electrons and the reactions are added.



Adding

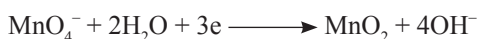


Some Important half reactions

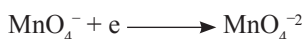
(a) acid medium



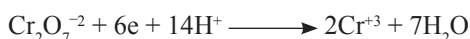
(b) aqueous or dil. Alkali



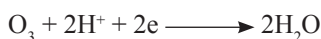
(c) strong alkaline medium



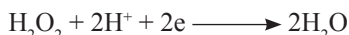
(d) acid medium



(e) O_3 in acid medium



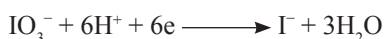
(f) H_2O_2 in acid



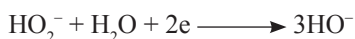
(g) $\text{S}_2\text{O}_8^{2-}$ in acid (oxidizes Mn^{+2} to MnO_4^-)



(h) IO_3^- in acid



(i) H_2O_2 in basic medium



(j) H_2O_2 in acid as reducing agent



(k) Bismuthate ion in acid (oxidizes Mn^{+2} to MnO_4^-)



(l) Periodate (IO_4^-) in acid (oxidizes Mn^{+2} to MnO_4^-)



PROBLEM

Balance the following redox reactions by ion-electron method.

- (i) $\text{MnO}_4^- + \text{H}^+ + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
 (ii) $\text{S}_2^{2-} + \text{ClO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{Cl}^-$

- (iii) $\text{H}_2\text{O}_2 + \text{NH}_3 \longrightarrow \text{N}_2\text{H}_4 + \text{HO}^-$
 (iv) $\text{H}_2\text{SO}_3 + \text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{SO}_4^{2-} + \text{Cr}^{+3}$
 (v) $\text{S}_2\text{O}_3^{2-} + \text{NO}_3^- \longrightarrow \text{SO}_3^{2-} + \text{NO}_2^-$

PRACTICE AND OBJECTIVE-TYPE QUESTIONS

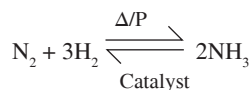
A Fill in the blanks

- The reaction,
 $\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$ is _____ a _____ reaction.
- In the reaction $\text{Ca} + \text{H}_2 \longrightarrow \text{CaH}_2$, hydrogen acts as _____.
- The minimum oxidation number of nitrogen possible is _____.
- The oxidation number of iron in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is _____.
- The reaction, $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$ is an example of _____.
- The oxidation numbers of oxygen in CrO_5 are _____ and _____.
- The oxidation number of iodine in $\text{IO}(\text{OH})_5$ is _____.
- The oxidation numbers of phosphorus in $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ is _____.
- Conversion of Pb into PbSO_4 requires _____ electrons.

- Oxidation of ferrous oxalate by acidified KMnO_4 releases _____ electrons per mole.
- The oxidation number of thallium in TlH_3 is _____.
- The ON of Ni in $\text{K}_4[\text{Ni}(\text{CN})_4]$ is _____.

True or False

- The ON of nitrogen atoms in $\text{RN}^+\text{H}_3\text{NO}_3^-$ is -3 and $+5$ respectively.
- The oxidation number of iodine in H_4IO_6^- is $+5$.
- The equivalent weight of NH_3 in the reaction is 8.5 .



- A sp^3 hybridized S goes to sp^2 in a reaction the change in ON is one unit down.
- The ON of Ni in $\text{Ni}(\text{CO})_4$ is $+2$.
- Amongst the alkali metals, the most negative reduction potential is of C.

OBJECTIVE-TYPE QUESTIONS

- Which among the given equation is balanced?
 (a) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{+3} + 7\text{H}_2\text{O} + 3\text{O}_2$
 (b) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 5\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{+3} + 9\text{H}_2\text{O} + 4\text{O}_2$
 (c) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 7\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{+3} + 11\text{H}_2\text{O} + 5\text{O}_2$
 (d) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 9\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{+3} + 13\text{H}_2\text{O} + 6\text{O}_2$
- The equivalent weight of $\text{Na}_2\text{S}_2\text{O}_3$ (Mol. Wt. = M) in the reaction
 $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$, is
 (a) $M/4$ (b) $M/3$
 (c) $M/2$ (d) M

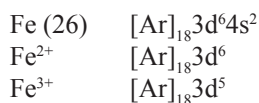
3. The oxidation numbers of Cl atoms in CaOCl_2 are
 (a) $(-1, -1)$ (b) $(+1, -1)$
 (c) $(+1, +1)$ (d) $(0, -1)$
4. The equivalent weight of MnSO_4 is half its molecular weight when it is converted to
 (a) MnO_4^- (b) Mn_2O_3
 (c) MnO_2 (d) MnO_4^{2-}
5. In the redox reaction of KMnO_4 and FeSO_4 in acid medium, the number of $\text{Fe}_2(\text{SO}_4)_3$ and KMnO_4 in balanced equation are
 (a) 1 and 5 (b) 5 and 2
 (c) 2 and 6 (d) 1 and 4
6. In the reaction $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$, reducing agent and change in its ON is
 (a) NH_4^+ and 4 (b) NH_3 and 3
 (c) NH_4^+ and 3 (d) N_2 and 3
7. The reaction, $2\text{Cu}^+_{(\text{aq})} \longrightarrow \text{Cu}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$, is
 (a) reduction
 (b) oxidation
 (c) disproportionation
 (d) decomposition
8. The oxidation number of P in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is
 (a) +3 (b) +2
 (c) +1 (d) +4
9. The number of electrons to balance the equation,
 $\text{NO}_3^- + \text{H}^+ + \text{e} \longrightarrow \text{NH}_4^+ + \text{H}_2\text{O}$ is
 (a) 5 (b) 7
 (c) 8 (d) 6
10. The oxidation number of S in $\text{H}_2\text{SO}_2\text{PO}_8$ is
 (a) +7 (b) +6
 (c) +8 (d) none
11. In the reaction the elements which can have negative oxidation number only is
 (a) S (b) S and O
 (c) F (d) H, O, S all

5

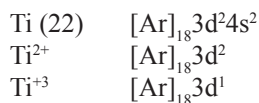
Transition Metals, Lanthanides and Actinides



Elements having partially filled inner d-orbitals $[(n - 1)d \text{ orbitals}]$ in their atoms or ions are known as transition elements. These elements are d-block elements and are present between s-block and p-block elements in the periodic table. For example, Fe (26)



Thus Fe, Fe^{2+} and Fe^{3+} are transition elements.



Transition elements



Not like transition elements as inner d orbitals have no electron ($3d^0$)

General electron configuration $(n - 1)d^xns^2$ or $(n - 1)d^xns^1$, $x = 1$ to 10

There are four transition series elements in the periodic table. They are

Table 5.1

| Group | 3 | 4 | 5 | 6 | 7 |
|---------------------------------|-----------------------|-------------------------------|------------------------|------------------------|------------------------|
| 3d-series or I-series | Sc (21) $3d^14s^2$ | Ti (22) $3d^24s^2$ | V (23) $3d^34s^2$ | Cr (24) $3d^54s^2$ | Mn (25) $3d^54s^2$ |
| 4d series or II-series | Y (39) $4d^15s^2$ | Zr (40) $4d^25s^2$ | Nb (41) $4d^45s^1$ | Mo (42) $4d^55s^1$ | Tc (43) $4d^55s^2$ |
| 5d – series or III-series | La (57) $5d^16s^2$ | Hf (72) $4f^{14}5d^26s^2$ | Ta (73) $5d^36s^2$ | W (74) $5d^46s^2$ | Re (75) $5d^56s^2$ |
| 6d – series or IV-series | Ac (89) $6d^17s^2$ | Rf (104) $5f^{14}6d^27s^2$ | Db (105) $6d^37s^2$ | Sg (106) $6d^47s^2$ | Bh (107) $6d^57s^2$ |

(Continued)

| Group | 8 | 9 | 10 | 11 | 12 |
|--------------------------------|-------------------------|-------------------------|------------------------|---------------------------|---------------------------|
| 3d-series or I-series | Fe (26) $3d^6 4s^2$ | Co (27) $3d^7 4s^2$ | Ni (28) $3d^8 4s^2$ | Cu (29) $3d^{10} 4s^1$ | Zn (30) $3d^{10} 4s^2$ |
| 4d series or II-series | Ru (44) $4d^7 5s^1$ | Rh (45) $4d^8 5s^1$ | Pd (46) $4d^{10}$ | Ag (47) $4d^{10} 5s^1$ | Cd (48) $4d^{10} 5s^2$ |
| 5d-series or III-series | Os (76) $5d^6 6s^2$ | Ir (77) $5d^7 6s^2$ | Pt (78) $5d^9 6s^1$ | Au (79) $5d^{10} 6s^1$ | Hg (80) $5d^{10} 6s^2$ |
| 6d – series or IV-series | Hs (108) $6d^6 7s^2$ | Mt (109) $6d^7 7s^2$ | Ds (110) | Rg (111) | |

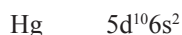
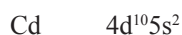
NOTES ON THE ABOVE TABLE

- (i) Electron configuration of Cr and Cu

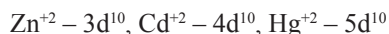


The $3d^5 4s^1$ and $3d^{10} 4s^1$ configurations are preferred due to greater stability of half and fully filled orbitals (HUND's Rule).

- (ii) Electron configuration of second and third transition series elements Nb, W, Ru, Rh, Pd and Pt is not similar to first transition series. The full explanation is beyond the scope of this book. It can only be said at this point that small energy gap with increasing atomic number is one of the reasons.
- (iii) Zinc, Cd and Hg have fully filled $(n-1)d^{10}$ orbitals in their configuration.



These elements exhibit oxidation state of +2 in their compounds. In +2 oxidation state, d-orbitals are fully filled.



Therefore, Zn, Cd and Hg do not exhibit general properties shown by transition elements but form a group (12) by themselves with similar properties.

- (iv) Elements Sc, Y and La exhibit the common oxidation states of +3, in which $(n-1)d$ orbitals are vacant (d^0). Therefore, these elements also do not show general characteristic properties of transition elements.
- (v) True transition elements, thus, are

Table 5.2

| | | | | | | | | | |
|-------|----|----|----|----|----|----|----|----|----|
| (i) | 3d | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
| (ii) | 4d | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag |
| (iii) | 5d | Hf | Ta | W | Re | Os | Ir | Pt | Au |
| (iv) | 6d | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg |

It is because all the above elements have partially filled $(n-1)d$ orbitals in their atoms or in one or more of the chemically important ions. Therefore, these are true transition elements in the strictest sense.

- (vi) Tc is the only transition element which is radio active before Po. It is β - active ($t_{1/2} = 2.12 \times 10^5 \text{y}$).
- vii) The configuration of Ru, Rh, Pd, Pt, Nb and W are not like other group members.
Iridium is the densest material found on earth.

GENERAL PROPERTIES

- (a) They all are metals.
- (b) They are hard, strong, high melting, high boiling metals that conduct heat and electricity.
- (c) Many are electropositive to dissolve in mineral acids, a few are noble (Pt, Au etc.)
- (d) They exhibit variable oxidation states.
- (e) Form paramagnetic compounds.
- (f) Form variety of complex compounds.
- (g) Many of the compounds are coloured.
- (h) Compounds undergo hydrolysis.
- (i) Many of the transition metals and their compounds act as catalyst.
- (j) Form very important alloys.

Atomic and Ionic radii

The atomic and ionic radii decrease from Sc to Cu, but the variation is small. The outer most electron configuration is $(n-1)d^x ns^2$. The screening power of d orbitals is small and electrons are being added in inner orbitals $[(n-1)d$ orbitals. Therefore, change in radii, atomic and ionic both, are small.

Table 5.3 Atomic radii

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|------------------|------|------|------|------|------|------|------|------|------|------|
| $r (\text{\AA})$ | 1.44 | 1.32 | 1.22 | 1.17 | 1.17 | 1.17 | 1.16 | 1.15 | 1.17 | 1.25 |

Table 5.4 Ionic radii

| | Ti ²⁺ | V ²⁺ | Cr ²⁺ | Mn ²⁺ | Fe ²⁺ | Co ²⁺ | Ni ²⁺ | Cu ²⁺ | Zn ²⁺ |
|------------------|------------------|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $r (\text{\AA})$ | 0.80 | 0.73 | 0.80 | 0.90 | 0.85 | 0.80 | 0.69 | 0.76 | 0.74 |

In a group, the atomic and the ionic radii increase with increase in atomic number (because new orbitals are added in the configuration). It is followed in the first and the second transition series. But the radii of the third transition series elements are almost equal to the second transition series elements. The reason for this equality, in radii is the lanthanide contraction.

Table 5.5 Radii in Å

| | | | | | | | | | | |
|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| r (Å) | Sc 1.44 | Ti 1.32 | V 1.22 | Cr 1.17 | Mn 1.17 | Fe 1.17 | Co 1.16 | Ni 1.15 | Cu 1.17 | Zn 1.25 |
| r (Å) | Y 1.62 | Zr 1.45 | Nb 1.34 | Mo 1.29 | Tc - | Ru 1.24 | Rh 1.25 | Pd 1.28 | Ag 1.34 | Cd 1.41 |
| r (Å) | La 1.69 | Hf 1.44 | Ta 1.34 | W 1.30 | Re 1.28 | Os 1.26 | Ir 1.26 | Pt 1.29 | Au 1.34 | Hg 1.44 |

Bonding in Transition metals and its effect on properties

All transition elements are metals. They are high melting, high boiling and have high heat of atomization and high densities. All these properties show that the atoms in transition elements are held together by strong metallic bonds. The strength of metallic bond very much depends upon number of valence electrons. Larger the number of valence electrons stronger is the metallic bond. In the transition elements a minimum of three electrons are present, $(n-1)d^1ns^2$. The presence of d – electrons contribute much towards metallic bonding (d – d overlap) and the strength increases with increase in the number of unpaired electrons in the orbitals. Also the difference between the mp and the bp is large. This indicates that metallic bond is present in molten state also.

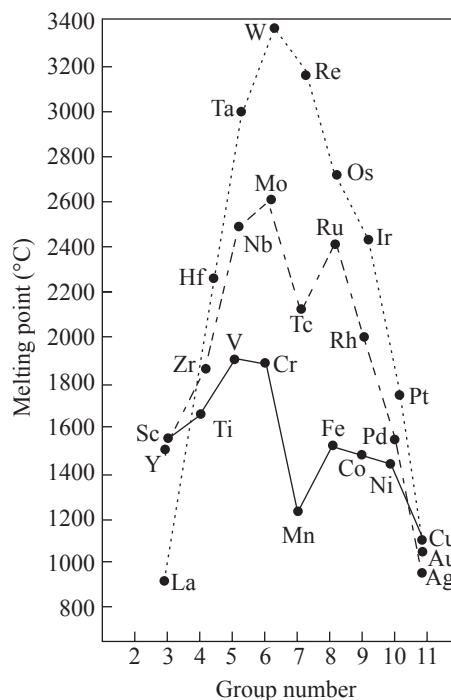
Melting points of Transition metals

The graph shows that-

- 5d metals have highest mp.
- mp increases with increase in the number of unpaired electron in d orbitals and then decreases, when number of unpaired electrons in d – orbitals decreases.
- Mn and Tc show anomalous values.
- W has highest mp.

Ionization energy

Variation of ionisation energy is not regular. The reason may be, irregular change in radii, increase in Z^* and difference in electron configuration.

**Figure 5.1**

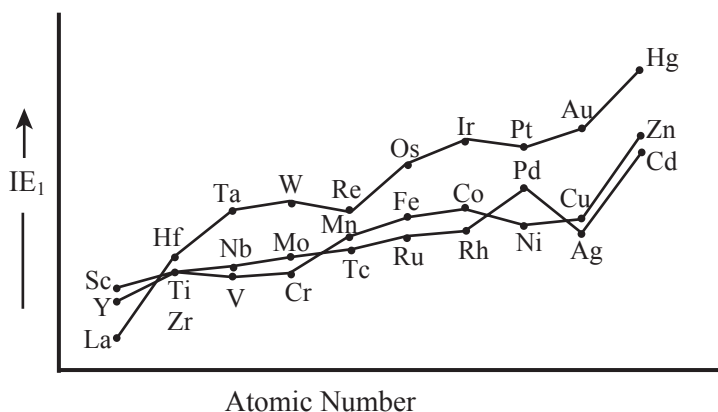


Figure 5.2

Conclusion on the above graph:

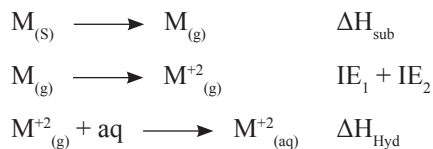
- (i) Overall variation is not regular.
- (ii) IE of 5d elements greater than 3d and 4d. It looks opposite but is logical. It is because of greater Z^* (4f least screening) and lanthanide contraction effect.
- (iii) IE of Pd is much larger than Ni. It is due to $4d^{10}$ configuration of Pd, Ni has configuration $3d^8 4s^2$.
- (iv) High IE of Au reflects its noble metal nature.
- (v) Hg has highest first IE. It is because its valence electrons ($6s^2$) is inert pair.

Electrode Potential

The stability of an oxidation state in aqueous medium depends very much on E^0 value. The reaction



Can also be represented as:



Therefore, $E = \Delta H_{\text{sub}} + (IE_1 + IE_2) + \Delta H_{\text{Hyd}}$. As variation of these properties is not regular, variation of E^0 is also not regular.

E^0 for +2 oxidations state (acid medium)

Table 5.7

| | | | | | | | | |
|--|-----------|-------|-------|-------|-------|-------|-------|-------|
| $M^{2+} + 2e \rightarrow M$ (volts) | Ti^{2+} | V | Cr | Mn | Fe | Co | Ni | Cu |
| | -1.6 | -1.18 | -0.91 | -1.18 | -0.44 | -0.28 | -0.24 | +0.34 |

Oxidation states

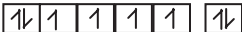
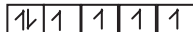
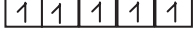

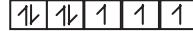
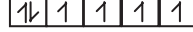
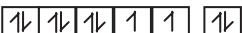
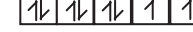
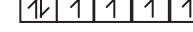
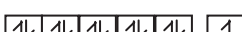
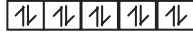
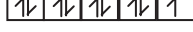
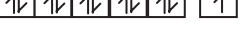
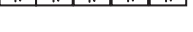




All transition metals exhibit variable oxidation states. It arises due to removal of electrons from inner d – orbital.



Table 5.8

| Element and oxidation states | Electron configuration | Arrangement of outermost electrons | Unpaired electrons |
|------------------------------|----------------------------|---|--------------------|
| Ti(22) | $[\text{Ar}]_{18}3d^24s^2$ | $\begin{array}{c} 3d \qquad 4s \\ \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \quad \boxed{\uparrow\downarrow} \end{array}$ | 2 |
| Ti ²⁺ | $[\text{Ar}]_{18}3d^2$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 2 |
| Ti ³⁺ | $[\text{Ar}]_{18}3d^1$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 1 |
| V(23) | $[\text{Ar}]_{18}3d^34s^2$ | $\begin{array}{c} 3d \qquad 4s \\ \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \quad \boxed{\uparrow\downarrow} \end{array}$ | 3 |
| V ²⁺ | $[\text{Ar}]_{18}3d^3$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \end{array}$ | 3 |
| V ³⁺ | $[\text{Ar}]_{18}3d^2$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 2 |
| V ⁵⁺ | $[\text{Ar}]_{18}$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 0 |
| Cr(24) | $[\text{Ar}]_{18}3d^54s^1$ | $\begin{array}{c} 3d \qquad 4s \\ \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \quad \boxed{1} \end{array}$ | 6 |
| Cr ²⁺ | $[\text{Ar}]_{18}3d^4$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{} \end{array}$ | 4 |
| Cr ³⁺ | $[\text{Ar}]_{18}3d^3$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \end{array}$ | 3 |
| Cr ⁶⁺ | $[\text{Ar}]_{18}$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 0 |
| Mn(25) | $[\text{Ar}]_{18}3d^54s^2$ | $\begin{array}{c} 3d \qquad 4s \\ \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \quad \boxed{\uparrow\downarrow} \end{array}$ | 5 |
| Mn ²⁺ | $[\text{Ar}]_{18}3d^5$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{1} \end{array}$ | 5 |
| Mn ⁴⁺ | $[\text{Ar}]_{18}3d^3$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{1} \boxed{1} \boxed{} \boxed{} \boxed{} \end{array}$ | 1 |
| Mn ⁶⁺ | $[\text{Ar}]_{18}3d^1$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 3 |
| Mn ⁷⁺ | $[\text{Ar}]_{18}$ | $\begin{array}{c} 3d \\ \boxed{1} \boxed{} \boxed{} \boxed{} \boxed{} \boxed{} \end{array}$ | 0 |

(Continued)

| | | | |
|------------------|--------------------------------------|---|---|
| Fe(26) | $[\text{Ar}]_{18}3d^64s^2$ |  | 4 |
| Fe^{2+} | $[\text{Ar}]_{18}3d^6$ |  | 4 |
| Fe^{3+} | $[\text{Ar}]_{18}3d^5$ |  | 5 |
| Co(27) | $[\text{Ar}]_{18}3d^74s^2$ |  | 3 |
| Co^{+2} | $[\text{Ar}]_{18}3d^7$ |  | 3 |
| Co^{+3} | $[\text{Ar}]_{18}3d^6$ |  | 4 |
| Ni(28) | $[\text{Ar}]_{18}3d^84s^2$ |  | 2 |
| Ni^{+2} | $[\text{Ar}]_{18}3d^8$ |  | 2 |
| Ni^{+4} | $[\text{Ar}]_{18}3d^6$ |  | 4 |
| Cu(29) | $[\text{Ar}]_{18}3d^{10}4s^1$ |  | 1 |
| Cu^{+} | $[\text{Ar}]_{18}3d^{10}$ |  | 0 |
| Cu^{+2} | $[\text{Ar}]_{18}3d^9$ |  | 1 |
| Ag(47) | $[\text{Kr}]_{36}4d^{10}5s^1$ |  | 1 |
| Ag^{+} | $[\text{Kr}]_{36}3d^{10}$ |  | 0 |
| Ag^{+2} | $[\text{Kr}]_{18}3d^9$ |  | 1 |
| Au(79) | $[\text{Xe}]_{54}4f^{14}5d^{10}5s^1$ |  | 1 |
| Au^{+} | $[\text{Xe}]_{54}4f^{14}5d^{10}$ |  | 0 |
| Au^{+3} | $[\text{Xe}]_{54}4f^{14}5d^8$ |  | 2 |

Besides, the above given oxidation states, lower oxidation state (0 or +1) are also exhibited by transition metals. But these are stable only in complexes especially with π -acid ligands. Compounds in different oxidation states differ in properties. Some common observations are:

- Most common oxidation state is +2 for first series. (It shows greater stability of 3d orbitals over 4s)
- The +1 state is stable (dry state) only for Cu in simple compounds.

- (iii) Bonds in +2 or +3 states are mostly ionic.
 (iv) +2 state forms basic oxide and hydroxides
 (v) Higher oxidation states +4, +5, +6, +7 etc., form covalent compounds (MnO_4^- has covalent Mn – O bond).
 (vi) Oxides (or hydroxides) in higher oxidation states are acidic.
 (vii) Higher oxidation state is more stable down a group
- | | | | | | | | |
|--|----|-----------------------|----|----------------------------------|--------------------------------------|------------------------|--------|
| | Fe | +2, +3 | Mn | +7, MnO_4^- S. O. agent | | VO | Basic |
| | Ru | +4, +6 | | Te | | V_2O_5 | Acidic |
| | Os | +8 (OsO_4) | | Re | +7, ReO_4^- not an O. agent | CrO | Basic |
| | | | | | | CrO_3 | Acidic |
- (viii) Higher oxidation states are found in oxygen and fluorine compounds only Mn_2O_7 , MnF_7 , CrO_4^- , MnO_4^- etc.
 (ix) Oxides in intermediate oxidation states are amphoteric
- | | | | | |
|--|-------------------------|---|--|------------|
| | TiO_2 | | | |
| | VO_2 | } | | Amphoteric |
| | Mn_2O_3 | | | |

Paramagnetic nature of transition metal compounds

Chemical substances having unpaired electrons in their structure are paramagnetic. It is represented in terms of paramagnetic moment, μ in Bohr magnetons,

$$\mu = \sqrt{n(n+2)} \text{ BM, where } n = \text{number of unpaired electrons.}$$

Transition metals and most of their compounds contain unpaired electrons in their different oxidation states. Therefore, they are paramagnetic.

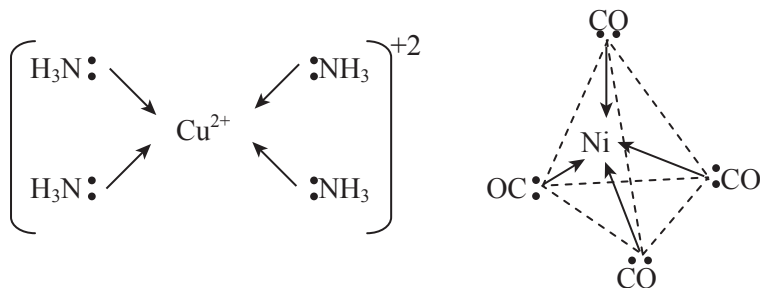
Magnetic moments for different numbers of unpaired electrons

Table 5.9

| Atomic ion | Configuration of d orbitals | Unpaired electrons | μ | | | | | | |
|--|---|--------------------|-----------------|-------|--|--|---|------------|------|
| | | | $\sqrt{n(n+2)}$ | Value | | | | | |
| Ti^{+3} , Cu^+ | <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td></td><td></td><td></td><td></td></tr></table> | 1 | | | | | 1 | $\sqrt{3}$ | 1.73 |
| 1 | | | | | | | | | |
| V^{+3} , Cr^{+4} , Ti^{2+} | <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td></td><td></td><td></td></tr></table> | 1 | 1 | | | | 2 | $\sqrt{8}$ | 2.83 |
| 1 | 1 | | | | | | | | |
| V^{+2} , Cr^{+3} | 1 1 1 | 3 | $\sqrt{15}$ | 3.87 | | | | | |
| Cr^{+2} | 1 1 1 1 | 4 | $\sqrt{24}$ | 4.90 | | | | | |
| Mn^{+2} , Fe^{3+} | 1 1 1 1 1 | 5 | $\sqrt{35}$ | 5.92 | | | | | |
| Fe^{2+} , Co^{+3} , Ni^{+4} | $\uparrow\downarrow$ 1 1 1 1 | 4 | $\sqrt{24}$ | 4.90 | | | | | |
| Co^{+2} | $\uparrow\downarrow$ $\uparrow\downarrow$ 1 1 1 | 3 | $\sqrt{15}$ | 3.87 | | | | | |
| Ni^{2+} | $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ 1 1 | 2 | $\sqrt{8}$ | 2.83 | | | | | |
| Cu^{2+} | $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ 1 | 1 | $\sqrt{3}$ | 1.73 | | | | | |

Complex compound formation

Formation of complex compound is a Lewis acid – base reaction. In it metal ion is Lewis acid i.e., electron pair acceptor and ligands are electron pair donors i.e., Lewis base. Example,

**Figure 5.3**

Transition metals or ions have partially filled $(n - 1)d$ orbitals in their valence shell and act as acceptor. Therefore, they form variety of complexes. The compounds are stable as ionic potential of transition metal ions is high, (C.f. “Coordination compounds”).

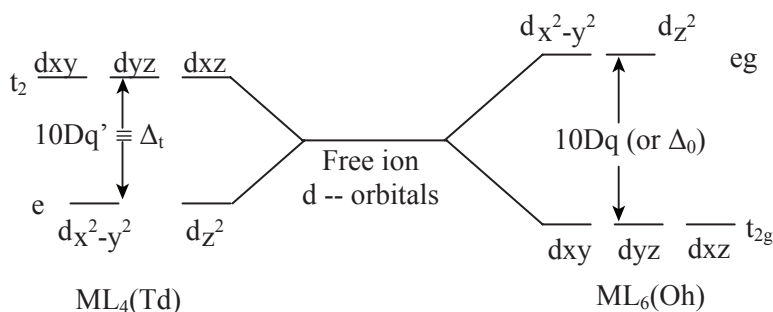
Colour of Transition metal compounds

A chemical substance looks coloured if it absorbs a portion of visible light ($\lambda = 3800 - 7800 \text{ \AA}$) and transmits the rest. For example, if a compound absorbs the yellow – red ($6000 - 7500 \text{ \AA}$) it appears green (i.e., transmitted light) i.e., the colour is complementary colour. Absorption of radiation excite electron to higher energy state. Therefore, when a substance looks coloured, it means that absorption of visible light and transition of electron must have taken place. Most of the transition metal compounds are coloured. It arises due to the following reasons:

- (i) d – d transition
- (ii) Charge transfer

The d – d transition

The five d-orbitals of a free ion are degenerate i.e., have equal energy. But in the presence of ligands (H_2O , NH_3 , CN^- , F^- etc.) the d – orbitals split. It depends on structure of the complex (Oh, Td, Sq, Pl etc.).

**Figure 5.4**

Let us consider $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. It is an Oh complex. The d – orbitals split as,

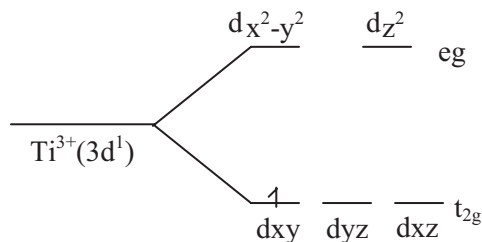


Figure 5.5

and single electron occupies t_{2g} level. When light falls on the complex, t_{2g} electron is excited to e_g level,

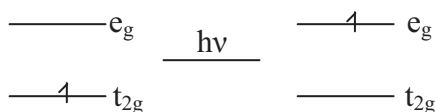
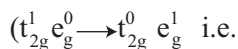


Figure 5.6

This excitation takes place when the compound absorbs radiation corresponding to $\lambda .5000\text{\AA}$, (greenish – yellow light). Therefore, transmitted wavelength corresponds violet light and the complex looks violet. As electron transition takes place from one group of d orbitals to the other, it is called d – d transition. The d – d transition is shown by transition metal ions of electron configurations, d^1 , d^2 , d^3 , d^4 , d^6 , d^7 , d^8 and d^9 .

Colour of aqua complexes

Table 5.10

| Aquaion | d – electrons | Colour |
|--|---------------|--------------|
| $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ | O | Colourless |
| $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | d^1 | Violet |
| $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ | d^2 | Blue |
| $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ | d^3 | Violet |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | d^4 | Sky – blue |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | d^5 | Colourless |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | d^6 | Pale – green |
| $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | d^7 | Pink |
| $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | d^8 | Green |
| $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ | d^9 | Blue |
| $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ | d^{10} | Colourless |

Colours due to d – d transition are faint. Metal ions which have d^0 , d^5 and d^{10} configurations are colourless, if at all coloured not due to d – d transition.

Colour and charge transfer

Many transition metal ions or compounds such as MnO_4^- , CrO_4^{2-} , Cu_2O , CdS etc are coloured. They have their d – orbitals either vacant or fully filled.

Table 5.11

| Ion or Compound | Oxidation state of transition metal | d – electrons | Colour |
|-----------------------|-------------------------------------|---------------|--------|
| MnO_4^- | Mn^{+7} | $3d^0$ | Purple |
| CrO_4^{2-} | Cr^{+6} | $3d^0$ | Yellow |
| Cu_2O | Cu^+ | $3d^{10}$ | Red |
| CdS | Cd^{+2} | $4d^{10}$ | Yellow |

Colour in such compounds is explained by charge transfer mechanism. In MnO_4^- , Mn^{+7} is oxidizing agent and O^{2-} is reducing agent. As oxidizing agent picks up electrons and reducing agent gives up electrons, electron moves from O^{2-} to Mn^{+7} .

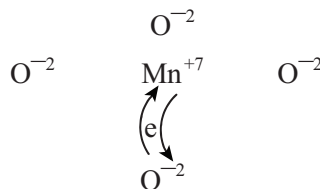


Figure 5.7

Due to such movement of electrons the ion is coloured.

The colour of brown ring compound, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$, and $\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]$ are also due to charge transfer.



Figure 5.8

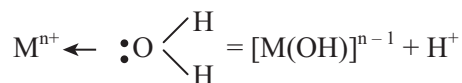
Colours due to charge transfer are intense (deep).

Hydrolysis of Transition metal compounds

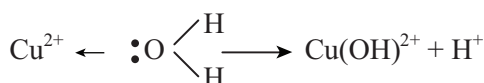
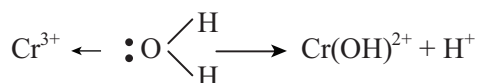
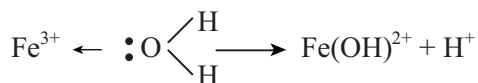
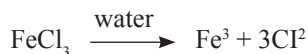
Splitting of water molecules by ions is known as hydrolysis. Cation hydrolysis takes place when charge density on the cation is high.

$$\text{Charge density} = \frac{\text{Charge}}{\text{Ionic radius}}$$

Transition metal ions on the average are small in size and the common oxidation states are +2, +3 etc. Therefore, their charge density is high and they under go hydrolysis.



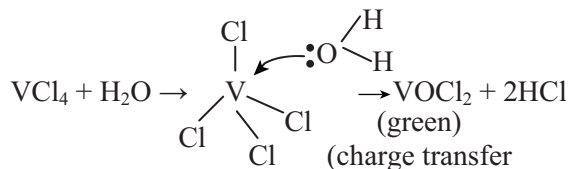
Thus, soluble salts of transition metals form slightly acidic solution,



Due to such hydrolytic reaction, cations, such as Mn^{+7} , Cr^{+6} , etc., are not stable in water.



Covalent transition metal compounds, such as TiCl_4 , VCl_4 etc., are hydrolyzed due to ability of transition metal ion to expand coordination number by the use of empty d – orbitals.



Catalytic property

Many transition metals and their compounds act as very useful catalysts.

Table 5.12

| Metal or compounds | Catalytic effect on |
|--------------------|---|
| Ni, Raney nickel | (a) Hydrogenation, (b) Anthraquinone \rightarrow anthraquinol in the production of H_2O_2 . |
| Cu | Manufacture of $(\text{CH}_3)_2\text{SiCl}_2$, (Rochow method) used to produce silicones. |
| Pt | Used in three stage converters for cleaning car exhaust fumes. |

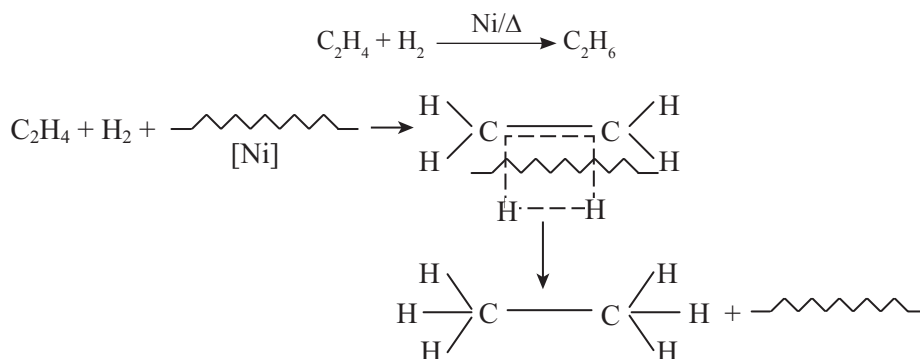
(Continued)

| Metal or compounds | Catalytic effect on |
|--|--|
| CuCl_2 | For Decon process of making Cl_2 from HCl |
| $\text{FeSO}_4 + \text{H}_2\text{O}_2$ (Fenton's reagent) | For Alcohol \rightarrow Aldehyde, oxidation |
| Fe (Promoted by Mo) | In Haber – Bosch process for synthesis of NH_3 . |
| V_2O_5 | In contact process for converting SO_2 to SO_3 . |
| TiCl_3 (Ziegler – Natta catalyst) | In the production of polythene |
| PdCl_2 | For oxidation of C_2H_4 to $\text{CH}_3 - \text{CHO}$, the Wacker process |
| Pt/PtO (Adams catalyst) | For reduction |
| $\text{RhCl}(\text{PPh}_3)_3$ (Wilkinson's catalyst) | Hydrogenation of alkenes |
| $(\text{ZnO} - \text{Cr}_2\text{O}_3)$ catalyst | Fischer – Tropsch synthesis of gasoline |
| Pd | Hydrogenation |

Catalysis by transition metals or their compounds is either,

- (i) Heterogeneous catalysis or
- (ii) Homogeneous catalysis.

For example, hydrogenation over Raney Ni is an example of heterogeneous catalysis



Homogeneous catalysis by transition metal compounds is due to the ability of transition metal ions to form intermediates by using their vacant d – orbitals.

Many biochemical reactions, i.e., reactions occurring in living systems, are catalysed by enzymes. Enzymes are protein molecules and many of them contain transition metal ions. Some examples are given with their functions:

Table 5.13

| Enzymes | Transition metal | Functions |
|---------------|------------------|--|
| Haemoglobin | Fe^{2+} | O_2 transport from the lungs to muscles |
| Ceruloplasmin | Cu^{2+} | Utilization of Fe |

(Continued)

| Enzymes | Transition metal | Functions |
|--------------------|------------------|--|
| Haemocyanin | | O ₂ transport in invertebrates |
| Arginase | Mn ⁺² | urea formation |
| Carbonic anhydrase | Zn ⁺² | Regulation of pH and CO ₂ formation |
| Carboxy peptidase | Zn ⁺² | Digestion of proteins |
| Nitrogenase | Fe, Mo | Fixation of nitrogen (N ₂) |

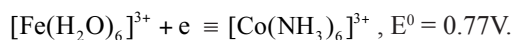
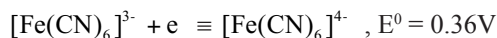
Stability of oxidation states in Aqueous Solution

Aqueous chemistry of a metal and the stability of its oxidation states mainly depend on:

- (i) redox potential i.e. E^0 and
- (ii) Complex forming tendency

Let us consider Sc. The E^0 for $\text{Sc}^{3+}/\text{Sc} = -2.08\text{V}$. It shows that Sc is a strongly electropositive metal which must be oxidized by a dilute acid (i.e., by H^+) to Sc^{3+} liberating H_2 gas. Also, Sc^{3+} exists in neutral and acid media as $[\text{Co}(\text{NH}_3)_6]^{3+}$ i.e., the aqua complex ion.

The relative stability is also affected by complex formation.



Therefore, an oxidation state can be stabilized through complexation. The Co^{3+} which oxidizes water to O_2 can be stabilized by complexing with NH_3 , CN^- and the like, $[\text{Co}(\text{NH}_3)_6]^{3+}$, a highly stable complex.

Aqueous chemistry stability of different oxidation. states of 3d metals are summerised in the table below:

Table 5.14

| Metal | O. State | E^0 (in V) | Remarks |
|-------|----------|---|--|
| Ti | 2+ | $\text{Ti}^{2+}/\text{Ti} = -1.63$ | Both reducing agent, reducing H^+ to H_2 |
| | 3+ | $\text{Ti}^{3+}/\text{Ti}^{2+} = -0.37$ | stable species in water, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ |
| | 4+ | — | Ti^{4+} has high charge density and is extensively hydrolyzed to TiO_2 . $\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}$ (Smoke reaction) |

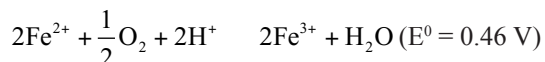
(Continued)

| Metal | O. State | E^0 (in V) | Remarks |
|---|----------|---------------------------|---|
| V | 2+ | $V^{2+}/V = -1.2$ | V a weaker reducing agent. than Ti. |
| | 3+ | $V^{3+}/V^{2+} = -0.26$ | It show that V^{2+} is not stable in water and in the presence of O_2 or air is oxidized to V^{3+} . |
| | 4+ | — | V^{4+} is amphoteric, forms VO_2 with alkali but with a strong base gives VO_4^{3-} ion. V^{4+} is reduced by Fe^{2+} or Zn in acid to blue vanadyl ion VO^{2+} . |
| | 5+ | — | V_2O_5 is acidic oxide. It dissolves in acid to pervanadyl ion VO_2^+ . In a base V_2O_5 forms VO_4^{3-} . |
| Cr. | 2+ | $Cr^{2+}/Cr = -0.91$ | Similar to Ti and V. Cr^{2+} is a reducing agent and is oxidized by air to Cr^{3+} . |
| | | $Cr^{3+}/Cr^{2+} = -0.41$ | Cr^{3+} stable and exists in water as $Cr(H_2O)_6^{3+}$ which is hydrolysed. $Fe(H_2O)_6^{3+} \rightleftharpoons Cr(HO)(H_2O)_5^{2+} + H^+$ In base $Cr(OH)_3$ precipitates. In water or acid, Cr^{3+} also forms $Cr(OH)_3$ when reacted with Na_2CO_3 or Na_2S . |
| | 3+ | — | Oxidized in a base to CrO_4^{2-} $Cr(OH)_3 + 5HO^- \rightarrow CrO_4^{2-} + 4H_2O$ ($E^0 = -0.13V$) |
| | 6+ | — | Strong oxidizing oxidation state, Cr^{6+} comes down to Cr^{3+} ($Cr_2O_7^{2-} / Cr^{3+} = +1.33V$) |
| Cr^{2+} is oxidized to Cr^{3+} and Cr^{6+} is reduced to Cr^{3+} . Thus, 3+ is most stable oxidation state of chromium. | | | |
| Mn | 2+ | $Mn^{2+}/Mn = -1.18$ | Mn is electro positive but not reducing like Ti, V and Cr. It is stable oxidation state ($3d^5$ ion). |
| | 3+ | $Mn^{3+}/Mn^{2+} = +1.51$ | Oxidation of Mn^{2+} to Mn^{3+} is difficult. Mn^{3+} not stable in water and disproportionates to Mn^{2+} and MnO_2 . ($MnO_2 / Mn^{3+}, E^0 = .95V$) |
| | 4+ | | Mn^{2+} is easily oxidized to MnO_2 ($E^0 = -0.05V$) |

(Continued)

| Metal | O. State | E^0 (in V) | Remarks |
|---|----------|---------------------------|---|
| | 6+ | | Mn^{4+} (MnO_2) is oxidized in basic medium to Mn^{6+} (MnO_4^{2-}) which is green and stable only in strong base. It disproportionates in aq. or acid to MnO_4^- and MnO_2 . |
| | 7+ | | Strong oxidizing agent, being reduced to Mn^{2+} (acid). ($E^0 = +1.51V$) |
| The above remarks show that Mn^{2+} is most stable oxidation state. | | | |
| Fe | 2+ | $Fe^{2+}/Fe = -0.44$ | Fe^{2+} thus a reducing agent, species in water is green $Fe(H_2O)_6^{3+}$ |
| | 3+ | $Fe^{3+}/Fe^{2+} = +0.77$ | Fe^{3+} an oxidizing agent. |

The E^0 of the couple Fe^{3+}/Fe^{2+} and O_2/O_2^{2-} , ($E^0 = +1.23V$) shows that O_2 will oxidize Fe^{2+} to Fe^{3+} in acid solution:



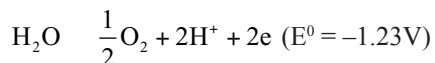
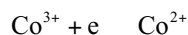
Ferric iron (Fe^{3+}), due to its high charge density hydrolyses to make acidic solution.



This equilibrium lies well towards left with decreasing p^H . Thus oxidation of Fe^{2+} to Fe^{3+} is quite slow in fairly acidic solution.

| | | | |
|----|----|---------------------------|---|
| Co | 2+ | $Co^{2+}/Co = +0.35$ | Stable oxidation state |
| | 3+ | $Co^{3+}/Co^{2+} = +1.82$ | Strong oxidizing agent being reduced to Co^{2+} |

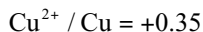
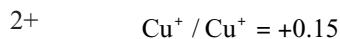
Co^{3+} oxidizes water to O_2 .



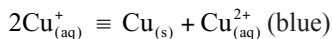
But Co^{3+} is quite stable in the presence of complexing agent (NH_3 , CN^-) etc.

It is due to high crystal field stabilization energy associated with $3d^6$ ion, (except CoF_6^{3-} , other common complexes are low spin).

| | | | |
|----|----|----------------------|--|
| Ni | 2+ | $Ni^{2+}/Ni = -0.25$ | Stable |
| | 3+ | - | Strong oxidizing agents, oxidizes water to O_2 |
| | 4+ | - | |
| Cu | 1+ | $Cu^+/Cu = +0.5$ | Non is reducing agent for H^+ |



Cu^+ is stable only in dry state or in insoluble salts (CuI , CuCN , CuCl , CuSCN). In aqueous solution Cu^+ disproportionate spontaneously.



This equilibrium moves well towards forward direction due to better stabilization of Cu^{2+} in water (through its high hydration energy).

The comparison of E^0 of Cr^{3+} with Ti^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Cu^{3+} shows that:

- (i) Elements before Cr (Ti^{3+} and V^{3+}) are good reducing agents.
- (ii) Elements after Cr i.e. Mn^{3+} , Fe^{3+} , Co^{3+} are strong oxidizing agents.

Lanthanides and Actinides

Elements (Ce to Lu) in which 4f orbitals are being filled are known as lanthanides, because of their chemical similarity to lanthanum. Thus the 15 elements La ($Z = 57$) through Lu ($Z = 71$) are lanthanides. They are third group elements and are placed at the bottom of the table to avoid making periodic table unnecessarily wide

Table 5.15

| Name | Symbol | Atomic no. | Configuration |
|------------------|-----------|------------|---|
| Lanthanum | La | 57 | [Xe] 5d¹6s² |
| Cerium | Ce | 58 | [Xe] 4f ¹ 5d ¹ 6s ² |
| Praseodymium | Pr | 59 | [Xe] 4f ³ 6s ² |
| Neodymium | Nd | 60 | [Xe] 4f ⁴ 6s ² |
| Promethium | Pm | 61 | [Xe] 4f ⁵ 6s ² |
| Samarium | Sm | 62 | [Xe] 4f ⁶ 6s ² |
| Europium | Eu | 63 | [Xe] 4f ⁷ 6s ² |
| Gadolinium | Gd | 64 | [Xe] 4f ⁷ 5d ¹ 6s ² |
| Terbium | Tb | 65 | [Xe] 4f ⁹ 6s ² |
| Dysprosium | Dy | 66 | [Xe] 4f ¹⁰ 6s ² |
| Holmium | Ho | 67 | [Xe] 4f ¹¹ 6s ² |
| Erbium | Er | 68 | [Xe] 4f ¹² 6s ² |
| Thulium | Tm | 69 | [Xe] 4f ¹³ 6s ² |
| Ytterbium | Yb | 70 | [Xe] 4f ¹⁴ 6s ² |
| Lutetium | Lu | 71 | [Xe] 4f ¹⁴ 5d ¹ 6s ² |

Conclusion

- (i) Configuration of Ce indicates that 4f orbitals become more stable than 5d orbitals at this point.
- (ii) The configuration $4f^7 5d^1 6s^2$ for Ga shows greater stability of half filled (i.e., $4f^7$) orbitals.
- (iii) At Lu the configuration is $4f^{14} 5d^1 6s^2$, it is for greater stability in full filled orbitals (i.e., $4f^{14}$).
- (iv) Promethium is the only lanthanide which is radioactive (β^- , $t_{1/2} = 2.64$ years). It occurs only in traces in U ores.

Atomic and Ionic Radii, Lanthanide Contraction

Atomic and ionic (M^{+3}) radii of lanthanides decreases from La through Lu: However, the decrease is very small.

In lanthanides, electrons are being filled in 4f orbitals. It is deep seated orbital and the screening of one 4f – electron by another from the effects of the nuclear charge is very weak due to the shapes of the f – orbitals. Hence, with increasing atomic number and nuclear charge, the effective nuclear charge felt by each 4f electron increases. This causes a decrease in the radii of the atoms or ions from La to Lu. This is known as the lanthanide contraction.

Radii, atomic and M^{+3} (Å)

Table 5.16

| Lanthanides | Atomic | Ionic M^{+3} |
|-------------|--------|----------------|
| Ce | 1.65 | 1.03 |
| Pr | 1.64 | 1.01 |
| Nd | 1.64 | 0.99 |
| Pm | 1.63 | 0.98 |
| Sm | 1.62 | 0.96 |
| Eu | 1.82 | 0.95 |
| Gd | 1.62 | 0.94 |
| Tb | 1.61 | 0.92 |
| Dy | 1.60 | 0.91 |
| Ho | 1.58 | 0.89 |
| Er | 1.57 | 0.88 |
| Tm | 1.58 | 0.87 |
| Yb | 1.70 | 0.86 |
| Lu | 1.56 | 0.85 |

Conclusions

- (i) Change in atomic radii is small from Ce to Lu.
- (ii) Eu and yb have anomalous values for atomic radii. It may be due to stability of +2 oxidation state ($Eu^{+2} 4f^7$ and $yb^{+2} 4f^{14}$).

- (iii) Variation in atomic radii is not regular.
 (iv) Ionic radii (of M^{+3}) decreases regularly from Ce to Lu.

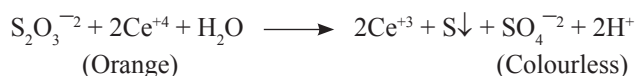
Oxidation states

The +3 oxidation state of lanthanides is common and most stable. It is because sum of the three ionisation energies are not very high.

Oxidation states of +2 and +4 are also found when it corresponds with stable electron configuration e.g.

- (i) Ce^{+4} ($4f^0$)
 (ii) Eu^{+2} and Tb^{+4} ($4f^7$)
 (iii) Yb^{+2} ($4f^{14}$)

However, Ce^{+4} [Orange sol. $Ce(SO_4)_2$] is a good oxidizing agent in which Ce^{+4} is reduced to Ce^{+3} , the common oxidation state of lanthanides.



Electron configuration of ions

Table 5.17

| Ions | Electron configuration | Ions | Electron configuration |
|-----------|------------------------|-----------|------------------------|
| Ce^{+3} | $[Xe] 4f^1$ | Ho^{+3} | $[Xe] 4f^{10}$ |
| Pr^{+3} | $[Xe] 4f^2$ | Er^{+3} | $[Xe] 4f^{11}$ |
| Nd^{+3} | $[Xe] 4f^3$ | Tm^{+3} | $[Xe] 4f^{12}$ |
| Pm^{+3} | $[Xe] 4f^4$ | Yb^{+3} | $[Xe] 4f^{13}$ |
| Sm^{+3} | $[Xe] 4f^5$ | Lu^{+3} | $[Xe] 4f^{14}$ |
| Eu^{+3} | $[Xe] 4f^6$ | Ce^{+4} | $[Xe] 4f^0$ |
| Gd^{+3} | $[Xe] 4f^7$ | Eu^{+2} | $[Xe] 4f^7$ |
| Tb^{+3} | $[Xe] 4f^8$ | Tb^{+4} | $[Xe] 4f^7$ |
| Dy^{+3} | $[Xe] 4f^9$ | Yb^{+2} | $[Xe] 4f^{14}$ |

Magnetic properties and colour

Most of the lanthanide ions have unpaired electrons and are paramagnetic. Only Ce^{+4} ($4f^0$) and Lu^{+3} ($4f^{14}$) have no unpaired electron and are diamagnetic. For example:

Nd^{+3} , $[Xe] 4f^3$,

| | | | | | | |
|---|---|---|--|--|--|--|
| 1 | 1 | 1 | | | | |
|---|---|---|--|--|--|--|

 Paramagnetic

Gd^{+3} , $[Xe] 4f^7$,

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|---|---|---|---|---|---|---|

 Paramagnetic

Most of the M^{+3} , lanthanide ions, are coloured in solid compounds or in solution. The colour is due to unpaired electrons in 4f orbitals. A similarity in colour is found for ions having $4f^x$ and $4f^{14-x}$ electrons.

Example,

$Ce^{+3} - 4f^1$ and $Yb^{+3} - 4f^{13}$ are both colourless.

Colour of M^{+3} ions**Table 5.18**

| Ions | $4f^x$ electrons | Colour | $4f^{14-x}$ electrons | Ions |
|------------------|---------------------|------------|--------------------------|------|
| La^{+3} | 0 | Colourless | Lu^{+3} | 14 |
| Ce^{+3} | 1 | Colourless | Yb^{+3} | 13 |
| Pr^{+3} | 2 | Green | Tm^{+3} | 12 |
| Nd^{+3} | 3 | Lilac | Er^{+3} | 11 |
| Pm^{+3} | 4 | Pink | Ho^{+3} | 10 |
| Sm^{+3} | 5 | Yellow | Dy^{+3} | 9 |
| Eu^{+3} | 6 | Pale Pink | Tb^{+3} | 8 |
| Gd^{+3} | 7 | Colourless | Gd^{+3} | 7 |

Some lanthanide ions show fluorescence or luminescence, e.g., Yb and Eu in oxides, silicates or transition metal oxide lattices. The Eu^{+2} show laser activity when trapped in CaF_2 lattice or in $[\text{Eu}\beta - \text{diket}_4]^-$.

Occurrence and Isolation

Source—Monazite sand, which is complex phosphate containing Th and lanthanides, is main source for thorium. It is found at Yaduguda (Jharkhand)

One of the lanthanides. Promethium (61), is radioactive and occurs only in traces in U ores (4×10^{-15} g per kilo). It is also produced in nuclear reactors as a fission product, ^{147}Pm (β^- , 2.64y). Small quantities of $^{147}\text{Pm}^{+3}$ (pink) can be isolated by ion-exchange methods.

Lanthanides are separated from each other either by solvent extraction method or by ion-exchange method.

Uses of Lanthanides

- As hydrogen carrier some intermetallic compounds like RECo_5 or RENi_5 (RE = lanthanides) can absorb large quantities of H_2 and give up on demand.
- $\text{Ce}(\text{SO}_4)_2$ solution is used as an oxidizing agent in volumetric analysis.
- As alloying metal e.g., Misch – metal [50% Ce, 40% La, 7% Fe and 3% other metals (Ca, Al, C) etc.]. It is added to steel to improve its strength and workability.
- La_2O_3 is used in Crook's lenses which protects from UV by absorbing it.
- Lanthanide oxides are used as phosphors in colour TV tubes.
- Alloys containing lanthanides are used as flints for lighters.
- Lanthanides are also used in warm super conductors (i.e., super conductivity at around 93K) e.g., $\text{La}_{(2-x)}\text{BaXCuO}_{(y-4)}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.
- To increase light emitting power of gas mantles, it is treated with 99% ThO_2 and 1% CeO_2 .

Actinides

Elements (Th to Lw) in which 5f orbitals are being filled are known as actinides. However, unlike lanthanides (Ce to Lu which is very similar to La), actinides (Th to Lr) are not very similar to Ac. All the elements of the actinide series are radioactive. Only Th, Pa and U are naturally occurring. Elements from Np onwards are made by nuclear reactions.

Table 5.19

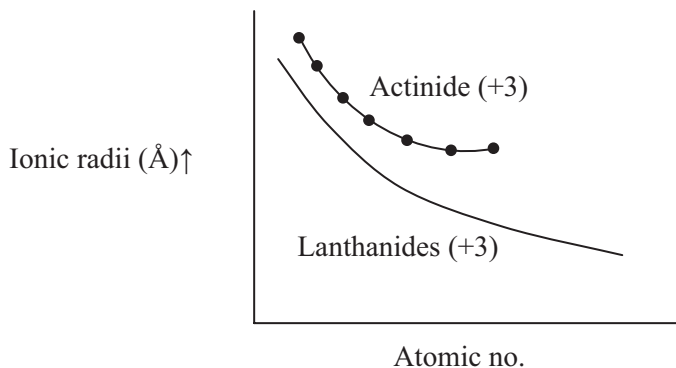
| Elements | Symbol | Atomic no. | Electron configuration |
|-----------------|-----------|------------|---|
| Actinium | Ac | 89 | [Rn] 6d¹7s² |
| Thorium | Th | 90 | [Rn] 6d ² 7s ² |
| Protactinium | Pb | 91 | [Rn] 5f ² 6d ¹ 7s ² |
| Uranium | U | 92 | [Rn] 5f ³ 6d ¹ 7s ² |
| Neptunium | Np | 93 | [Rn] 5f ⁴ 6d ¹ 7s ² |
| Plutonium | Pu | 94 | [Rn] 5f ⁶ 7s ² |
| Americium | Am | 95 | [Rn] 5f ⁷ 7s ² |
| Curium | Cm | 96 | [Rn] 5f ⁷ 6d ¹ 7s ² |
| Berkelium | Bk | 97 | [Rn] 5f ⁸ 6d ¹ 7s ² |
| Californium | Cf | 98 | [Rn] 5f ¹⁰ 7s ² |
| Einsteinium | Es | 99 | [Rn] 5f ¹¹ 7s ² |
| Fermium | Fm | 100 | [Rn] 5f ¹² 7s ² |
| Mendelevium | Md | 101 | [Rn] 5f ¹³ 7s ² |
| Nobelium | No | 102 | [Rn] 5f ¹⁴ 7s ² |
| Lawrencium | Lr | 103 | [Rn] 5f ¹⁴ 6d ¹ 7s ² |

Conclusion

- (i) The 5f orbitals become more stable than 6d from Pu.
- (ii) The energies of 5f, 6d, 7s are comparable. So configuration is not distinct
- (iii) The configuration of Cm, (5f⁷6d¹7s²) is due to greater stability associated with half filled (5f⁷) orbitals.
- (iv) The configuration of Bk is anomalous.
- (v) The configuration of Lr, 5f¹⁴6d¹7s² is due to greater stability of full filled (5f¹⁴) orbitals.

Atomic and Ionic radii and Melting Point

Atomic radii and mp do not vary regularly. However, ionic radii decreases with increasing atomic number, i.e., an ‘actinide contraction’ similar to lanthanide contraction.

**Figure 5.9**

Oxidation states

Actinides exist in a greater range of oxidation states +3 to +7 (unlike lanthanides). Highest oxidation states are found with Np and Pu, +3 to +7. Oxidation states decreases with increase in atomic number. High range, of oxidation states, is due to the fact that the 5f, 6d and 7s orbitals are of comparable energies. Such large range of oxidation states makes chemistry of these elements complex. The other factor responsible for complexity in chemistry is their high radioactivity.

PRACTICE QUESTIONS

- Classify the following as transition metal or ion.
 Sc , Sc^{+3} , Cu^+ , Cu^{2+} , Zn , Zn^{+2} , Ti^{+4} , Fe^{3+} , Mn^{+4} , Ag^+ , Au^{+3} , Hg^{2+} , Cr , Cr^{+6}
 Find out unpaired electrons in each case.
- The ionization energies of 6s and 5s – electrons are almost similar, why?
- $\text{Cu}^+_{(\text{aq})}$ is unstable in aqueous solution, why?
- Which of the five d orbitals is used in dsp^2 hybridization and sp^3d hybridization?
- Explain the following:
 - Au and Pt do not react with conc HNO_3 but dissolves in aquaregia ($3\text{HCl} + \text{HNO}_3$).
 - Au goes in solution when there is O_2 and NaCN .
 - Electron configurations of Cr is $3\text{d}^5 4\text{s}^1$ and Cu $3\text{d}^{10} 4\text{s}^1$.
 - A light blue colored solution of CuSO_4 becomes green when conc HCl is added in it.
- Write balanced equations for the following changes:
 - (a) KMnO_4 is treated with conc. H_2SO_4 , when greenish brown oil like substance is formed.
 (b) The oil like substance is dissolved in water.
 - (a) When NaOH solution is gradually added to CrCl_3 solution till a greenish solid separates.
 (b) After that excess NaOH added in the greenish solid when a deep green colour develops.
 - (a) When MnO_2 (Pyrolusite) is fused with KOH and KNO_3 to give a green solid.
 (b) The green solid is dissolved in water and Cl_2 is passed in it.
 - (a) When KMnO_4 solution is added in FeSO_4 solution (or oxalic acid) till colourless solution.
 (b) Then KMnO_4 is added in excess in the above colourless solution till a black ppt. is obtained.
 - (a) MnCl_2 is heated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in acid medium.
- Black cupric sulphide (CuS) is highly insoluble ($K_{\text{sp}} = 8 \times 10^{-37}$). But CuS dissolves in HNO_3 (50%) when heated. Write balance equation for this dissolution.
- A colourless solution containing Mn^{+2} is treated with NaOH to give a white ppt. 'A'. When left in air the white ppt. turns to a red compound 'B'. When dil. H_2SO_4 is added to the red compound colourless solution and black particles 'C' are obtained. When the black particle is heated with Na_2CO_3 in air the black compound turns to a green compound 'D'. When the acid is added to the green compound black particles 'C' and a deep violet solution containing the compound 'E' is produced. Identify A to E and write equations for each change.

$$\begin{array}{ll} \text{A} \longrightarrow \text{Mn}(\text{OH})_2, & \text{B} \longrightarrow \text{Mn}^{+3}_{(\text{aq})}, \\ \text{C} \longrightarrow \text{MnO}_2, & \text{D} \longrightarrow \text{K}_2\text{MnO}_4, \\ \text{E} \longrightarrow \text{HMnO}_4 \end{array}$$
- Write balanced equation for the following changes:
 - A small piece of Zn is dissolved in NaOH solution
 - HCl is added in the solution from (a) until a white ppt appears.
 - When the ppt from (b) is heated there is loss in weight but no loss of Zn .
 - The product from (c) is dissolved in dil. HCl .

6

Coordination Chemistry



Many metal ions form aggregate with Lewis bases which are stable in solution, such species are known as coordination compounds or complex compounds. A complex may be positive ion, a negative ion or even neutral. It depends upon the charge of the metal ion and the donor. Example,

$[\text{Co}(\text{NH}_3)_6]^{+3}$, O.N. of cobalt is +3 and NH_3 is neutral.

$[\text{Fe}(\text{CN})_6]^{4-}$, O.N. of iron is Fe^{2+} and cyanide ion (CN^-) is uninegative

$[\text{Cu}(\text{H}_2\text{NCH}_2\text{COO}^-)_2]$, O.N. of copper is +2 and glycinate ion is uninegative.

Complex compound are made by chemical species which have independent existence, such as Co^{+3} , Fe^{3+} , Cu^{2+} , NH_3 , CN^- etc. Thus, complexes are chemical compounds which contain a metal ion, surrounded by Lewis bases and the aggregate retain its identity in solution. Lewis bases which form complexes are known as Ligands (G, ligare – to bind).

COORDINATION NUMBER

The number of ligands surrounding a metal ion is coordination number of the metal ion. In case of polydentate ligands the number of coordinating centres determine coordination number. For example, ethylene diamine, a bidentate ligand, satisfies two coordination position.

Most common coordination numbers found are 4 and 6.

Table 6.1

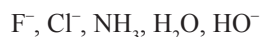
| Complex | Coordination number |
|-----------------------------------|---------------------|
| $[\text{Ag}(\text{NH}_3)_2]^+$ | 2 |
| $[\text{Cu}(\text{NH}_3)_4]^{+2}$ | 4 |
| $[\text{Fe}(\text{CN})_6]^{4-}$ | 6 |
| $[\text{CoCl}_4]^{-2}$ | 4 |

Types of Ligands

Lewis bases which form complexes are known as Ligands (G., ligare – to bind). They are classified as:

(i) *Monodentate*

Ligands which donate one electron pair to M^{n+} are called monodentate. Example,



Those ligands which can donate two electron pairs to M^{n+} , are known as bidentate. These are most common.

Cobalt ammines were subjected to reaction with silver nitrate solution. The results are given below:

Table 6.3

| Complex | No. of Cl^- ions | Number of ions |
|------------------------------------|---------------------------|----------------|
| $\text{CoCl}_3 \cdot 6\text{NH}_3$ | 3 (3AgCl) | 4 |
| $\text{CoCl}_3 \cdot 5\text{NH}_3$ | 2 (2AgCl) | 3 |
| $\text{CoCl}_3 \cdot 4\text{NH}_3$ | 1 (AgCl) | 2 |

It shows that in $\text{CoCl}_3 \cdot 6\text{NH}_3$ all chloride ions are identical. But in $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ there are two different kinds of chlorides. One type being similar to that in NaCl , which precipitated as AgCl , whereas other is bonded strongly with Co^{+3} and so did not precipitate.

Conductance measurement provided useful information about the ions present in solutions. The greater the number of ions in a solution, the greater is the electrical conductance. Therefore, the conductivities of different complexes having the same conc were compared. It provided information about the number of ions present in each complex. It was studied for several series of complexes. Some of the results are given below:

Table 6.4

| Complex | No. of ions | Conductance |
|------------------------------------|-------------|----------------|
| $\text{CoCl}_3 \cdot 6\text{NH}_3$ | 4 | ↓ Decreases |
| $\text{CoCl}_3 \cdot 5\text{NH}_3$ | 3 | |
| $\text{CoCl}_3 \cdot 4\text{NH}_3$ | 2 | |

Table 6.5

| Complex | No. of ions | Molar conductivity Ohm^{-1} | |
|------------------------------------|-------------|--------------------------------------|-----------|
| $\text{PtCl}_4 \cdot 6\text{NH}_3$ | 5 | 523 | ↓ |
| $\text{PtCl}_4 \cdot 5\text{NH}_3$ | 4 | 404 | |
| $\text{PtCl}_4 \cdot 4\text{NH}_3$ | 3 | 229 | |
| $\text{PtCl}_4 \cdot 3\text{NH}_3$ | 2 | 97 | |
| $\text{PtCl}_4 \cdot 2\text{NH}_3$ | 0 | 0 | |
| | | | Decreases |

Taking the above observations into consideration, the above observations. Werner developed a method to write coordination complexes. He suggested that complex unit which is stable in solution should be kept within square bracket and grs ionizable outside the bracket, viz.,

[Complex unit] Ionizable grs.

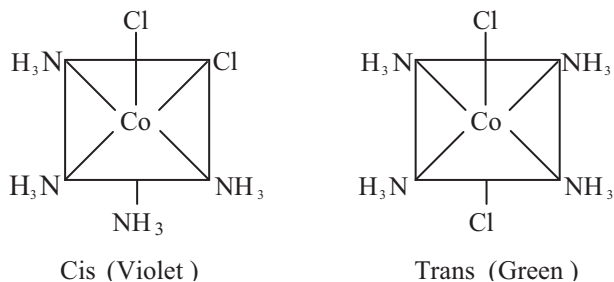
Thus, the above complexes may be formulated as,

Table 6.6

| Complex | Formulation |
|------------------------------------|--|
| $\text{CoCl}_3 \cdot 6\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_6]^{3+}, 3\text{Cl}^-$ |
| $\text{CoCl}_3 \cdot 5\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}, 2\text{Cl}^-$ |
| $\text{CoCl}_3 \cdot 4\text{NH}_3$ | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+, \text{Cl}^-$ |
| $\text{PtCl}_4 \cdot 6\text{NH}_3$ | $[\text{Pt}(\text{NH}_3)_6]^{4+}, 4\text{Cl}^-$ |

Isomer Analysis

The compound $\text{CoCl}_3 \cdot 4\text{NH}_3$ is found in two different colours, green and violet. Werner proposed that it is due to existence of isomers. This compound forms two isomers so there is difference in colour.

**Figure 6.2**

Isomers differ not only in colours, properties also. For example, the α and β forms of $\text{PtCl}_2 \cdot 2\text{NH}_3$ are both cream coloured but they differ in solubility and chemical reactivity. The cis isomers of $\text{PtCl}_2 \cdot 2\text{NH}_3$ (cis-platin) has anticarcinogenic property.

Based on the above observations Werner proposed his coordination theory (1893) at the age of only 26. For this work he was awarded Noble Prize in 1913. Warner's coordination theory is:

- (1) Metals possess two types of valencies
 - (a) Primary valency, it is satisfied by negative groups and is ionisable (in modern terms it is oxidation state of the metal).
 - (b) Secondary valency, it may be satisfied by negative groups or neutral molecules and is not ionizable (in modern terms it is coordination number of the metal).
- (2) The secondary valencies are directed towards fixed position in space. Therefore, every complex has a definite structure, depending upon its coordination number.



Structure of six coordinated complexes

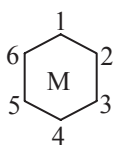
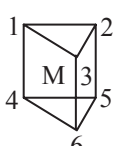
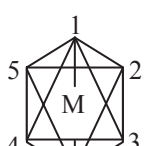
Werner determined structure of six coordinated complexes (ML_6) using isomer analysis method. Before the use of X-ray analysis, spatial configuration was determined by comparing known isomers with isomers theoretically possible for different structures.

A six coordinated complex may have the following structures:

- (a) Hexagonal planar
- (b) Trigonal prismatic
- (c) Octahedral

Possible isomers for a complex of the type MA_4B_2 are shown for different structures.

Table 6.7

| Complex |  |  |  | Actual no. of isomer found |
|---------|---|---|---|----------------------------|
| | Hexagonal planar | Trigonal prism | Octahedral | |

| | | | | |
|--|----------------------|----------------------|-----------------|---|
| Isomers (MA ₄ B ₂) | 3 (1,2; 1,3; 1,4) | 3 (1,2; 1,4; 1,6) | 2 (1,2; 1,6) | 2 |
|--|----------------------|----------------------|-----------------|---|

Actual number of isomers found were only two for several cases. It compared with octahedral structure only. Therefore, Werner proposed an octahedral structure for all six coordinated complexes.

Nomenclature

The naming of coordination compounds follows rules developed by International Union of Pure and Applied Chemistry (IUPAC). Important points are:

1. Cations are named first then the anions (like slats, NaCl, sodium chloride not chloride sodium).
2. For writing formula of a complex metal is written first then the ligands [$M^{n+}L_s$].
3. For writing name of a complex ligands are named first then the metal ion and its oxidation state at last in small bracket in roman numerals. $L_s M^{n+}$ (oxidation number).
4. Naming of ligands

(a) Some ligands have special names.

| | | | |
|------------------|--------|----|----------|
| H ₂ O | aqua | NO | nitrosyl |
| NH ₃ | ammine | CO | carbonyl |

(b) Name of negative ligands end in 'O'.

| | | | |
|-----------------|---------|---|---------|
| F ⁻ | fluoro | CH ₃ COO ⁻ | acetato |
| CN ⁻ | cyano | O ⁻² | oxo |
| HO ⁻ | hydroxo | O ₂ ⁻² | peroxo |
| H ⁻ | hydrido | C ₂ O ₄ ⁻² | oxalato |

(c) Most ligands receive their ordinary names.

| | |
|--------------------------------------|---------------------|
| en | Ethylene diamine |
| Py (C ₅ H ₅ N) | Pyridine |
| PPh ₃ | Triphenyl phosphine |

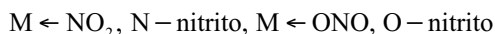
(d) N₂ and O₂ as ligands are named as dinitrogen and dioxygen.

(e) For two or more ligands the following prefixes are used.

| | | | | | |
|-------|------|------|--------|-----|------|
| Two | di, | Four | tetra, | Six | hexa |
| Three | tri, | Five | penta | | |

If the name of the ligand, bears number, their numbers are denoted as
2(en) → bis – (en), 3(en) → tris (en) etc.

- (f) For different ligands alphabetical order is generally used.
- (g) Naming of Ambidentate ligands: Ligands which can join with a metal through different atoms in different conditions are called Ambidentate. Atom linking with metal is included in its name. for example, NO₂



5. (a) Names of neutral complexes and complex cations have no special ending.
(b) Name of anionic complexes end in 'ate' (ferrate, cuprate, etc.)
6. A particular isomer is indicated by cis, trans, fac, Mer, dextro and lavo.

7. A bridging ligand is denoted by μ , for example, $[(\text{NH}_3)_5\text{Cr} - \text{OH} - \text{Cr}(\text{NH}_3)_5]\text{Br}_5$
 μ – hydroxobis [pentammine chromium (III)] bromide.

Name of the some complexes are given

| | |
|---|---|
| $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ | Hexamine cobalt (III) chloride |
| $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ | Pentammine carbonato cobalt(III) chloride |
| $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ | Tetraqualdichloro chromium (III) chloride |
| $\text{K}_4[\text{Fe}(\text{CN})_6]$ | Potassium hexacyanoferrate (II) |
| $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ | Trioxalato ferrate (III) |
| $[\text{Ni}(\text{Dmg})_2]$ | bis (dimethylglyoximate) nickel (II) |
| $[\text{Cu}(\text{gly})_2]$ | diglycinato copper (II) |
| $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ | bis-(ethylene diamine) dichloro cobalt (III) chloride |
| $\text{Cr}(\text{en})_3]^{3+}$ | tris (ethylene diamine) chromium (III) ion |
| $\text{Na}[\text{Co}(\text{CO})_4]$ | Sodium tetra carbonyl cobaltate (–I) |
| $\text{K}_4[\text{Ni}(\text{CN})_4]$ | Potassium tetracyano nickelate (0) |
| $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ | Pentammine N-nitrito cobalt (III) chloride |
| $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ | Pentammine O-nitrito cobalt (III) chloride |
| $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ | Hexamine chromium (III) hexacyano cobaltate (III) |
| $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ | tris (triphenyl phosphine) chloro Rhodium (I) |
| $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{PyNO}_2]^+$ | ammine hydroxylamine pyridine N-nitrito platinum (II) ion |

Valence bond model for complexes

Linus Pauling, first of all, proposed valence bond model for coordination compounds. According to this model:

1. Metal ion (or metal atom) provides vacant orbitals. For coordination number four, metal ion uses either sp^3 or dsp^2 hybrid orbitals leading to tetrahedral or square planar complex. For coordination number six, the hybrid is either d^2sp^3 or sp^3d^2 leading to octahedral complex.
2. Ligands provide electron pair for metal – ligand bond.



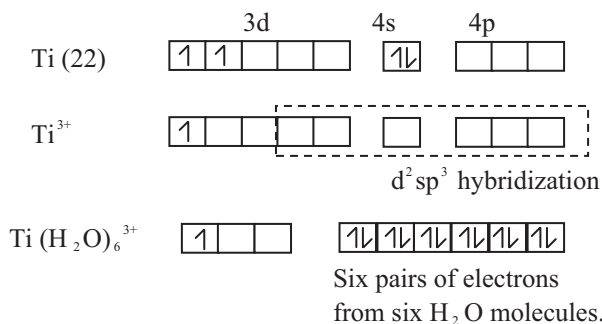
Figure 6.3

The bond is of σ – type.

3. There can be M – L π bonds also if ligands have vacant d – orbitals or vacant π^* MOs and metal ion has electrons in d – orbitals.

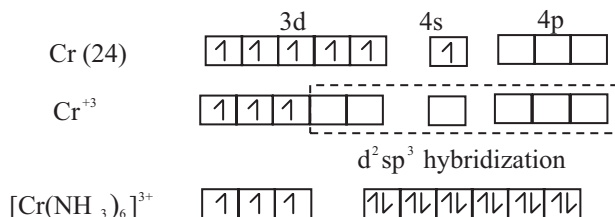
1. Formation of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

In this complex oxidation number of Ti is +3 which has one electron in 3d orbital, that is, $3d^1$ configuration.



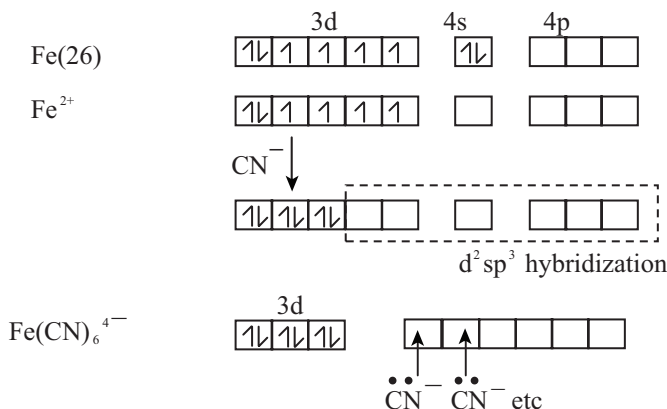
As the complex has unpaired electron, it is paramagnetic ($\mu = \sqrt{3\text{BM}}$)

2. $[\text{Cr}(\text{NH}_3)_6]^{3+}$. This complex has Cr in +3 oxidation state, that is, Cr^{+3} which has $3d^3$ configuration.



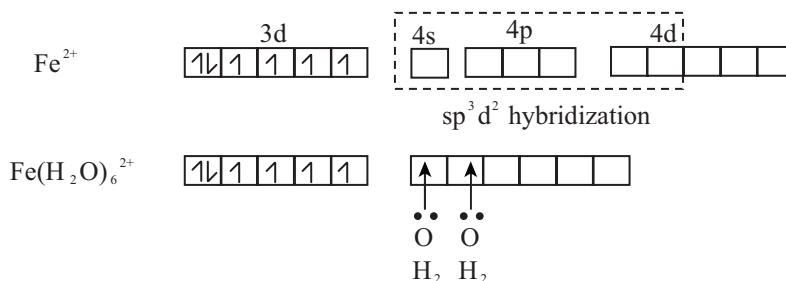
This complex ion has 3 unpaired electrons, it is paramagnetic, ($\mu = \sqrt{15\text{BM}}$)

Formation of many complexes requires pairing of electron in orbitals against Hund's Rule. It happens due to presence of ligands. For example formation of $\text{Fe}(\text{CN})_6^{4-}$, that is, ferrocyanide ion. This complex has iron in +2 oxidation state, Fe^{2+} , which has six electrons in 3d orbitals ($3d^6$). The CN^- causes pairing of d – electrons. The Fe^{2+} is d^2sp^3 hybridized.



It results into an octahedral complex. As the complex has no unpaired electrons, it is diamagnetic. Such complexes are known as inner orbital complexes or low spin or spin paired complexes. That is, an inner orbital complex is that which uses (n – 1)d orbitals for hybrid formation.

On the contrary, there are many others in which metal ion uses outer d orbitals (nd) for hybrid formation to form the complex. For example, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$. This complex has iron in +2 oxidation state, that is, Fe^{2+} , $3d^6$ electron configuration. Here no pairing of electrons takes place in 3d orbitals.



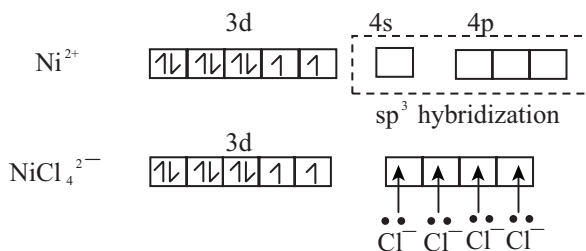
This complex is also octahedral but 4d is involved in hybrid formation. Such complexes are called outer orbital or high spin or spin free complexes. Thus an outer orbital complex is that which uses nd orbitals for hybridization.

Formation of four coordinated complexes may also be explained in the same way. A metal ion may use either sp³ or dsp² hybrids for four coordinated complexes.

Td complexes



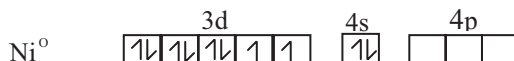
This complex has Ni in +2 oxidation state, that is, Ni^{2+} , having $3d^8$ electron configuration.



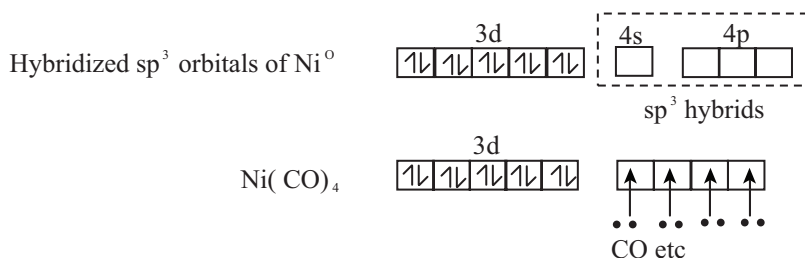
A Td complex thus results. As the complex has unpaired electrons, it is paramagnetic. ($\mu = \sqrt{8}$ BM).



The oxidation number of Ni in this complex is zero having electron configuration.



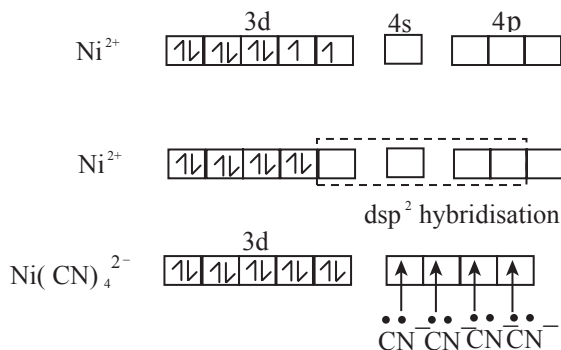
But the complex is found diamagnetic. It is possible only when 4s electrons pair up in 3d to make it $3d^{10}$, a diamagnetic situation. It happens during complex formation.



Nickel tetracarbonyl is thus a Td complex.



The oxidation number of Ni in this complex is +2, that is, Ni^{2+} which has electron configuration in $3d^8$. This complex is also found diamagnetic. That is 3d electrons pair up to leave one 3d orbital vacant. The hybridization then is dsp^2 and the complex is square planar.



The complex is diamagnetic as it has no unpaired electron.

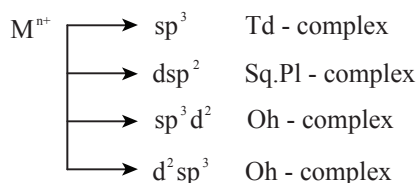
Some important points

- (i) M^{n+} ions which have one, two or three electrons in 3d orbitals always form inner orbital Oh complexes.
- (ii) M^{n+} ions which have d^8 and d^9 configurations always form outer orbital Oh complexes.
- (iii) M^{n+} ions having d^4 , d^5 , d^6 may form outer or inner orbital complexes. It depends on ligands.
- (iv) CN^- and CO always forms inner orbital Oh complexes.
- (v) F^- , H_2O , $\text{C}_2\text{O}_4^{2-}$ always forms outer orbital Oh complexes.
- (vi) NH_3 , H_2O and $\text{C}_2\text{O}_4^{2-}$ form inner orbital Oh complex with Co^{+3} i.e., $[\text{Co}(\text{NH}_3)_6]^{3+}$ is inner orbital, diamagnetic complex.
- (vii) Cl^- , Br^- , I^- , PPh_3 mostly form Td complexes, with 3d metals.
- (viii) M^{n+} (Pt^{+2} , Pd^{+2} , Ni^{+2} , Au^{+3} etc.,) having 8 d – electrons mainly form square planar complexes, in coordination number four.
- (ix) PtCl_4^{2-} is square planar.
- (x) M^{n+} having d^0 , d^5 and d^{10} prefer Td complexes.

Merits of VB model

It explains:

- (i) Complex formation
- (ii) Geometry of the complex



Demerits of VB model

It fails to explain:

- (i) Colour and electronic spectra of complexes.
- (ii) Reason for inner and outer orbital complexes.
 FeF_6^{3-} Outer orbital
 $\text{Fe}(\text{CN})_6^{3-}$ Inner orbital, there are many others.
- (iii) Temperature dependent magnetic moment.
- (iv) Stability and ligand exchange reactions are difficult to explain.

Crystal Field Model of Bonding

This model compares a complex compound with an ionic crystal. In an ionic crystal cations are surrounded by anions in definite number (the crystal coordination number).

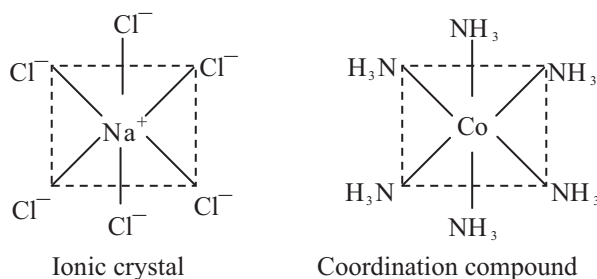


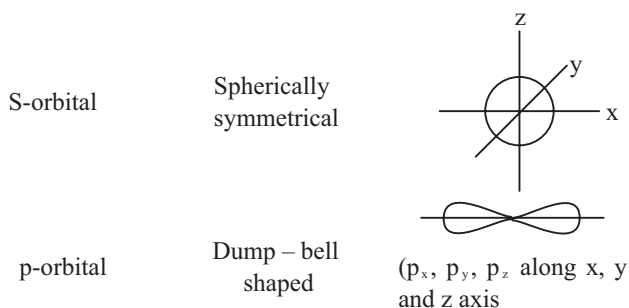
Figure 6.4

Similarly, in a complex compound metal ion is surrounded by a definite number of ligands (coordination number of the M^{n+}). A complex is thus compared with an ionic crystal. As interaction between ions in an ionic crystal is mainly electrostatic, so it was assumed that the interaction between the metal ion and ligands is electrostatic.

Assumptions of crystal field model

1. Ligands are taken as point charge or point dipole.
2. Metal ions are assumed to have orbitals.
3. M^{n+} ion and ligands, interaction is purely electrostatic.

Shape of orbitals



p_x , p_y , p_z are degenerate orbitals but differ in orientation.

d-orbitals

 (i) d_{xy} , d_{yz} and d_{xz}

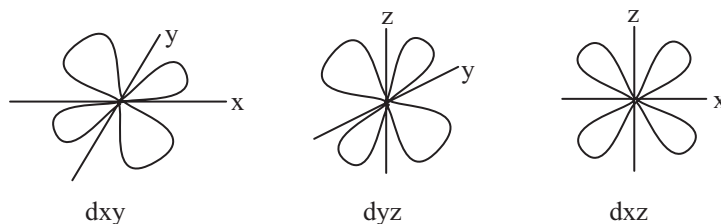
 These orbitals are oriented between the given axes (i.e., at 45°)


Figure 6.5

 (ii) The $d_{x^2-y^2}$ and d_{z^2}

Orbitals are oriented along the given axes

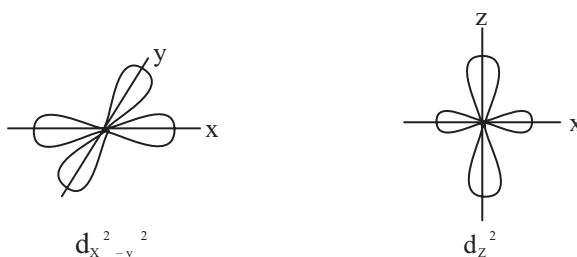


Figure 6.6

The five d orbitals are degenerate but differ in orientation.

Interaction of six ligands with metal d orbitals (i.e., octahedral complex case).

Comparison of the position of ligands in octahedral field and orientation of d orbitals shows that:

- The $d_{x^2-y^2}$ and d_{z^2} orbitals are facing the ligands i.e., interact more with the ligands.
- The d_{xy} , d_{yz} and d_{xz} orbitals do not face the ligands rather the ligands lie in between the lobes of these orbitals.

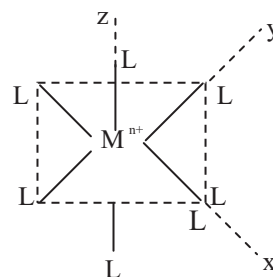


Figure 6.7

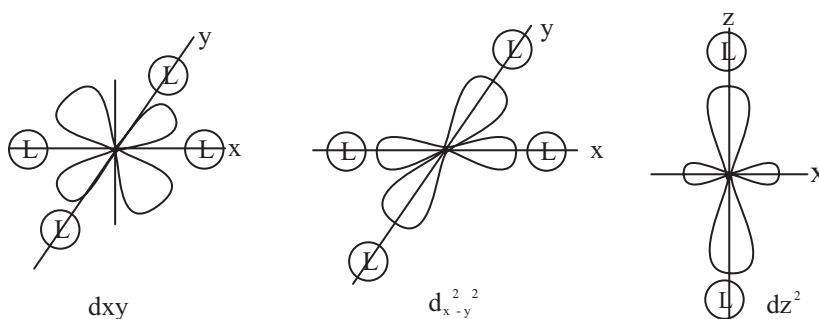


Figure 6.8

Therefore, in an Oh crystal field, d-orbitals of the M^{n+} ion split in two levels as

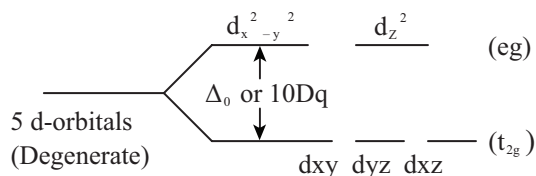


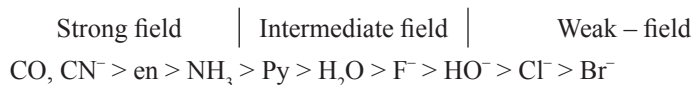
Figure 6.9

This is called crystal field splitting. The energy gap between t_{2g} and e_g levels is denoted either by Δ_0 or $10Dq$. The energy per electron in t_{2g} level is $-2/5\Delta_0$ (or $-4Dq$) and in e_g level is $+3/5\Delta_0$ (or $+6Dq$). The crystal field splitting extent depends on many factors:

- (i) Ligands,
- (ii) Transition series of M^{n+} ,
- (iii) Oxidation state of the M^{n+} ,
- (iv) Geometry of the complex.

Ligands

All ligands do not interact equally with metal d orbital. Some interact more and others less. Therefore, extents of Δ_0 differ from ligand to ligand. In general, ligands can be arranged in a series in order of their ability to cause d-orbital splitting. It is known as Spectro Chemical Series.



Td – complexes

The splitting of d-orbitals in Td-fields is opposite to that in the octahedral complexes.

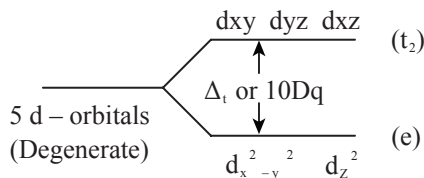


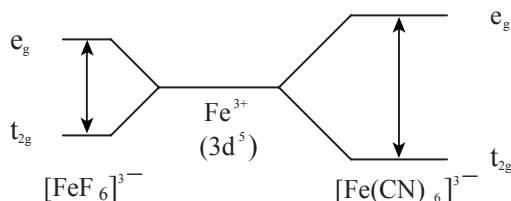
Figure 6.10

However, splitting in Td-complexes is smaller. Therefore, only high-spin Td complexes are known for the first transition series metal ions. Crystal field model can explain:

- (i) Stability of the complexes
- (ii) Magnetic property of the complex
- (iii) Colour of the complexes

Stability and CF model

Complexes in which d-orbitals split to a larger extent are more stable, thermodynamically. Therefore, $[Fe(CN)_6]^{3-}$ is more stable than $[FeF_6]^{3-}$ as CN^- is strong field ligand than F^- and causes greater splitting of d-orbitals.

**Figure 6.11**

Actually, stability determining factor is Crystal Field Stabilization Energy (CFSE). It is defined as: gain in energy due to the preferential filling of electrons in lower lying orbitals (e.g., t_{2g}) is called CFSE

It is calculated as:

$$\begin{aligned} \text{CFSE} &= t_{2g}^x e_g^y \\ &= (\text{electrons in } e_g \text{ level} \times \frac{3}{5} \Delta_0 - (\text{electrons in } t_{2g} \text{ level}) \times \frac{2}{5} \Delta_0 \end{aligned}$$

Table 6.8

| Complex | Configuration in complex | CFSE |
|---------------------------------|--------------------------|--|
| $[\text{FeF}_6]^{3-}$ | $t_{2g}^3 e_g^2$ | $+\frac{3}{5} \times 2 \Delta_0 - \frac{2}{5} \times 3 \Delta_0 = 0$ |
| $[\text{Fe}(\text{CN})_6]^{3-}$ | t_{2g}^4 | $-\frac{2}{5} \times 5 \Delta_0 = -2 \Delta_0$ |

It shows that decrease in total energy for cyano complex is greater. Thus the complex $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than the complex $[\text{FeF}_6]^{3-}$.

CFSE for d^1, d^2, d^3, d^8, d^9 and d^{10} in oh – field

| d-electrons | Configuration in complex in t_{2g} & e_g term | CFSE |
|-------------|---|-------------------------|
| 1 | t_{2g}^1 | $-\frac{2}{5} \Delta_0$ |
| 2 | t_{2g}^2 | $-\frac{4}{5} \Delta_0$ |
| 3 | t_{2g}^3 | $-\frac{6}{5} \Delta_0$ |
| 4 | $t_{2g}^4 e_g^0$ | $-\frac{6}{5} \Delta_0$ |
| 5 | $t_{2g}^5 e_g^0$ | $-\frac{3}{5} \Delta_0$ |

For configuration like d^4, d^5, d^6 and d^7 , two possibilities exists, e.g., for d^4 they may be $t_{2g}^4 e_g^0$ or $t_{2g}^3 e_g^1$. Out of these two the ground state is determined by comparing Δ_0 and the pairing energy (say P).

When:

- (i) $P > \Delta_0$, (i.e., for weak crystal field) electrons occupy t_{2g} and e_g levels both giving a high spin complex.
 (ii) $P < \Delta_0$, (i.e., for strong crystal field) electrons remain in t_{2g} level only, giving a low spin complex.

CFSE for d4, d5, d6 and d7 ions in weak and strong crystal field.

| d-electrons | Weak Field ($P > \Delta_0$) | CFSE | Strong Field ($P < \Delta_0$) | CFSE |
|----------------|-------------------------------|----------------------------|---------------------------------|-----------------------------|
| d ⁴ | $t_{2g}^3 e_g^2$ | $-\frac{3}{5}\Delta_0$ | (t^4_{2g}) | $-\frac{8}{5}\Delta_0 + P$ |
| d ⁵ | $t_{2g}^3 e_g^2$ | 0 | t^6_{2g} | $-2\Delta_0 + P$ |
| d ⁶ | $t_{2g}^5 e_g^2$ | $-\frac{2}{5}\Delta_0 + P$ | t^6_{2g} | $-\frac{2}{5}\Delta_0 + 3P$ |
| d ⁷ | $t_{2g}^5 e_g^2$ | $-\frac{4}{5}\Delta_0 + P$ | $t^6_{2g} e_g^1$ | $-\frac{9}{5}\Delta_0 + 3P$ |

Magnetic properties and CF model

Transition metal compounds are generally paramagnetic. It arises due to unpaired electrons in the d-orbitals of the metal ions. Paramagnetism is denoted in terms of magnetic moment, μ which is given by,

$$\mu = \sqrt{n(n+2)} \text{ BM, where } n = \text{number of unpaired electrons.}$$

This μ is known as spin only (S.O) value, $\mu_{s.o.}$, as it considers electronic spin only to calculate μ .

Table 6.9 Unpaired es and $\mu_{s.o}$

| Ion | e configuration (d – orbitals) | Unpaired electrons | $\mu_{s.o}$ (calculated) |
|------------------|--------------------------------|--------------------|--------------------------|
| Ti ³⁺ | ↑ | 1 | 1.73 ($\sqrt{3}$) |
| Ti ²⁺ | ↑ ↑ | 2 | 2.84 ($\sqrt{8}$) |
| V ²⁺ | ↑ ↑ ↑ | 3 | 3.87 ($\sqrt{15}$) |
| Cr ²⁺ | ↑ ↑ ↑ ↑ | 4 | 4.9 ($\sqrt{25}$) |
| Mn ²⁺ | ↑ ↑ ↑ ↑ ↑ | 5 | 5.92 ($\sqrt{35}$) |
| Fe ²⁺ | ↑↓ ↑ ↑ ↑ ↑ | 4 | 4.9 |
| Co ²⁺ | ↑↓ ↑↓ ↑ ↑ ↑ | 3 | 3.87 |
| Ni ²⁺ | ↑↓ ↑↓ ↑↓ ↑ ↑ | 2 | 2.84 |
| Cu ²⁺ | ↑↓ ↑↓ ↑↓ ↑↓ ↑ | 1 | 1.73 |

According to CF model d-orbitals split in the complexes. It gives number of unpaired electron and hence the magnetic moment (μ).

Let us consider $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ ions in which 1st one is paramagnetic ($\mu \sim 4.9$) whereas 2nd is diamagnetic ($\mu=0$). Both are Oh-complexes but H_2O is a weak ligand and CN^- is a very strong ligand w.r.t. d-orbitals splitting. Therefore, energy gap between split orbitals differ the d-electrons in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ occupy both t_{2g} and e_g orbitals whereas in $[\text{Fe}(\text{CN})_6]^{4-}$ all electrons occupy t_{2g} orbitals.

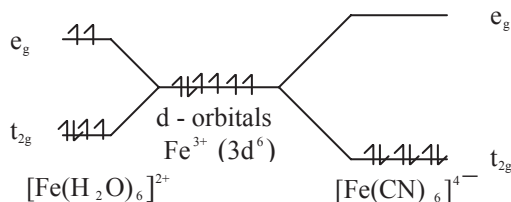


Figure 6.12

As $[\text{Fe}(\text{H}_2\text{O})]^{2+}$ has four unpaired electrons, $t_{2g}^4 e_g^2$ its μ is around 4.9 whereas $[\text{Fe}(\text{CN})_6]^{4-}$ has no unpaired electrons t_{2g}^6 , it is diamagnetic. In some cases reduced paramagnetism is also found. Example $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. Both these complexes contain iron in +3 oxidation states, Fe^{3+} , a $3d^5$ systems. Fluoride is much weaker ligand compared to cyanide, (CN^- causes splitting almost five times than F^-).

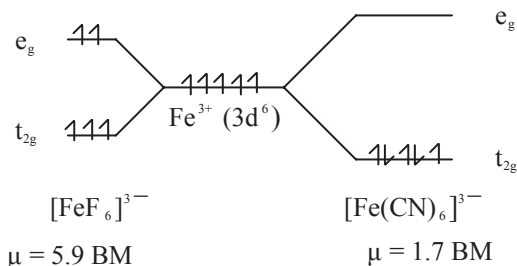
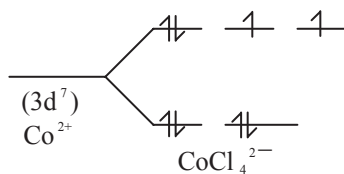


Figure 6.13

Thus, the fluoro complex FeF_6^{3-} , has five unpaired electrons and its μ is 5.9 B.M. But the cyano complex shows paramagnetism for one unpaired electron (i.e., reduced paramagnetism), $\sqrt{3}$ B.M.

Tetrahedral complexes are dealt in the same way. However, splitting in Td complexes is always small. Therefore, only high spin Td complexes are known.



$$\mu = \sqrt{2(2 + 2)} = \sqrt{8} \text{ BM}$$

Figure 6.14

Colour and CF model

A substance looks coloured when it absorbs wavelength of the visible range of radiation and transmits the rest. The visible range is $\lambda = 3800\text{\AA}$ to 7800\AA . Many of the transition metal complexes are coloured. Crystal field theory explains colour easily. Let us consider the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, which is violet. The complex is Oh, oxidation number of Ti is +3 i.e., there is only one electron in 3d orbital of Ti^{3+} . The d orbital split in Oh field and has the electron configuration, t_{2g}^1 .

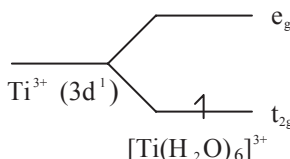


Figure 6.15

When light falls on the complex, the t_{2g} electron is excited to e_g level. This excitation takes place in greenish yellow region ($\sim 5000\text{\AA}$), the rest is transmitted. The colour is violet, (the complementary colour).

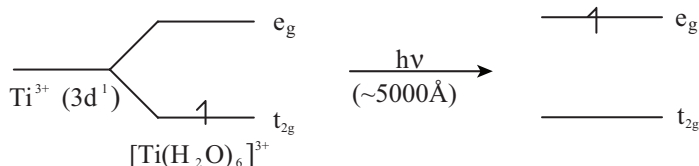


Figure 6.16

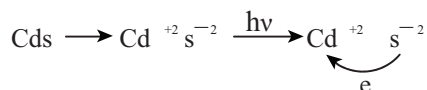
Colour due to this mechanism is called $d \rightarrow d$ transition.

In the absence of ligands crystal field splitting does not occur, colour disappears. Example, anhydrous TiCl_3 , CuSO_4 etc, are colourless.

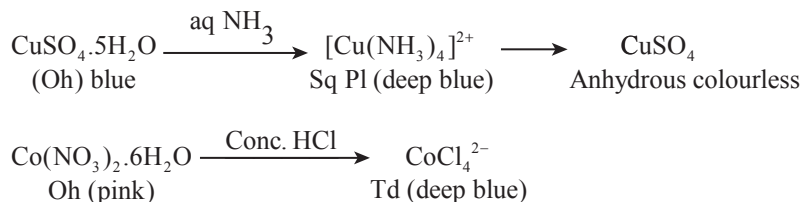
Table 6.10

| Compounds | Colour |
|--|------------|
| $\text{Ti}(\text{H}_2\text{O})_6\text{Cl}_3$ | Violet |
| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | Blue |
| CuSO_4 | Colourless |
| TiCl_3 | Colourless |

Some anhydrous salts are also found coloured. It is due to charge transfer, Example, NiS (black), Cu_2O (Red), CdS (yellow) etc.



Colour change in coordination compounds is followed with change in coordination number. Example,



Some important points

- Splitting of d-orbitals in Oh crystal field is larger than Td field.
- Splitting of d-orbitals in Td field is opposite to that in Oh field.

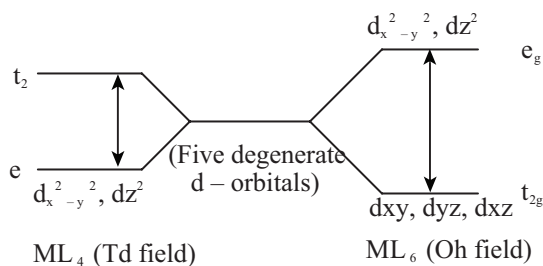
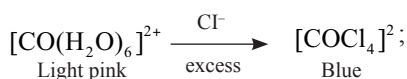
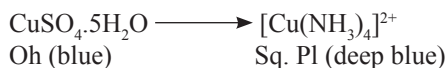


Figure 6.17

- (iii) Carbon monoxide (CO) and CN^- strong field ligands and always form low spin complexes. They are two electron donors.
- (iv) NO is a strong ligand and is a three electron donor.
- (v) Water (H_2O), F^- , Cl^- , $C_2O_4^{2-}$ weak field ligands and always form high spin complex.
- (vi) Complexes in which metal ion has d^1 , d^2 , d^3 , d^4 , d^6 , d^7 , d^8 , d^9 electrons are coloured due to d-d transition.
- (vii) Complexes having M^{n+} in which there are d^0 , d^5 and d^{10} electrons are generally coloured due to charge transfer.
- (viii) Charge transfer colours are deep whereas colours due to d-d transition are not so deep.
- (ix) Complexes having 1, 2 and 3 d – electrons are always high spin.
- (x) Complexes having 4, 5, 6, 7 d – electrons can be high spin or low spin.
- (xi) Complexes having d^8 and d^9 electrons always have similar magnetic property.
- (xii) Colour of anhydrous salts is due to charge transfer. Example Cd s (yellow), SnI_4 (violet), Ni s (black), Cu_2O (red) etc.
- (xiii) Change in coordination number follows with colour charge.



Isomerism in coordination compounds

Molecules or ions which have the same molecular formula but different structures are called isomers. Werner visualized that ligands are arranged around the central metal ion in specific orientation in space, e.g.,

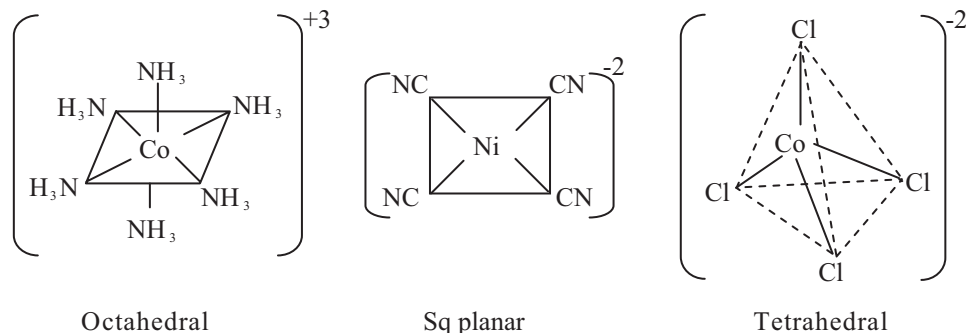


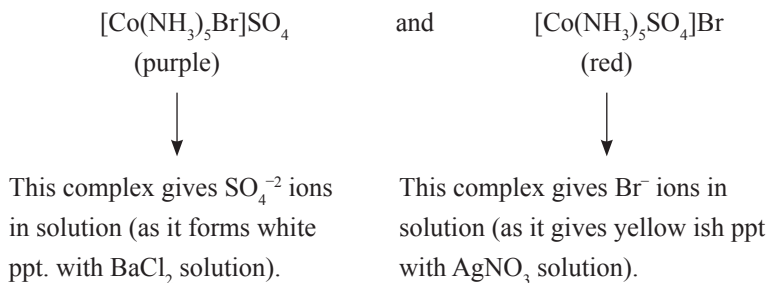
Figure 6.18

This three-dimensional picture of complexes gives rise to the possibility of isomerism. Coordination compounds show structural as well as stereo isomerism.

Structural isomerism

(i) Ionisation isomerism

Isomers which give different ions in solution are called ionisation isomers. It becomes possible when the negative ligands interchange position between the coordination sphere and out side it, e.g.,



The other example is



(ii) Linkage isomerism

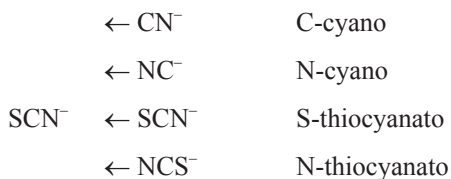
It is possible with ambidentate ligands. i.e., ligands which can coordinate with the metal ions through different atoms. The NO_2^- group can coordinate either through N ($\leftarrow \text{NO}_2$) or through O atom ($\leftarrow \text{ONO}$), e.g.,



Pentaammine N-nitrito Co(III) ion Pentaammine O-nitrito Co(III) ion.

Other ligands which can form linkage isomers are

CN^- it may use either C or N as donor atom.



(iii) Hydrate isomerism

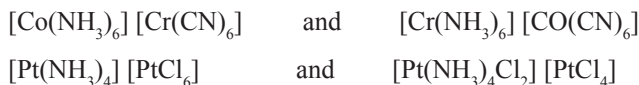
Such isomers result from replacement of a coordinated group by water of hydration, example, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ may represent three isomers which differ in physical and chemical properties.

- | | |
|--|--|
| (a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) | hexaqua Cr(III) chloride |
| (b) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (green) | pentaquachloro Cr(III) chloride monohydrate |
| (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (green) | tetraqua dichloro Cr(III) chloride dihydrate |

- (a) Does not lose water over conc. H_2SO_4 and all Cl^- ions are precipitated by Ag^+ .
 (b) Loses one H_2O over conc. H_2SO_4 and 2Cl^- pptd by Ag^+ .
 (c) Loses two H_2O over conc. H_2SO_4 and only one Cl^- is pptd by Ag^+ .

(iv) Coordination isomerism

In compounds where both cation and anion are complex, ligand exchange can form isomers known as coordination isomers, e.g.,



(v) Ligand isomerism

When a ligand itself possesses isomeric possibilities ligand isomers exist, example, $[\text{Co}(1,2\text{-diaminopropane})_2\text{Cl}_2]^+$ and $[\text{Co}(1,3\text{-diaminopropane})_2\text{Cl}_2]^+$.

Stereo isomerism

Stereo isomerism in coordination compounds arises due to different spatial arrangement of ligands around the central metal ion.

Geometrical isomerism

In complexes ligands may occupy different sites. When the ligands in question occupy adjacent positions it is called 'Cis' (Cis, Latin, meaning "on this side") and when they occupy opposite sites, it is called 'trans' (trans, Latin meaning "across"). Therefore, geometrical isomerism is also called 'Cis-Trans' isomerism. This type of isomerism is not possible for complexes of CN 2 or 3 or for CN 4, tetrahedral complexes.

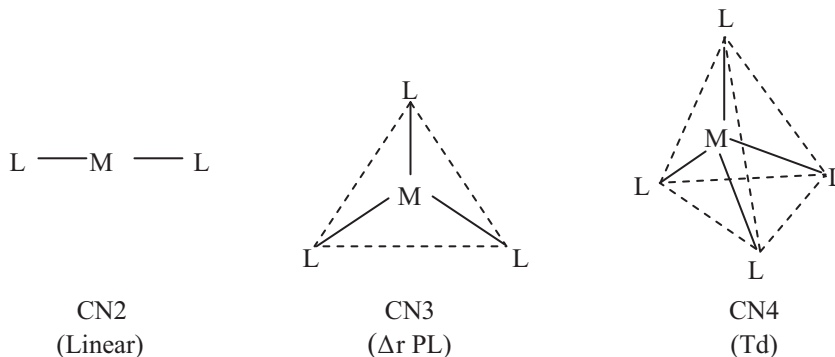


Figure 6.19

In these complexes, all ligand positions are adjacent not opposite. However, cis-trans isomerism is common in square planar and octahedral complexes.

Sq PL

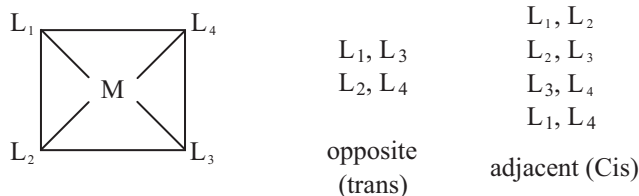


Figure 6.20

Oh

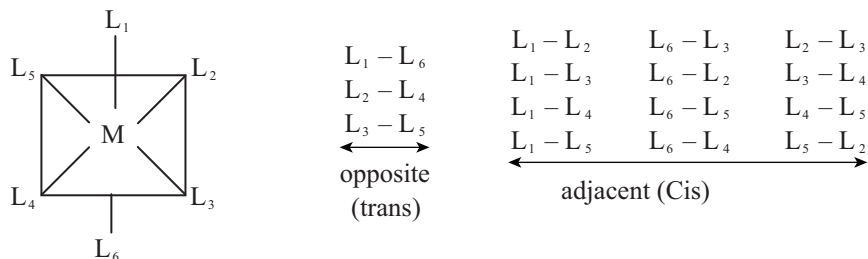


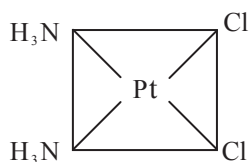
Figure 6.21

CN – 4 Sq planar complexes

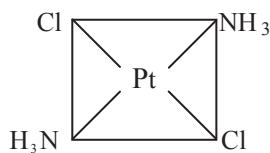
The following types of four coordinated square planar complexes show cis–trans isomerism.

(i) MA_2B_2 

diammine dichloro Pt (II)



Cis

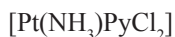
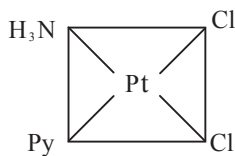
(Cl[−] and NH₃ ligands are adjacent)

trans

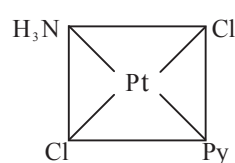
(Cl[−] and NH₃ ligands are opposite)

Figure 6.22

Cis and trans isomers may be distinguished by dipole moment measurement.

(ii) $MABX_2$ (Py = pyridine C₅H₅N)

Cis



trans

Figure 6.23

(iii) $[MABCD]$ 

In such complexes three of the ligands (B, C, or D) may be trans to A.

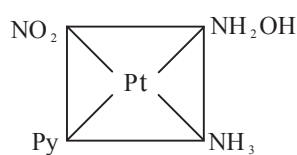
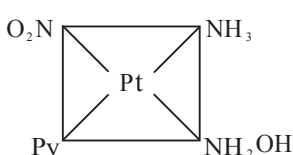
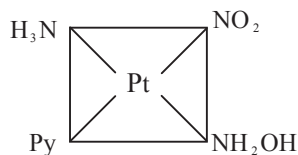


Figure 6.24

It such complexes are denoted as $[M < AB > CD]$, the ligands in the angular brackets are trans to each other, and they have no isomers.

- (v) Geometrical isomerism is also found in square planar complexes containing unsymmetrical bidentate ligands. example, $[M(AB)_2]$, gly = $NH_2 - CH_2 - COO^-$

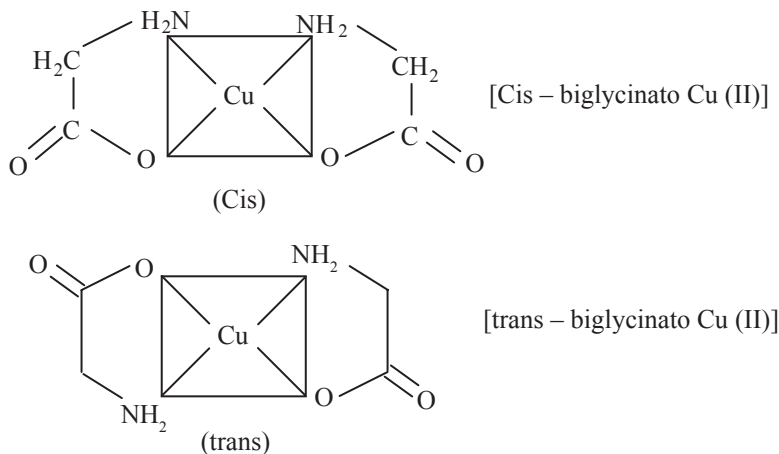


Figure 6.25

CN – 6

Geometrical isomerism in octahedral complexes is also very common. The familiar examples include compounds of the type:

- (i) $[MA_4X_2]$
- (ii) $[MA_4XY]$
- (iii) $[M(AA)_2X_2]$
- (iv) $[M(AA)_2XY]$
- (v) $[MA_2X_2Y_2]$

Where M = Co (III), Cr (III), Rh (III), Pt (IV) etc.

A – A = Symmetrical bidnetate ligands

X and Y = \ominus ive ligands.

For example,

- (i) $[Cr(NH_3)_4Cl_2]^+$

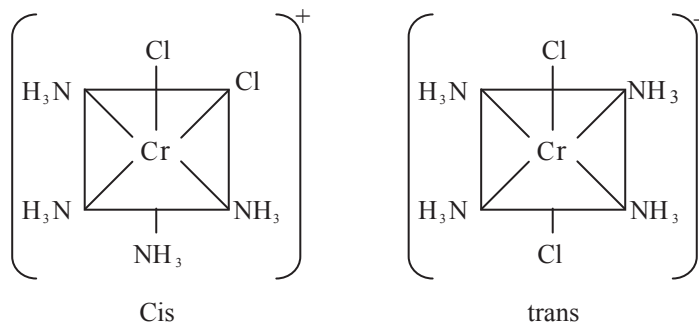
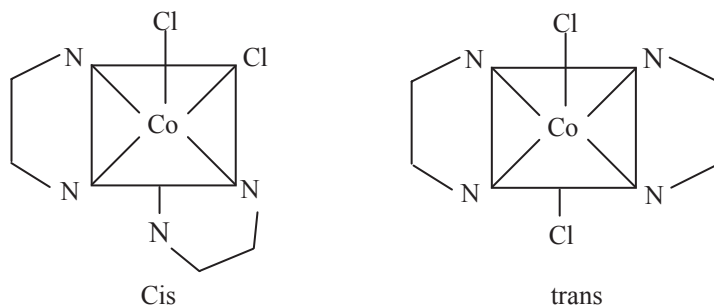
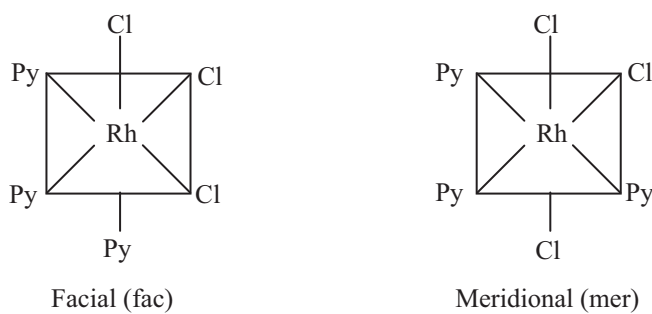


Figure 6.26

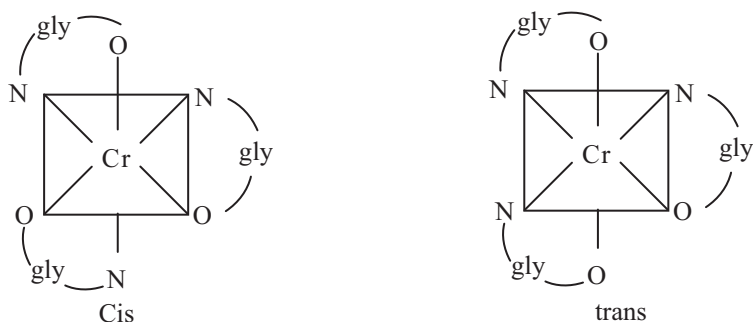
(ii) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ **Figure 6.27**

A few complexes of the type $[\text{MA}_3\text{X}_3]$ are also known. Example, $[\text{Rh Py}_3\text{Cl}_3]$

**Figure 6.28**

Largest numbers of geometrical isomers are found for complex of the type $[\text{M ABCDEF}]$ where each ligand is different. Example, $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)\text{Cl Br I}]$.

Unsymmetrical bidentate ligands also produce cis-trans isomers. Example, $[\text{Cr}(\text{gly})_3]$.

**Figure 6.29**

Optical isomerism

Optical isomers are molecules (or ions) which are not superimposable on their mirror images. Such species lack either a centre or a plane of symmetry. The most important difference is that each isomer rotates plane polarized light in opposite directions. The isomer which rotates plane polarized light right handed is called dextro rotatory (d) and that which rotates plane polarized light towards left is said lavo ratoatory (l). Because of this property, the isomers are said to be optically active.

Optical isomerism in CN 4

Four coordinated square planar complexes are very seldom optically active. In most cases the molecular plane is a plane of symmetry.

Four coordinated T_d – complexes are highly reactive, which makes separation of isomers extremely difficult. Some tetrahedral complexes containing two unsymmetrical bidentate ligands have been isolated. e.g., bis (benzoylacetonato) beryllium (II).

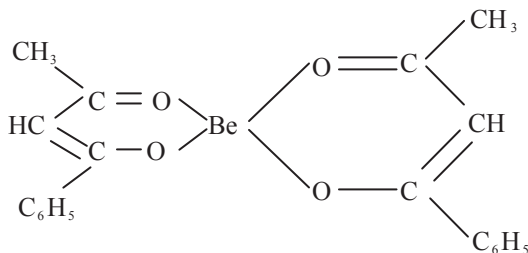
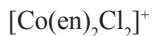
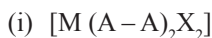


Figure 6.30

Unlike four coordinated complexes, six coordinated complexes give many optical isomers. The following types are common:



The cis-isomer of this complex forms non super imposable mirror images. The mirror images are optical isomers.

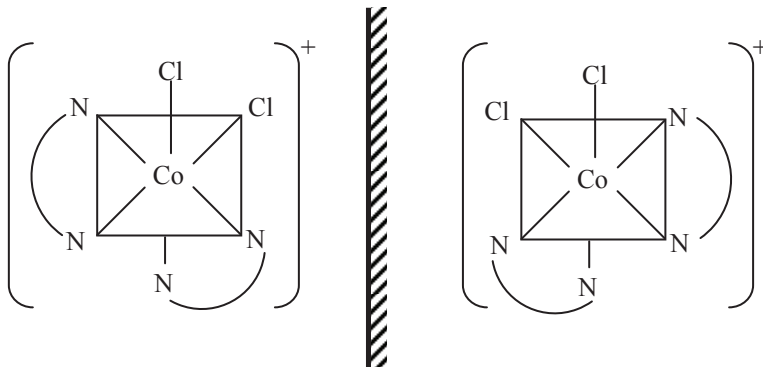


Figure 6.31

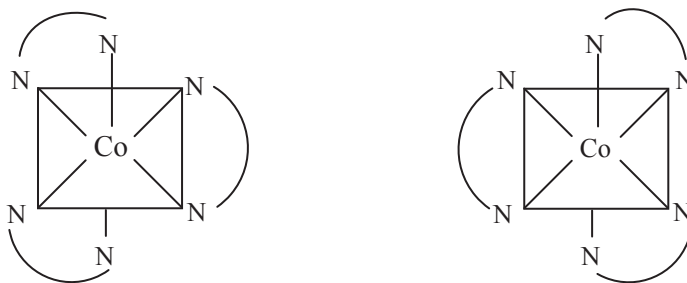
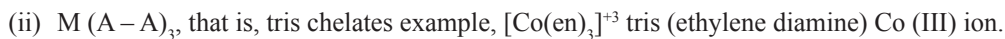


Figure 6.32

These structures can also be represented as

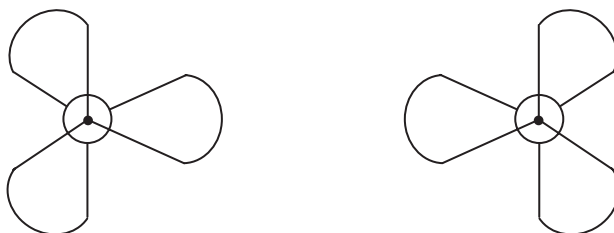


Figure 6.33

This looks like a ship's propeller. These are non-super imposable optical isomers.

(iii) $M(A-A)_2X_2$ Example,

$[Co(en)(NH_3)_2Cl_2]^+$ diammine ethylene diamine dichloro Co (III) ion

One of the isomers of this complex can exist in non identical mirror image forms. They are optical isomers

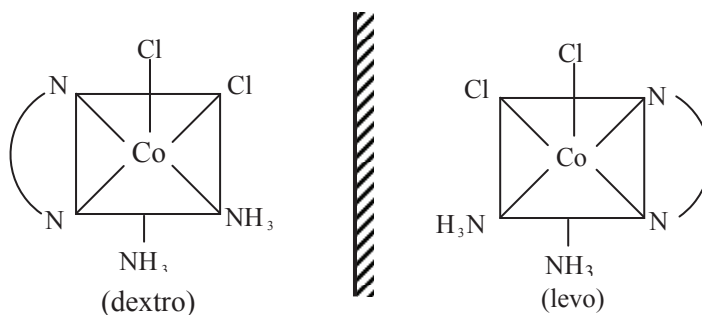


Figure 6.34

(iv) $[M(ABCDEF)]$ Example,

$[Pt(Py)NH_3NO_2ClBrI]$

Such complexes lack symmetry elements. Therefore, they are optically active and form optical isomers.

(v) Multidentate ligands can also form optical isomers. Example, $[Co(EDTA)]^-$

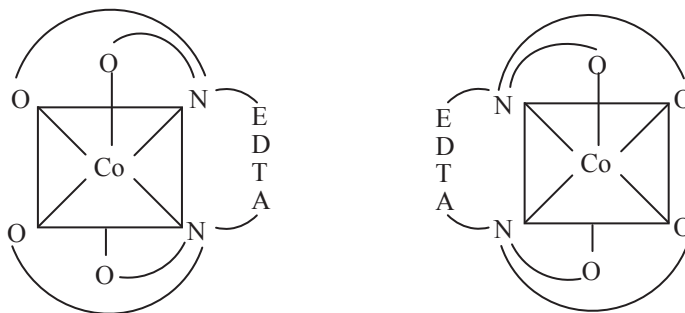


Figure 6.35

Preparations of complex compounds

Complex compounds are generally prepared by the following methods:

(i) Substitution reaction in aqueous solutions

This method involves a reaction between a metal salt in aq solution and a coordinating agent. Example aq. solution of CuSO_4 and excess NH_3 forms a Cu^{2+} ammine.



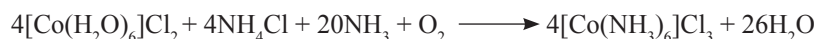
(ii) Substitution reactions in the absence of solvent

Direct reaction between anhydrous metal salt and liquid NH_3 produces metal amines. Example,



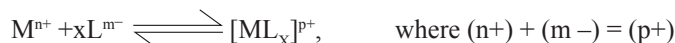
(iii) Redox reactions

Co(II) salt forms a Co(III) complex



Stability of complex compound in a solution

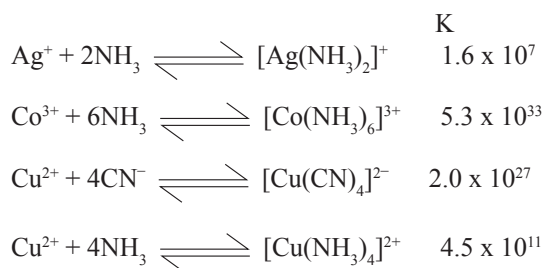
Complex formation can be seen as a Lewis acid–base reaction. The M^{n+} is Lewis acid and the ligands are Lewis bases. If the interaction between M^{n+} and the ligands is strong, the complex is thermodynamically stable. The reactions between M^{n+} and the ligands can be written as



The equilibrium constant k is stability constant and it is defined as

$$k = \frac{[\text{ML}_x]^{p+}}{[\text{M}^{n+}][\text{L}^{m-}]^x}$$

The numerical value of k gives an indication of thermodynamic stability. Some stability constants are given below:



The value of k for Cu^{2+} complexes with NH_3 and CN^- show that cyanocomplex is more stable than NH_3 complex.

Applicability of complex compounds

1. Uses of complexes in analytical chemistry

(a) Qualitative chemistry

Many ions are detected in salt analysis due to complex formation-

- (i) Fe^{3+} forms blue solution with $\text{K}_4[\text{Fe}(\text{CN})_6]$. The blue solution is due to a complex $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.
- (ii) NO_3^- is tested as brown ring compound. It also involves a complex. The complex is $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$. There are many such examples.

(b) Quantitative chemistry

- (i) Hardness of water can be determined using multidentate ligand EDTA.
- (ii) Ni can be estimated as $\text{Ni}(\text{Dmg})_2$ complex.

(c) Many complexes are involved in sustaining life processes, chlorophyll, Haemoglobin and many other metallo enzymes contain Cu, Zn, Cd, Mo etc.

(d) In electroplating industry

Many Ag and Au complexes are used in the process of electroplating.

(e) Medical application

Many complexes are used in chemotherapy, cyanocobalamine, cis-platine etc.

(f) Many complexes are used as catalysts.

Table 6.11

| Catalyst | Application |
|--|--|
| Ziegler – Natta $[(\text{C}_2\text{H}_5)_3\text{Al TiCl}_4]$ | Polymerization of ethene |
| Wilkinson $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ | Hydrogenation of alkenes |
| $[\text{C}_2\text{H}_4\text{PdCl}]_2$ | Wacker process (C_2H_4 to CH_3CHO , a cyclic process) |

Organometallic compounds

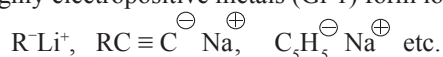
Substances having carbon–metal bonds are defined as organometallic compounds. For example, CH_3^-Li^+ , $(\text{C}_2\text{H}_5)_4\text{Pb}$, RMgX , R_2Hg etc.

Sodium methoxide ($\text{CH}_3\text{O}^-\text{Na}^+$) and sodium acetate $\text{CH}_3\text{COO}^-\text{Na}^+$, are not organometallic compounds as organic group is bound to Na through oxygen. The compounds of less metallic elements (metalloids) B, Si, Ge, Se, As etc. are also included in this category. The nature of C – M bond varies from ionic, $\text{HC}\equiv\text{C}^-\text{Na}^+$ (sodium acetylide) to covalent, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $(\text{Et})_2\text{Hg}$ etc.

Classification of organometallic compounds

(a) Ionic compounds

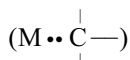
Highly electropositive metals (Gr 1) form ionic organo metallic compounds.



They are highly reactive. Sodium and Korganometallics are most reactive. Insoluble in non polar solvents. They inflame in air, react violently with water, CO₂ etc. organometallics containg stabilized carbanions (by delocalization) are relatively more stable, although still quite reactive e.g., (C₅H₅⁻)Ca⁺² and (C₆H₅)₃C⁻Na⁺.

(b) σ – bonded compounds

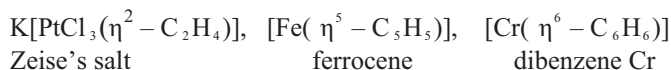
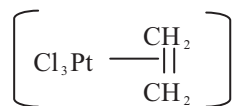
Less electropositive metals and non metals form such compounds. The metal is bound with the organic residue by a normal 2 – electron bond.



(C₂H₅)₂Zn, (C₂H₅)₄Sn, R₂Hg, (Et)₄Pb, (CH₃)₃SnCl, RMgX etc.

(c) π–bonded organometallics

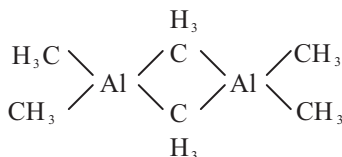
The π–electrons of alkenes, alkynes benzene or other aromatic systems can form complexes with transition metals. These are termed as π–complexes.



In π–bonded organometallics the number of carbon atoms bonded to the metal is indicated. It is done by using η (eta) (Greek letter) followed by a number at right upper side i.e., η², η⁵, η⁶ etc. Thus in [η² – C₂H₄PtCl₃]⁻, η² means that both the carbon atoms of C₂H₄ are bound to the metal. Similarly, (η⁶ – C₆H₆)₂Cr and (η⁵ – C₅H₅)₂Fe show that all six and five carbon atoms of C₆H₆ and C₅H₅⁻ are bound to Cr and Fe(II) respectively.

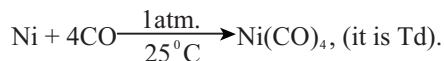
(d) Alkyls of metals

Such compounds are formed by B, Al etc. These compounds have bridging alkyl groups because there is electron deficiency like B₂H₆. For example, trimethyl aluminium actually exists as a dimer, with two methyle groups as bridging groups.



(e) Metal carbonyls

The transition metal carbon monoxide complexes are known as carbonyls. The M–C bond in carbonyls has both σ and π character. Such compounds Ni(CO)₄ and Fe(CO)₅ were first discovered by Mond (1890 – 1891).



Some more examples are

- (i) $M(CO)_6$, $M = Cr, Mo, W$
It is octahedral

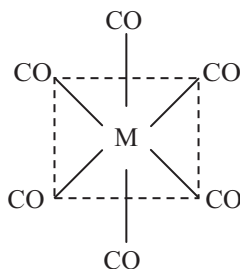


Figure 6.36

- (ii) $Fe(CO)_5$, (it is tpb)

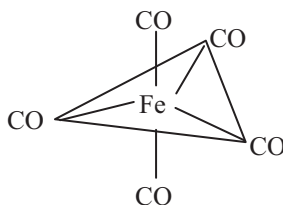


Figure 6.37

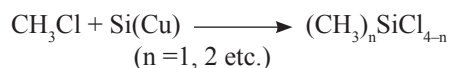
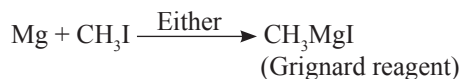
The formation of $Ni(CO)_4$ is used in the metallurgy of Ni. This carbonyl decomposes at higher temperature to produce pure metal and CO.

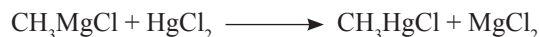


Preparation of organometallies

(a) Direct reaction of metals

The first organometallic was synthesized by Frankland (1845).



(b) Reaction of an organometallic reagent with metal halide

(c) Direct reaction between metal and metal alkyl

(d) Synthesis of π -complexes

(i) Zeise's salt: Ethylene reacts with $[\text{PtCl}_4]^{-2}$ in dil. HCl to produce Zeise's salt.



(ii) Benzene reacts with Cr vapour to give this complex



(iii) Cyclopentadienyl complexes

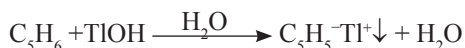
Ferrocene $[(\text{C}_5\text{H}_5)_2\text{Fe}]$



(Cyclopentadiene)



TIOH may also be used to generate C_5H_5^{-}


Bonding in organometallic compounds

Bonding in metal carbonyls is prototype for other organometallics. It involves two steps:

(a) Overlap of filled carbon σ orbital with empty orbital of the metal.

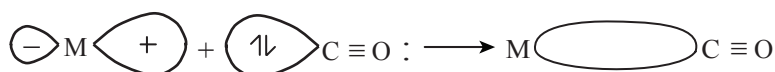


Figure 6.38

(b) A dative overlap of metal filled $d\pi$ orbital with empty π^* orbital of CO.

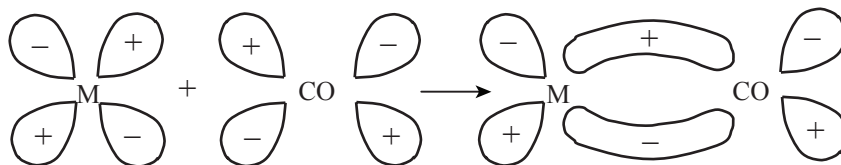


Figure 6.39

This bonding mechanism is termed synergic bonding. Here, CO behaves in the first step as a Lewis base, giving electron pair to vacant metal σ type orbital. This donation makes CO slightly positive. Therefore, in the second step of bonding it accepts metal $d\pi$ electrons easily. Thus the effects of σ bonding helps π bonding and vice versa.

Experiments show that in metal carbonyls, there is reduction in CO bond orders. It causes increase in carbon oxygen bond distance. The greater is the extent of $M - C$ back bonding, the larger is the increase in CO bond distance. Thus in isoelectronic species $Mn(CO)_6^+$, $Cr(CO)_6$ and $V(CO)_6^-$ the order of $dC - O$ found is $V(CO)_6^- > Cr(CO)_6 > Mn(CO)_6^+$.

Such ligands which form π bonds by use of their vacant π^* orbitals are known as π -acid ligands. Some more such ligands include CN^- , PPh_3 etc.

Bonding in alkene complexes

The bonding in alkene complexes involves two interdependent components:

- Overlap of the π -electron of the alkene with a σ type acceptor orbital on the metal atom.
- A back-bond due to flow of electrons from filled metal $d\pi$ orbitals into π^* orbital on the alkene.

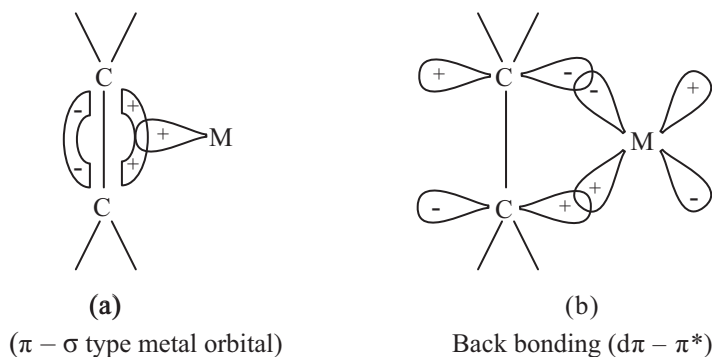


Figure 6.40

PRACTICE QUESTIONS

A. 1. Explain using VB model:

- $Fe(CN)_6^{4-}$ is diamagnetic but $[Fe(H_2O)_6]^{2+}$ has four unpaired es.
- $NiCl_4^{2-}$ is paramagnetic for 2 unpaired es but $Ni(CN)_4^{2-}$ is diamagnetic.

(c) Fe^{3+} has five unpaired es but the complex ion $Fe(CN)_6^{3-}$ shows Paramagnetism for one unpaired only.

2. Write IUPAC name of the following complexes.

- $[Co(NH_3)_6]Cl_2$

- (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$
- (c) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
- (d) $[\text{Cu}(\text{gly})_2]$
- (e) $\text{K}_3[\text{Fe}(\text{OX})_3]$
- (f) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
- (g) $\text{Na}_3[\text{Co}(\text{ONO})_6]$
- (h) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
- (i) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- (j) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$
3. Explain the following:
 - (a) $\text{Cu}(\text{NH}_3)_4^+$ is completely colourless but $\text{Cu}(\text{NH}_3)_4^{2+}$ is intensely blue.
 - (b) Cd^{+2} and S^{-2} are colourless when isolated i.e., in solution but solid CdS is intensely yellow.
 - (c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is found in two colours (violet and green).
4. For the complex ions $[\text{NiCl}_4]^{-2}$ (HS), $[\text{Ni}(\text{CO})_4]$ (LS), $\text{Fe}(\text{CN})_6^{3-}$ (LS), FeF_6^{3-} (HS), work out the following:
 - (a) Unpaired es in the d orbitals of the metal ions in the complex ions.
 - (b) Spin – only magnetic moment
 - (c) Hybridization of the metal ions.
5. Spin-only magnetic moments of the following complexes are as:

| | | |
|--|---|--------|
| $[\text{Cr}(\text{NH}_3)_6]^{3+}$ | ~ | 3.88BM |
| $[\text{Mn}(\text{CN})_6]^{4-}$ | ~ | 1.73BM |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | ~ | 5.10BM |
| $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ | ~ | 5.0BM |

Work out

 - (a) Unpaired es in the d orbitals of the metal ions in the complex
 - (b) Hybridization of the central metal ion.
6. Draw the possible isomers of the following:
 - (a) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 - (b) $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Cu}(\text{NH}_2 - \text{CH}_2 - \text{COO})_2]$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$
 - (c) $[\text{Pt}(\text{gly})_2]$ and write IUPAC names?
7. A complex of the type $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is known to be optically active. What information it gives about the structure of the complex?
8. Draw possible isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.
9. (a) Draw possible isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Cu}(\text{gly})_2]$.
(b) Indicate which isomers will have dipole moment and why?
10. Write down the formulae of the following complexes:
 - (a) Ammine chlorobis (ethylene diammine) cobalt (III) ion.
 - (b) Diammine tetrachloroplatinum (IV)
 - (c) Nitrosopentaque iron (II) sulphate.
 - (d) Dichlorobis (ethylene diamine) Cr (III) ion.
 - (e) Ethylene trichloro platinate (II) chloride.
11. (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless, explain.
(b) Write the formula of Wilkinson's catalyst and name it.
12. Two Co^{+3} complexes are made out of five ammonia molecules and one SO_4^{2-} ion or one Br^- ion (in CN = 6).
 - (a) Formulate them.
 - (b) What type of isomerism do they represent?
13. Ethylene diamine is a bidentate ligand denoted as 'en'. Which of the following can exist as optical isomer $[\text{Co}(\text{NH}_3)_4\text{en}]^{3+}$, cis- $[\text{Co}(\text{NH}_3)_2\text{en}_2]^{3+}$ and trans- $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$?
14. Solution of a $\text{Co}(\text{II})$ compound 'A' is used as a colourless ink. The write up is heated gently; the invisible writing becomes blue coloured compound B. Formulate A and B and write their IUPAC names.
15. What is a complex compound? How does it differ from a double salt?
16. The following aggregates behave as given below, formulate them as complex compounds.
 - (a) $\text{CoCl}_3 \cdot 4\text{NH}_3$ forms only one mole AgCl with AgNO_3 solution.

- (b) $\text{Co}(\text{NO}_3)_2 \cdot 5\text{NH}_3$ forms only one mole BaSO_4 with BaCl_2 solution.
- (c) $\text{Co}(\text{SO}_4)\text{Br} \cdot 5\text{NH}_3$ forms only one mole AgBr with AgNO_3 solution.
- (d) $\text{CoCl}_3 \cdot 3\text{NH}_3$ forms no any ppt with AgNO_3 solution.
17. What are the basis of Werner's coordinate theory? Write the postulates of the theory.
18. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ exists in violet and green forms. Write the structure of both the forms.
20. $[\text{FeF}_6]^{3-}$ is outer orbital but $[\text{Fe}(\text{CN})_6]^{3-}$ is inner orbital complex, explain.

B. True or False

State whether each of the following is true or false.

- The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$.
- The ground state electron configuration of Pd is $4d^{10}$.
- Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3d orbital of neutral atom.
- Both potassium ferrocyanide and potassium ferricyanide are diamagnetic.
- Copper has electronic configuration $3d^9 4s^2$.

C. Fill in the blanks

- The reaction between KMnO_4 and oxalic acid is catalysed by _____, which is known as _____.
- The IUPAC name of $\text{K}[\text{Ag}(\text{CN})_2]$ is _____.
- The IUPAC name of $\text{K}_4[\text{Fe}(\text{CN})_6]$ is _____.
- The IUPAC name of $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ is _____.
- The complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic. The state of hybridization of iron is _____.
- The complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic. The state of hybridization of iron is _____.
- The magnetic moment of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ would be _____ Bohr magneton.
- The type of magnetism exhibited by $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion is _____.
- The IUPAC name of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is _____.
- The IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ is _____.
- The IUPAC name of $\text{K}_3[\text{Cr}(\text{CN})_6]$ is _____.

OBJECTIVE-TYPE QUESTIONS

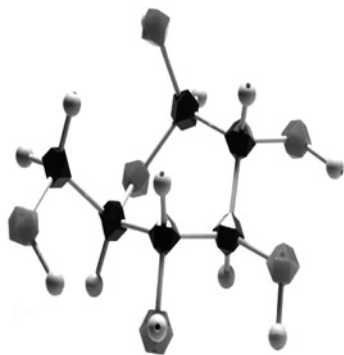
- Among the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by
 - $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$
 - $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- The aqueous solution of the following salts will be coloured in the case of (a) $\text{Zn}(\text{NO}_3)_2$
 - LiNO_3
 - $\text{Co}(\text{NO}_3)_2$
 - CrCl_3
- Among $\text{Ni}(\text{CO})_4$, $[\text{Ni}(\text{CN})_4]^{2-}$ and NiCl_4^{2-}
 - $\text{Ni}(\text{CO})_4$ and NiCl_4^{2-} are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic.
 - NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $\text{Ni}(\text{CO})_4$ paramagnetic.
 - $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and NiCl_4^{2-} is paramagnetic.
 - $\text{Ni}(\text{CO})_4$ is diamagnetic and NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic.
- Amongst the following ions, which one has the highest paramagnetism?
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- When excess of NH_4OH is added to the aqueous solution of CuSO_4 , the compound crystallized after the addition of alcohol is
 - $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$

- (b) $[\text{Cu}(\text{NH}_3)_4](\text{SO}_4)$
 (c) $[\text{Cu}(\text{NH}_3)_4](\text{SO}_4) \cdot \text{H}_2\text{O}$
 (d) $[\text{Cu}(\text{NH}_3)_4](\text{SO}_4) \cdot 2\text{H}_2\text{O}$
6. The IUPAC name $[\text{Ni}(\text{CO})_4]$ is
 (a) tetracarbonylnickel (II)
 (b) tetracarbonylnickel (0)
 (c) tetracarbonylnickelate (II)
 (d) tetracarbonylnickelate (0)
7. Chlorophyll is a/an
 (a) magnesium complex
 (b) cobalt complex
 (c) iron complex
 (d) chromium complex
8. Haemoglobin is a/an
 (a) iron (II) complex
 (b) cobalt (III) complex
 (c) magnesium (II) complex
 (d) chromium (III) complex
9. Vitamin B_{12} is a complex of
 (a) Cobalt (II) ion
 (b) Cobalt (III) ion
 (c) Chromium (II) ion
 (d) Chromium (II) ion
10. The number of ions produced by the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is
 (a) 2 (b) 3
 (c) 4 (d) 6
11. The IUPAC name of $[\text{Ni}(\text{CN})_4]^{2-}$ is
 (a) tetracyanonickel (II) ion
 (b) tetracyanonickel (0) ion
 (c) tetracyanonickelate (II)
 (d) tetracyanonicklate (0) ion
12. The IUPAC name of $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ is
 (a) potassium (I) hexanitrocobaltate (II)
 (b) potassium (I) hexanitrocobaltate (III)
 (c) potassium hexanitrocobalt (0)
 (d) potassium hexanitrocobaltate (III)
13. The IUPAC name of $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$ is
 (a) tetramminechloronitroplatinum (II) sulphate
 (b) tetramminechloror itroplatinum (IV) sulphate
 (c) chlorotetramminenitroplatinum (IV) sulphate
 (d) chloronitrotetrammineplatinum (IV) sulphate
14. Which of the following facts about the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is wrong?
 (a) The complex involves d^2sp^3 hybridization and is octahedral in shape.
 (b) The complex is paramagnetic.
 (c) The complex is diamagnetic.
 (d) The complexes give white precipitate with silver nitrate.
15. Which of the following statements about the complex $[\text{CoF}_6]^{3-}$ which is paramagnetic in nature is correct
 (a) Cobalt involves d^2sp^3 hybridization
 (b) Cobalt involves sp^3d^2 hybridization
 (c) F is in zero oxidation state
 (d) Co is in +2 oxidation state
16. Which of the following statements is not correct?
 (a) The complex $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in the state of hybridization of nickel.
 (b) The complex $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in the magnetic properties.
 (c) The complex $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in the geometry.
 (d) The complex $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in the primary valencies of nickel.
17. Which compound is formed when excess KCN is added to aqueous solution of copper sulphate?
 (a) $\text{Cu}(\text{CN})_2$
 (b) $\text{K}_2[\text{Cu}(\text{CN})_4]$
 (c) $\text{K}[\text{Cu}(\text{CN})_2]$
 (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
18. In nitroprusside ion, the iron and NO exists as Fe^{II} and NO^+ rather than Fe^{III} and NO . These forms can be differentiated by
 (a) Estimating the concentration of iron
 (b) Measuring the concentration of CN
 (c) Measuring the solid state magnetic moment
 (d) Thermally decomposing the compound
19. Identify the complex which are expected to be coloured.
 (a) $\text{Ti}(\text{NO}_3)_4$

- (b) $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$
(c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
(d) $[\text{K}_3(\text{VF}_6)]$
20. The geometry of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ are
(a) Both square planar
(b) Tetrahedral and square planar, respectively
(c) Both tetrahedral
(d) Square planar and tetrahedral, respectively

ANSWERS

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (c) | 3. (c) | 4. (b) | 5. (d) | 6. (b) | 7. (a) | 8. (a) | 9. (b) | 10. (a) |
| 11. (b) | 12. (d) | 13. (b) | 14. (c) | 15. (b) | 16. (d) | 17. (d) | 18. (c) | 19. (c) | 20. (c) |



Abundance and Metallurgy

CHEMICAL ELEMENTS

Chemical elements are distributed in the earth's crust, in the universe and in the oceans. The average relative amount of an element in any natural system (earth, stars, solar system, oceans etc.) is called its abundance.

Chemical elements in the Earth's Crust

There are only 16 most abundant elements in the earth's crust. Out of these 16, only 8 are main elements. They are O, Si, Al, Fe, Ca, Na, K and Mg. They constitute about 98% by weight. Oxygen and Si are most abundant and form about 75% of the crust.

% of main elements

| Elements | O | Si | Al | Fe | Ca | Na | K | Mg |
|------------|------|------|-----|-----|-----|-----|-----|-----|
| % (by wt.) | 49.5 | 25.7 | 7.5 | 4.7 | 3.4 | 2.6 | 2.4 | 1.9 |

The remaining 8 elements are less than 1% each.

Elements less than 1%

| Elements | H | Ti | Cl | P | Mn | C | S | Ba |
|------------|-----|-----|-----|-----|------|------|------|------|
| % (by wt.) | 0.9 | 0.6 | 0.2 | 0.1 | 0.09 | 0.08 | 0.06 | 0.04 |

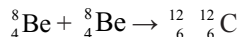
The transuranic elements and short lived Tc, Pm, At, and Fr are not present in the earth's crust.

Cosmic abundance of elements

The amount of elements in the universe is cosmic abundance. Available data shows that;

- The abundance does not vary uniformly with increasing atomic number.
- Hydrogen and He are most abundant. It is believed that three fourth of cosmic matter is H and He.
- The relative abundance of elements with even number of protons is higher than that having odd number of protons (it is similar to abundance on earth's crust).
- Iron is found in higher concentration. It is due to its very high nuclear binding energy (~8 Mev per nucleon).

- (v) Low abundance of Li, Be, B may be due to their ability to react with α -particles producing relatively large atoms.



Now-a-days, automatic space laboratories are in use to study space chemistry. It is studied mainly by means of spectrographic analysis. The study of lunar soil, in particular, has been the basis of such a development.

Abundance in oceans

Oceans are the great storehouse of chemicals and chemical elements. Sea water is a leading source of bromine. Elements like Cl, Br, Na, Mg are obtained from sea water. Natural gas, oil, coal, gold, S, Sn are also extracted from seas. The ocean floor is richer in copper, Ni, Zn. Sea weeds are an important source of agar-agar and iodine.

Occurrence of Metals

Elements may occur in free and combined states. It depends upon their nature. Gold, Pt, Cu, Hg, Pd etc., are found in native state because of their lesser chemical reactivities. However, most metals are reactive and are found in combined forms. It is due to the fact that universe is par excellence a chemical laboratory. Soluble metal compounds are mainly found in oceans. The important natural metal compounds are oxides, sulphides, chlorides, carbonates, sulphates, silicates, phosphates etc. Ores of some common metals are given below:

Table 7.1

| Ore type | Examples |
|------------|--|
| Native | Au, Pt, Ag, Cu, Hg, Pd |
| Oxides | Al_2O_3 , TiO_2 , MnO_2 , Fe_2O_3 , Fe_3O_4 , Cu_2O , SnO_2 , FeCr_2O_4 , WO_3 |
| Carbonates | CaCO_3 , FeCO_3 , PbCO_3 , BaCO_3 , SrCO_3 , ZnCO_3 , MnCO_3 , CaCO_3 , MgCO_3 , CuCO_3 , $\text{Cu}(\text{OH})_2$ |
| Halides | NaCl , KCl , AgCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NaCl and MgCl_2 (seawater) |
| Sulphides | Ag_2S , Cu_2S , PbS , ZnS , HgS , FeS , NiS , MoS_2 |
| Sulphates | BaSO_4 , SrSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, PbSO_4 , $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ |
| Silicates | $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, Zn_2SiO_4 , NiSiO_3 , MgSiO_3 |
| Phosphates | LaPO_4 , CePO_4 , $\text{Th}_3(\text{PO}_4)_2$, $\text{LiF} \cdot \text{AlPO}_4$ |

(Ores are minerals from which metals can profitably be extracted).

Extraction of elements

Isolation of an element from its natural source is known as extraction. Metals are present in their positive oxidation states, that is, in oxidized form. So, they are isolated by reduction process. Non-metals are found in oxidized and reduced forms both. Therefore, they are isolated by reduction as well as oxidation methods.

METALLURGY

The process of extraction of a pure metal from its ore is called metallurgy. It is a three-step process:

- (i) Concentration of the ore.
- (ii) Isolation of metal from the concentrated ore.
- (iii) Purification of the isolated metal.

Metallurgy, on the basis of reaction conditions, can be classified into three groups:

Electro-metallurgy

In this method, fused ore or a suitable compound of the metal is electrolysed to get the metal. Highly electropositive metals are obtained by this method. Thus, group 1, 2 metals and Al is isolated by this method.

Note: Above metals cannot be isolated by C reduction method, as they are stronger reducing agents than C.

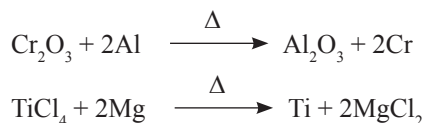
Table 7.2

| Metal | Compound used as electrolyte |
|-------|--|
| Na | NaCl |
| K | KOH |
| Mg | MgCl ₂ |
| Ca | CaCl ₂ |
| Al | (Al ₂ O ₃ + Na ₃ AlF ₆) |

Thermometallurgy

In this method concentrated ore is reduced to get the metal. Common reducing agents used are H₂, C, metals (Al, Mg) etc. Less electropositive metals are obtained by reduction of their oxides by C. For example, Fe, Zn, Sn, Pb etc are obtained by this method.

Aluminium, Mg etc., are used as reducing agents for transition metals,



Transition metals form stable hydride and carbides with H and C. Therefore; they are not isolated by C and H reduction method.

Hydrometallurgy

It is also called wet process. In this method, ore or the native metal is brought into solution by a reagent. From this solution metals are recovered. Ag and Au are isolated by this method.

Terms used in metallurgical process

Minerals

Solid compounds of metals which are found in nature are called minerals. Thus, NaCl, CaCO₃, ZnS, Cu₂S, FeS₂, Fe₂O₃ etc., are minerals.

Ore

Ore is that mineral from which a metal can be isolated easily and economically. Therefore, all ores are minerals but all minerals are not ores.

Table 7.3

| Metals | Minerals | Ores |
|--------|--|---|
| Na | Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ Chile – salt petre NaNO_2 | Rock salt, NaCl (Major source is sea water). |
| K | Carnalite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ Felspar $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ | Sylvine KCl |
| Mg | Asbestos CaSiO_3 3MgSiO_3 | Magnesite MgCO_3 Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$ Karnalite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sea water is also a source) |
| Ca | Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$ Cypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | Lime stone CaCO_3 |
| Al | Cryolite NaAlF_6 | Bauxite $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ |
| Fe | Iron pyrite FeS_2 | Haematite Fe_2O_3 Magnetite Fe_3O_4 |
| Cr | X | Chromate FeCr_2O_4 |
| Mn | X | Pyrolusite MnO_2 |
| Zn | X | Zinc blende ZnS Zincite ZnO Calamine ZnCO_3 |
| Ag | X | Silver glance Ag_2S Horn silver AgCl |
| Au | X | Native gold |
| Hg | X | Cinnabar HgS |
| Sn | X | Cassiterite (Tin stone) SnO_2 |
| Pb | X | Galena Pbs |

Gangue (or Matrix)

Ores contain impurities. Many of the impurities are present in the phase of the ore. They are known as gangue. Thus, a gangue is that impurity which is present in the phase of the ore.

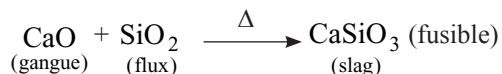
Silica (SiO_2) in iron ores (Fe_2O_3 and Fe_3O_4), Fe in Cu ore (CuFeS_2), is gangue.

Flux

A chemical substance, which is used to remove gangue from an ore, is called flux. A flux can be acidic or basic. Acidic flux is used to remove basic gangue and basic one to remove acidic gangue. Flux and gangue react to form slag.

Slag

Slag is a substance, which is formed when a flux reacts with gangue. It is fusible and is formed at high temperature during the process of metallurgy.



METALLURGY

Metallurgy is a three-step process:

- (i) Concentration of ore.
- (ii) Concentrated ore to metal.
- (iii) Purification of isolated metal.

Table 7.4

| Flux | Gangue | Slag |
|------------------|------------------|--------------------|
| CaO | SiO ₂ | CaSiO ₃ |
| SiO ₂ | FeO | FeSiO ₃ |

Concentration of ore

Ores contain impurities. The process of removing impurities to get actual ore material is called ‘Concentration of ore’. Ores contain two types of impurities:

- (a) One that is not present in the phase of the ore.
- (b) Those which are present in the phase of the ore.

The first type of impurities are removed by physical methods and the second type by chemical methods.

Physical methods of concentration of ore

Gravity separation

This method is used when ore is heavier than the impurities. Finely powdered ore is washed with an upward stream of running water. Impurities are washed away and ore particles settle at the bottom. Hematite (Fe₂O₃), Cassiterite (SnO₂) etc., are concentrated by this method.

Froth floatation method

This method is employed, when the ore is lighter than the impurities. It is generally used for sulphide ores – Zinc blende (ZnS), Copper pyrite (CuFeS₂), Galena (PbS), Cinnabar (HgS) etc. This process is based on the principle that

- (a) Ore is wetted by oils.
- (b) Impurities by water.

Finely powdered ore is mixed with water, pine oil and fatty acid (collector) and cresols + aniline (froth stabilizers). Then agitated by air. Froth is formed which carries ore with it and wetted impurities sink to the bottom. The froth is skimmed off, acidified to break up the froth. Ore is filtered and dried.

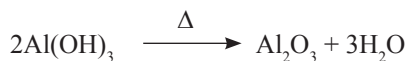
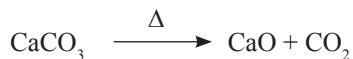
Magnetic separation

It is used when either of the two ore or impurities is magnetic. The powdered ore is carried on a travelling band over a magnetic roller. Magnetic and non-magnetic materials form separated piles. Magnetite (Fe₃O₄), Pyrolusite (MnO₂) and Chromite (FeCr₂O₄) are concentrated by this method. It is also useful to separate W-ore from SnO₂.

Chemical methods of concentration**Calcinations**

Strong heating of ore below its m.p. is called calcinations. At this stage

- (i) Volatile impurities are removed (S, As, Sb etc.).
- (ii) Carbonates and hydroxides are decomposed to metal oxides.



Chemical reactions other than the above do not take place. Calcination is generally done in reverberatory furnace.

Roasting

Heating of the ore in a regular supply of air below the m.p. of the metal is known as roasting. It is usually applied to sulphide ores. Chemical reactions do take place such as:

- (i) S, As, Sb etc are removed as oxides.
- (ii) Sulphide ores changes to oxides, sometimes to sulphate also.



- (iii) In some cases sulphide itself acts as reducing agent producing metal, (e.g., Cu and Pb ores).



- (iv) HgS converts to metallic Hg.



Roasting of sulphide ores is an essential requirement. It is because ΔG of most metal sulphides are greater than those for H_2S and CS_2 , Carbon disulphide and H_2S are endoergic compounds. Therefore, neither H nor C are suitable reducing agents for metal sulphides.

However, reduction of ZnO by C at high temperature is energetically favourable, as in seen below:



Thus, for



$$\Delta G = -439 - (-377) = -62\text{kJ}$$

Therefore, at higher temperature, the reduction of ZnO by C is possible, as ΔG is now negative (−62kJ)

Smelting

Calcined and roasted ore is employed for smelting. It is performed in blast furnace. Heating of concentrated ore at high temperature ($> \text{mp}$ of metal) with a flux and a reducing agent (coke) is called smelting.

Chemical reactions do take place. Gangue is removed as slag on reaction with flux. Metal may or may not be isolated; Fe is recovered in blast furnace but not the Cu.

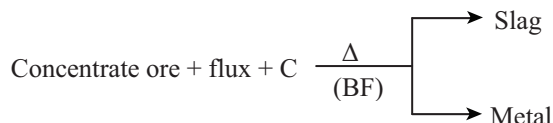


Figure 7.1

Leaching

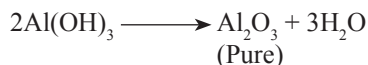
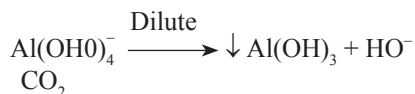
This process takes place in solution. The ore is brought into solution by a suitable reagent. Some examples are

1. Bayer's process

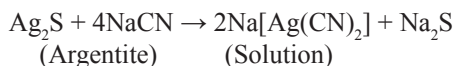
Pure Al_2O_3 is obtained from bauxite. Leaching agent is concentrated solution of NaOH, which dissolves Al_2O_3 of bauxite leaving behind impurities. From solution pure Al_2O_3 is recovered.



(Bauxite)



2. Ag and Au ores are concentrated by using NaCN or KCN as leaching agent in the presence of air.



Ag is then isolated by reacting the solution with more reactive metal like Zn or Fe etc.

Isolation of metal from concentrated ore

Chemical methods of ore concentration produce metal oxide. It has metal in positive oxidation state (M^{+n}). Metals are, therefore, isolated by reduction. Reducing agent and mode of reaction is selected considering nature of the metal. Various reduction processes used are

- (i) Thermal reduction (chemical reduction)
- (ii) Auto reduction
- (iii) Electrolytic reduction
- (iv) Displacement of a less reactive metal by more reactive metal in solution (i.e., wet metallurgy).

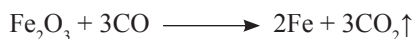
Thermal (or chemical reduction)

In this method metal oxides are reduced to metal. Reducing agents generally used are C, H metals (Al, Mg, Na) etc.

Reducing metal oxides is energetically favourable as free energy of formation of CO_2 , H_2O and Al or Mg oxides is higher than metal oxides. However, reducing metal sulphide is not profitable as formation constants for CS_2 and H_2S is low (CS_2 an endothermic compound).

(a) C as reducing agent

Zinc, Fe, Sn, Pb, Cd etc are obtained by reduction of their oxides with C. In thermal condition C may change to CO which is also a reducing agent.



Ellingham Diagram

(b) H as reducing agent

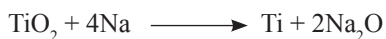
H_2 is highly inflammable. So its use as reducing agent is limited. Mo and W are obtained by H – reduction method.

**(c) Metals as reducing agents**

Carbon and H are not suitable for transition metal isolation as both form stable carbide and hydride (interstitial) with transition metals. Metals like Na, Mg, Al are used as reducing agent. Chromium and Mn are obtained by reduction of their oxides with Al.



These reactions are highly exothermic. Therefore, reactions proceed on their own temperature. This method is known as aluminothermic process or Gold Schmidt thermite process (for motion constant of Al_2O_3 is highest among metal oxides). Titanium is obtained by reducing TiO_2 with Na or Mg.

**Auto reduction**

In a few cases reducing agent is not required. Redox reaction during roasting produces the metal. In case of Cu metallurgy, Cu_2O obtained by partial oxidation of Cu_2S reacts with Cu_2S to produce Cu.



Here, sulphide ion is reducing agent.

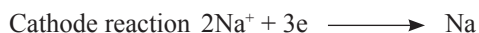
Pb is also obtained by self-reduction.



Electrolytic method of reduction

Highly electropositive metals of group 1, 2 and Al are stronger reducing agents than either C or H. Therefore, they are not obtained by C and H reduction methods. Such metals are obtained by electrolytic reduction method.

Na, Mg Ca etc., are obtained by electrolysis of their fused chlorides. Al is isolated by electrolysis of fused ($\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6$).



Displacement of one metal by the other

A more reactive metal displaces a less reactive metal from its compound. For example, Ag and Au are displaced from their cyano complexes by Zn.



Purification of isolated metals

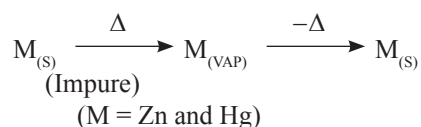
Metallurgical processes may not produce pure metals. Therefore, metals obtained are further purified. It all depends on the nature of the metal. Some methods used are:

(i) Liquation

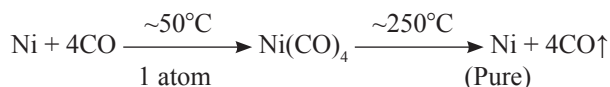
Low melting metals are purified by this method. For example, Sn and Pb. Liquid metal is allowed to flow on a slopping surface. Pure liquid metal slides down leaving behind higher melting impurities.

(ii) Distillation method

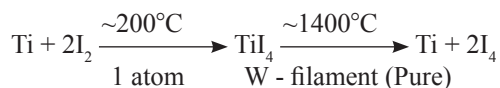
Metals having low boiling points are purified by this method. Zinc and Hg are purified by distillation method.



- (i) Alkali metals, alkaline earth metals and Al are stronger reducing agents than H, C. Therefore, these metals are obtained by electrolytic reduction method.
- (ii) Fe, Zn, Sn are obtained by carbon reduction method.
- (iii) Lead and Cu are obtained by self-reduction method.
- (iv) Hg is obtained by decomposition of HgO formed during roasting of HgS.
- (v) Ag and Au are obtained by wet process. In this method cyano complexes of Ag and Au $[M(CN)_2]^-$ are reduced by more active metals like Zn etc.
- (vi) Transition metals are obtained by special methods such as:
 - (a) Ni by Mond's process



- (b) Ti by Van Arkel – de Boer method



- (c) Chromium is obtained by reduction with Al, the thermite process or alumino thermic reduction (Gold schmidt's alumino – thermic process).



This reaction is favourable as oxidation of Al to Al_2O_3 liberates a large amount of energy 1675KJ/mol.

Sodium (Na) (Latin Name: Natrum)

Source

Seawater is major source, contains 2.6 to 2.9% NaCl.

Chile salt petre NaNO_3 (Chile and Peru)

Various silicates and alumino silicates also contain Na.

Manufacturing

Sir Humphry Davy (1807) first isolated Na from NaOH.

Sodium is very strong reducing agent ($\text{Na}_{(s)} \longrightarrow \text{Na}_{(aq)}^+ + e$, $E^\circ = 2.71\text{V}$). Therefore, it is not obtained by chemical reduction methods with C, H_2 , Mg, Al etc. It is also not obtained by electrolysis of aq. solution of its compounds. It is obtained by electrolytic reduction of either NaCl or NaOH:

(a) Down's process (1924)

In this method sodium is produced by electrolysis of fused NaCl. The mp. of NaCl is high (83°C). Therefore, it is mixed with CaCl_2 (NaCl 40% and CaCl_2 60%). Impurity lowers mp. The mp of the mixture (NaCl + CaCl_2) is 600°C . The cell used is the Down's cell. It consists of a circular steel cell lined with firebrick.

Anode \longrightarrow Carbon

Cathode \longrightarrow Iron

Cathode and anode are separated by iron screen to check mixing of Na and Cl₂.



Cathode reaction $\text{Na}^+ + e \longrightarrow \text{Na}$

Anode reaction $\text{Cl}^- \longrightarrow \frac{1}{2} \text{Cl}_2 + e$

Chlorine (Cl₂) is a valuable by product of this process.

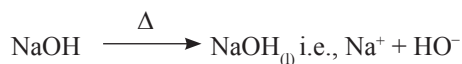
(a) Castner's process

In this method Na is obtained by electrolysis of fused NaOH.

Cathode \longrightarrow Iron

Anode \longrightarrow Ni

Cathode and anode are separated by iron gauge, to check reaction between Na and O₂ produced in electrolysis.



Cathode reaction $\text{Na}^+ + e \longrightarrow \text{Na}$

Anode reaction $2\text{HO}^- \longrightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e$

Uses

- (i) As a reducing agent [Na + alcohol or Na(Hg) + alcohol].
- (ii) In the extraction of some metals



- (iii) Liquid Na or its alloy with K, as a coolant in nuclear power plants. It is because liquid Na is an excellent heat conductor. [A Na – K alloy with 77.2%K has a mp of –12.3°C].
- (iv) In discharge (sodium vapour) lamps.
- (v) Na is also used in detection of nitrogen in organic compound (Lassaigne's test).
- (vi) In Dyes, drugs and perfume industry.

Magnesium

Davy (1808) was first to isolate impure Mg. Later Bussy (1829) obtained pure Mg by decomposition of anhydrous MgCl₂ with K.



Source

It is widely distributed, in rocks, spring and seawater. Many silicates also contain Mg.

Common ores

| | |
|------------|--|
| Magnesite | MgCO ₃ |
| Dolomite | MgCO ₃ ·CaCO ₃ |
| Carnalite | KCl·MgCl ₂ ·6H ₂ O |
| Epsom salt | MgSO ₄ ·7H ₂ O |

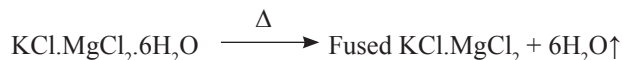
Alloy – Duralumin - $\text{Al} + \underset{4\%}{\text{Cu}} + \underset{.5\%}{\text{Mg}} + \underset{0.25-1\%}{\text{Mn}} + \text{low Fe Si}$

Seawater contains Mg as MgCl_2 and MgBr_2 . Mg is an important constituent of Chlorophyll, the green plant pigment. Magnesium is mostly extracted from carnalite.

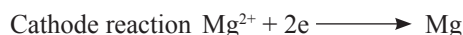
Magnesium is a strong reducing agent. Therefore, it is not obtained by chemical reduction. It is obtained by electrolytic reduction of fused MgCl_2 .

Mg from carnalite

Fused carnalite on electrolysis gives Mg.



Fused salts contain ions, K^+ , Mg^{2+} and Cl^- .



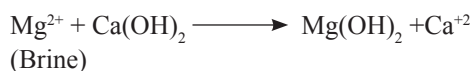
Potassium (K) is also produced at cathode. But it reacts with MgCl_2 to produce Mg and again converted into K^+ .



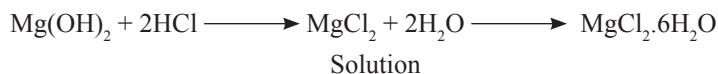
Mg from Seawater: Dow process

Seawater contains Mg as soluble MgCl_2 and MgBr_2 . Steps in the extraction:

(i) Seawater (brine) is treated with Ca(OH)_2 , the slaked lime. It precipitates Mg(OH)_2 .



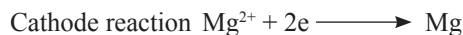
(ii) Precipitate is converted to MgCl_2 when dissolved in dil. HCl, and crystallized.



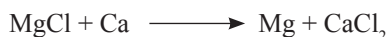
(iii) Preparation of fused MgCl_2

Hydrated magnesium chloride is partly dehydrated by passing dry HCl gas over it. Partially dehydrated $\text{MgCl}_2.x\text{H}_2\text{O}$ ($x < 6$) thus obtained is added to a mixture of fused NaCl and CaCl_2 . In this way anhydrous fused MgCl_2 is produced.

(iv) The fused mixture MgCl_2 , NaCl and CaCl_2 is electrolyzed to get Mg.



Any Na or Ca produced during electrolysis reacts with MgCl_2 to form Mg.



It is due to the fact that Na and Ca are more reactive than Mg.

Mg from Magnesite (MgCO_3)

Magnesite when heated with CaO, MgO is formed. Magnesium oxide is reduced by C to Mg.



(This reaction takes place easily because CaO is more basic than MgO).



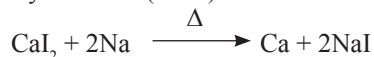
Magnesium can also be produced by reducing MgCl_2 with Na or K.

**Uses**

- (i) Mainly for light weight structural alloys
 - (a) Manelium (Al + Mg) aircraft, balances piston of motor engine.
 - (b) Duralumin (Cu + Al + Mg), aircrafts.
 - (c) Elektron Mg (~90%) + Cu + Zn + Mn + Si.
- (ii) As reducing agent in the metallurgy of Be, Ti and Zr.
- (iii) Mg powder in flash powders and bulb.
- (iv) To prepare Grignard reagent R-Mg-X .
- (v) As a laboratory reagent

Calcium (Ca)

Calcium is third most abundant of all metals. Davy (1808) first isolated impure Ca. The pure metal was prepared by Moissan (1898) as

**Ores**

| | |
|--------------|---|
| Lime stone | CaCO_3 |
| Gypsum | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| Fluorspar | CaF_2 |
| Phosphorite | $\text{Ca}_3(\text{PO}_4)_2$ |
| Lime felspar | $\text{CaAl}_2\text{Si}_2\text{O}_8$ |
| Anhydrite | CaSO_4 |

In India, Ca sources are:

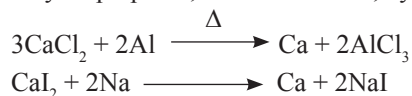
- Marble (CaCO_3) : Madras, Madhya Pradesh, Punjab and Rajasthan.
- Lime stone (CaCO_3) : Madhya Pradesh, Punjab.
- Fluorspar (CaF_2) : Jabalpur (M.P.) and Rajasthan.
- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): Large quantities are found in Bikaner and Jodhpur of Rajasthan.

Metallurgy

Calcium is a strong reducing agent. Therefore, it is neither obtained by chemical reduction method nor by electrolysis of its aqueous salt solution. It is manufactured by electrolysis of fused CaCl_2 .

Small-scale preparation

Calcium may be prepared, on a small scale, by reducing Ca – salts with Al or Na.

**Preperation**

On a large scale Ca is obtained by electrolysis of fused anhydrous CaCl_2 . Major source of Ca is carbonate ore, the lime stone CaCO_3 . Steps are

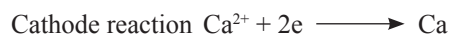
- (i) $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \uparrow\text{CO}_2$
- (ii) $\text{CaO} + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
- (iii) $\text{CaCl}_2 \xrightarrow{\text{Crystallization}} \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
- (iv) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{CaCl}_2 + 6\text{H}_2\text{O}\uparrow$
- (v) $\text{CaCl}_2 \xrightarrow{\text{Electrolysis}} \text{Ca (at cathode)}$

Electrolyte \rightarrow Fused anhydrous $\text{CaCl}_2 + \text{CaF}_2$, CaF_2 is mixed to lower mp of CaCl_2 .

Cathode \rightarrow It is a water – cooled iron rod which can be with drawn on need.

Anode \rightarrow Graphite

Cell \rightarrow Steel – cell with graphite wall linings which act as an anode.

**Note**

- (a) CaO is a refractory substance. It does not melt. So, Ca cannot be obtained from CaO .
- (b) Unlike NaOH and KOH , Ca(OH)_2 can not also be used to obtain Ca as Ca(OH)_2 on heating converts into CaO .
- (c) $\text{CaCl}_{2(aq)}$ gives Ca(OH)_2 and Cl_2 on electrolysis.
- (d) CaO cannot be reduced by C or H_2 as Ca is stronger reducing agent.

Uses

- (a) As reducing agent.
- (b) As a ‘getter’ for removing last traces of air (N_2 , O_2 etc.) in thermionic valves.
- (c) As a dehydrating agent (for organic compounds like alcohol).

Aluminium (Al)

Apart from oxygen and silicon, Al is most abundant and widely distributed element in the earth’s crust.

The industrial method of production of Al was developed by Hall (1886, US) and Herroult (Europe).

Ores

Bauxite (Hydrated aluminium oxides) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

Feldspar : KAlSi_3O_8

Mica : $\text{KAlSi}_3\text{O}_{10}(\text{OH})_2$

Cryolite : Na_3AlF_6

Mica is found in Jharkhand, Orissa, Madhya Pradesh, Maharastra, Tamil Nadu and Jammu and Kashmir. India is the largest supplier of mica.

Aluminium is extracted from bauxite. It involves two stages:

- (i) Production of pure alumina (Al_2O_3) from bauxite.
- (ii) Electrolysis of Al_2O_3 dissolved in cryolite to obtain Al.

Bauxite contains Fe_2O_3 and SiO_2 as impurities. Therefore, production of pure alumina from bauxite depends on amount of impurity (i.e., Fe_2O_3 or SiO_2). Different methods are used for this purpose. They are

| | |
|----------------------|--|
| (a) Baeyer's process | These are used when Fe_2O_3 impurity is present in large amount. |
| (b) Hall's process | |
| (c) Serpek's process | It is used when SiO_2 is present in large amount. |

Bauxite $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (Fe_2O_3 and SiO_2)

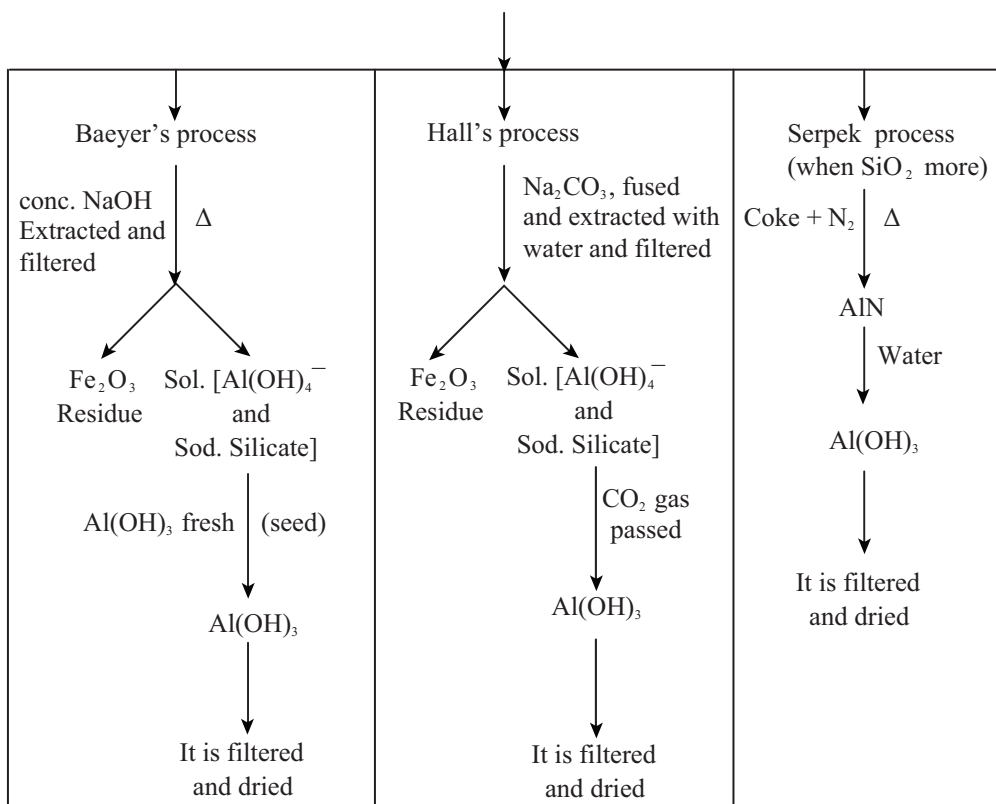
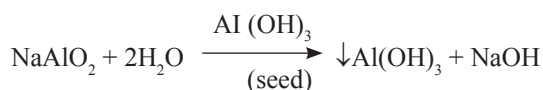
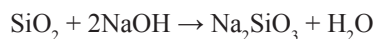
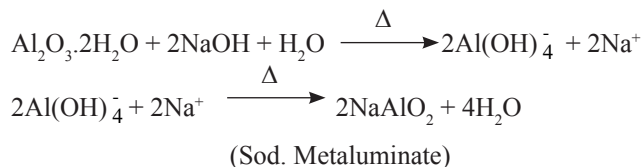
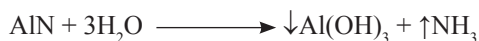


Figure 7.2

Note

- (i) Fe_2O_3 is not amphoteric, so it does not react with NaOH and Na_2CO_3
 (ii) Al_2O_3 amphoteric and SiO_2 acidic, so reacts with NaOH and Na_2CO_3 .

Reactions in Baeyer's process**Reactions in Hall's process****Reactions in Serpek's process**

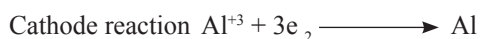
Aluminium hydroxides obtained in the above processes is calcined to get pure Al_2O_3 (alumina).



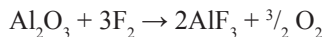
Bauxite is thus concentrated by leaching method.

Pure alumina to Al

Alumina is a refractory substance i.e., it does not fuse. Therefore, alumina is dissolved in a fused mixture of cryolite Na_3AlF_6 and a little CaF_2 . Cell is made of steel lined with graphite which acts as cathode. Anode is a graphite rod. Electrolysis produces Al at the cathode. Reactions at electrodes



Anode reaction $2\text{F}^- \longrightarrow \text{F}_2 + 2\text{e}^-$



The F_2 formed at anode acts as an agent to convert Al_2O_3 (a poor conductor) into AlF_3 (a good electrolyte).

Oxygen produced at anode reacts with it producing CO and CO_2 . Anode is also destroyed by liberated F_2 . Therefore, anode needs to be replaced periodically. This process produces Al which is about 99.5% pure.

Pure Al

It is obtained by Hopp's process. It gives 99.99% pure Al.

Uses

- (i) As reducing agent in the extraction of Cr, Mn (thermite process).
- (ii) In the manufacture of stainless steel.
- (iii) Al – cable is used for transmission of electricity.
- (iv) In the production of construction materials (house and automobiles).
- (v) To produce foils which are used in many ways.
- (v) To produce light and strong alloys used in aircrafts and transportation vehicles.

| | |
|-----------|---|
| Magnelium | $\text{Al} + \text{Mg}$ |
| Duralumin | $\text{Al} + \text{Mg} + \text{Cu} + \text{Mn}$ |

Iron – Fe [Ferrum]

Iron is second most abundant element after Al, and the fourth most abundant in the earth's crust. It is also found in meteorites i.e., iron is present in the solar system.

Iron has been known since prehistoric days. Egyptian tools date as far back as 1500 – 2000 B.C. In India iron and steel were produced as early as 600 B.C. It was known as 'Wootz' and was manufactured in Hyderabad and Madras (Now Chennai). Asoka pillar in Delhi and also at many other places stand even today without being affected. It shows great skill of the iron manufacturers in ancient India. Chinese also used steel as early as 2500 B.C.

Ashoka Pillar at Delhi

It is made of wrought iron and is highly corrosion resistant. Its composition found is W. iron – 99.72%, C – 0.08%, Si – 0.04%, S – 0.06%, P – 0.114%.

Ores

| | |
|-------------|------------------------------------|
| Haematite | Fe_2O_3 |
| Magnetite | Fe_3O_4 (magnetic) |
| Siderite | FeCO_3 |
| Iron pyrite | FeS_2 (Fool's gold) |
| Limonite | $\text{FeO}(\text{OH})$ |

Iron is extracted from oxide ores or carbonate ore.

Iron is not extracted from sulphide ores. It is because

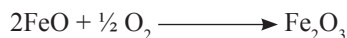
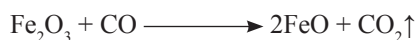
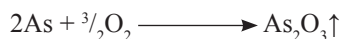
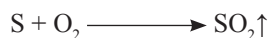
- (i) It is very difficult to remove S from Fe as it has high affinity for S and,
- (ii) Presence of S in iron makes it brittle.

Steps in extraction

- (a) Crushed ore is washed with water and then concentrated by magnetic separation method.

(b) Calcinations and Roasting

Concentrated ore is heated with coke. Sulphur, As etc are removed as SO_2 , As_2O_3 and C as CO_2 . Ferrous oxide is oxidized to ferric oxide. Ore becomes porous.



(c) Smelting

Calcined and roasted ore is mixed with lime stone (CaCO_3 , the flux) and coke. This mixture is called 'charge'. The reduction of oxide ore is carried out in a blast furnace. Blast furnace is a vertical arrangement. Temperature at different parts is different:

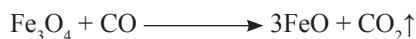
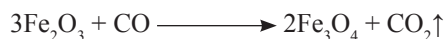
Upper part $400^\circ - 600^\circ\text{C}$

Middle part $\sim 600^\circ - 1100^\circ\text{C}$

Lower part $\sim 1500^\circ\text{C}$

Reactions in blast furnace

- (i) Upper Zone

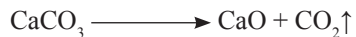


Some Fe is produced as



- (ii) Middle Zone

It is heat absorption zone. The reactions are





Silica is removed as CaSiO_3 slag and some Fe is also produce.

(iii) Lower Zone

It is known as smelting zone.



Fused iron is obtained. It sinks below fused slag, CaSiO_3 . Therefore, Fe is protected from being oxidized. This iron contains Si, P, Mn etc., as impurities due to reduction of SiO_2 , Mn_2O_3 , and $\text{Ca}_3(\text{PO}_4)_2$. Carbon is also present in iron. The mp of iron is 1500°C but it melts around 1200°C due to impurities.

Cast iron or Pig iron

The product of the blast furnance is known as pig iron or cast iron. It contains about 3 – 5% carbon in addition to Si, P, S, Mn etc. Cast iron can either be (i) Grey (ii) White. It depends upon speed of cooling.

Grey cast iron

When cooled slowly grey cast iron is formed. It contains carbon as tiny flakes of graphite. It is relatively soft and tough.

White cast iron

When cooled rapidly white cast iron is produced. It contains carbon as iron carbide, Fe_3C which is called cementite. White cast iron is about 75% cementite and is extremely hard and brittle.

Wrought iron or Malleable iron

It is purest form of iron and has minimum carbond content (0.15 to 0.25%). It is obtained from cast iron by puddling process.

A special type of reverberatory furnance, lined with Fe_2O_3 , is used. Pig iron is melted and air is passed in it. Impurities are oxidized by reaction with oxygen of air or Fe_2O_3 . Slag is also formed.



As the purity of iron increases, its mp rises and a semi-solid is produced. It is collected as large lumps. The lumps are beaten under steam hammers to squeeze out slag as far as possible. The product is known as Wrought iron. It is:

- Soft, gray, tough, fibrous in structure.
- Malleable and can be forged and welded
- It softens around 1000°C, mp 1530°C.
- It is more resistant to corrosion than any other form of iron.

Steel

Steel is an alloy of iron and carbon. Its grade and properties depends on carbon content:

Table 7.5

| Name | % C | Properties and Use |
|-------------------------|------------|--|
| Mild steel or low steel | 0.15 – 0.3 | Ductile and used for tubes, forgings. |
| Medium steel | 0.3 – 0.6 | It can be hardened and tempered used for axles, springs etc. |
| High carbon steel | 0.6 – 0.8 | |
| Tool steel | 0.8 – 1.6 | Hard, used to make tools. |

Special steel

Steel which contains various transition metals (V, Cr, Mn, Ni, W etc.) in small quantities are known as special steel. They are corrosion resistant and possess special properties, discussed later on.

Conversion of Iron into Steel

It involves the following steps:

- Removal of the impurities from iron by oxidation.
- Addition of alloying elements.

Haematite to steel conversion therefore, involves:

- Reduction of Fe – oxides to Fe.
- Removal of the impurities from Fe by oxidation.
- Addition of alloying elements.

It can be summerised as

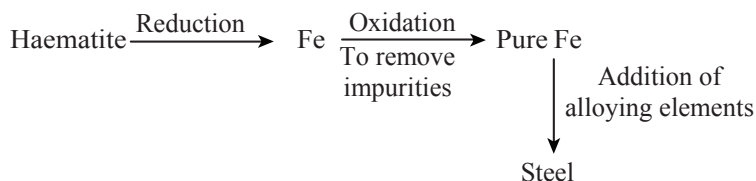


Figure 7.3

Methods of making steel

- Steel form Pig Iron
- Steel from Wrought Iron

Steel from Pig Iron

- Bessemer's method
- Siemen's Martin open-hearth process

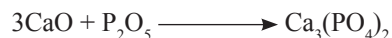
- (iii) L – D process
- (iv) Electrical process

Bessemer's method

The impurities of Pig iron are removed by oxidation. Then Spiegel (Fe, Mn, C mixture) is mixed in the oxidized product to produce steel. This method uses SiO_2 lined Bessemer converter. It is filled with a perforated bottom to blow air. Impurities are removed by oxidation and Mn as MnSiO_3 . Wrought iron is the product. It is mixed with speigel to produce steel.

When pig iron contains P as the major impurity, $(\text{MgO} + \text{CaO})$ mixture lined furnace is used. Phosphorous is removed as basic slag $\text{Ca}_3(\text{PO}_4)_2\text{CaO}$.

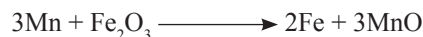
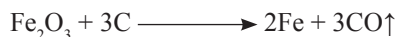
Chemical reactions involved:



Siemen's Martin open-hearth process

This process is carried out in a producer gas fired–furnance. SiO_2 or $(\text{CaO} + \text{MgO})$ lined furnace is used. In this method the impurities are removed by oxidation with Fe_2O_3 and also as slag. The charge consists of pig iron + scrap iron + haematite ore. Although slow, this method produces steel of superior quality.

Chemical reactions involved:



Note:

The above processes have one major drawback. That is taking up of nitrogen by the molten iron. When simply above 0.01% N, makes steel brittle. In addition to that nitriding of the surface of iron makes it unfit for welding.

L–D process

It is modern method of steel making. This method uses pure O_2 for removal of the impurities. A jet of hot O_2 is held above molten iron surface. The impurities are removed quickly, only in 20 to 30 minutes. Then



In India, Rourkela iron plant uses this method of steel making. L – D process produces superior steel compared to Bessemer and open hearth process.

Electrical process

This method produces high-grade steel. For this purpose, steel from Bessemer method is used. Silica and dolomite ($\text{CaCO}_3 + \text{MgCO}_3$) lined furnance is used. Graphite is electode. Low-grade Steel melts by heating effect of current; slag is produced and is removed. Then alloying metal is mixed to produce Spiegel steel.

Some special steels:

Table 7.6

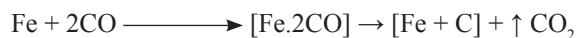
| Special steel | Constituents | Properties | Application |
|----------------------------------|------------------------|---------------------------------|---|
| Silicon steel | ~ 3.5% Si + little C | | Electromagnets, transformers |
| Manganese steel | Mn 12 – 15 % | Very hard | Rail, helmets, safes, rock crushing machinary |
| Chromium steel (Stainless steel) | Cr ~12% | Hard, corrosion resistant | Cutlery |
| W – Cr steel | Cr ~ 4% W ~10 – 20% | Very tough & strong | Tools |
| Ni – steel | Ni ~3.5% | Tough and high tensile strength | Motor cars, cables propeller shafts |
| V – Cr steel | Cr ~ 1% V ~0.15% | Load bearing, hard, elastic. | Bearings, gears, cable, axel etc. |

Steel from Wrought iron

Wrough iron has lesser carbon content than steel. Therefore, steel is produced by adding carbon to Wrought iron (steel is made by removing carbon from pig iron).

Bars of wrought iron are packed, with charcoal in-between, in fire–clay boxes. It is heated in a furnance to about 1000°C . Carbon and O_2 reacts to produce CO which is absorbed in iron. Carbon monoxide absorbed in iron decomposes to C and CO_2 . CO_2 escapes and C remains and spreads in iron. The evolution of CO_2 leaves a blistered surface. The product is therefore, known as Blister steel. This process is called cementation. It produces high carbon steel.

Reaction



Comparison Pig iron, Wrought and Steel**Table 7.7**

| Properties | Cast iron | Wrought iron | Steel |
|---------------|----------------------------|----------------------------|---|
| C % | 2.0 to 4.5 | 0.1 to 0.25 | 0.1 to 1.5 |
| P,S, Si, Mn | Highest % | Very little | Less than cast iron |
| Structure | Crystalline | Fibrous | Granular |
| Melting pt | 1200°C | 1500°C | 1300° – 1400°C |
| Malleability | Brittle | Malleable | Brittle and malleable (depending upon C content) |
| Hardness | Hard | Soft | Hard and soft both (hardness increases with C content). |
| Magnetization | No permanent magnetization | No permanent magnetization | Magnetized permanently |
| Welding | Not possible | Easily welded | Welding with difficulty |
| Tempering | X | X | Tempered |
| Uses | For RCC work | Wire, chain etc. | Tools, rails, magnet etc. |

Heat treatments of steel

The elasticity and hardness of steel changes when it is heated strongly and cooled. The change in properties depends, actually, on temperature and method of cooling.

Quenching of steel

The process of heating steel to red hot then cooling suddenly by plunging into water (or oil) is called quenching. Quenched steel

- (i) is brittle,
- (ii) is extremely hard and
- (iii) has very low elasticity

Tempering of Steel

When quenched steel is heated at different temperatures for different times and cooled slowly, brittleness is reduced. It is called tempering. Desired elasticity and hardness is developed in steel by this method. A coloured thin film of oxide is formed on the surface of steel. The actual colour of oxide film depends on temperature of heating.

Table 7.8

| Colour of the surface | Temperature (°C) | Uses |
|-----------------------|------------------|--------------------------|
| Light yellow | ~ 340 | For blades |
| Grey yellow | ~230 – 260 | Tools for cutting |
| Pink | ~ 275 | Scissor, fork, etc |
| Bright blue | ~ 288 | Sword, spring of watches |
| Deep blue | ~ 300 | |

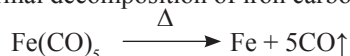
Annealing

The process of slow cooling of a bright red hot steel is called annealing. It makes steel ductile and soft. Such an steel is used in fabrication process.

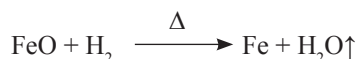
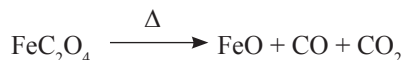
Chemically pure iron

It can be prepared by

- (i) Thermal decomposition of iron carbonyl



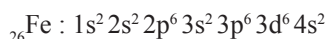
- (ii) Reduction of pure FeO with H_2 . Pure FeO is obtained by heating FeC_2O_4 or FeCO_3 or $\text{Fe}(\text{NO}_3)_2$.

**Brief chemistry of Iron**

Iron is an element of Group – 8 (or VIII)

Period – 4

At. No. – 26



This electron configuration has partially filled 3d orbitals. Therefore, iron is a transition metal.

The metal (Fe)

Pure iron is white, lustrous metal. It has lattice structure. Lattice contains Fe^{+3} ions. This ion has 5 unpaired electrons in 3d orbitals.

These d – electrons are also involved in metallic bonding. It makes lattice more stable. So, Fe has high mp (1535°C)

**Figure 7.4**

Allotropy of Fe

Iron shows allotropy. Allotropic forms are α -iron, β -iron, γ -iron and δ -iron. Forms are temperature dependent.

Table 7.9

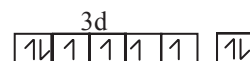
| | α -form | β -form | γ -form | δ -form |
|-------------------|----------------|---------------|----------------|----------------|
| Temperature (°C) | < 770 | 770 – 906 | 906 – 1401 | > 1401 |
| Crystal structure | BCC | BCC | FCC (or CCP) | BCC |
| Magnetism | Ferromagnetic | Paramagnetic | Paramagnetic | Paramagnetic |

Note:

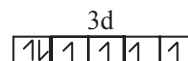
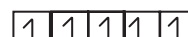
- Ferromagnetism in Fe below 770°C arises due to domain formation i.e., lattice interaction.
- This temperature i.e., 770°C, after which Fe becomes paramagnetic is called Curie temperature.
- Above Curie temperature (>770°C) lattice interaction is stopped. Therefore, Fe becomes paramagnetic due to unpaired electrons.

General physical properties

- Valence orbitals and electrons ($3d^6 4s^2$)



- Oxidation states

Fe²⁺ (ferrous)Fe³⁺ (ferric)

- Ionisation Energy

Fe²⁺554 Kcal mol⁻¹**Figure 7.5**Fe³⁺ 1246 Kcal mol⁻¹

- Atomic radius (Å)

Fe

1.26 Å

- Ionic radius

Fe²⁺

0.85 Å

Fe³⁺ 0.63 Å

- Electronegativity

Fe

1.64

Fe²⁺ 1.83Fe³⁺ 1.96

- mp

1535°C

- bp

2735°C

- E°

Fe²⁺ + 2e⁻ \equiv Fe

-0.44V

Fe³⁺ + 3e⁻ \equiv Fe

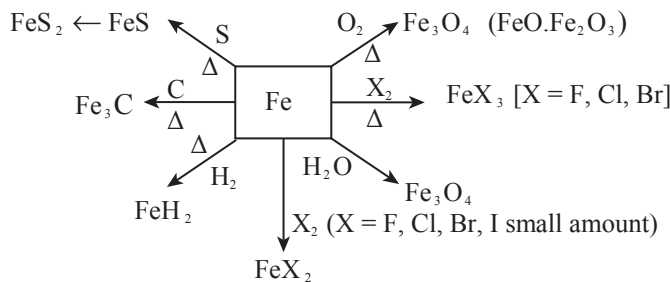
+0.77V

Note:

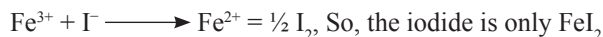
- Electronegativity changes with oxidation states.
- E° shows that Fe²⁺ is a reducing agent and Fe³⁺ is an oxidizing agent.
- Ferrous (Fe²⁺) and Ferric (Fe³⁺) compounds are paramagnetic as there are unpaired electrons in both the ions.

Chemical properties

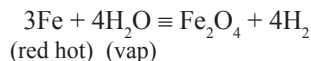
Iron is moderately reactive.

(i) Binary compounds**Figure 7.6**

- (a) Ferric iodide (FeI_3) is not stable. It is due to the fact that Fe^{3+} is a strong enough oxidizing agent for a good reducing agent like I^- .



- (b) Red hot iron reacts with water vap only. The reaction is reversible.



- (c) Reaction of Fe with S forms FeS which further reacts with S to produce FeS_2 .

(ii) Reactions in solution

- (a) Fe reacts with dil. HCl and dil. H_2SO_4 to give H_2 .



- (b) Dil. HNO_3 forms ferrous nitrate and NO.

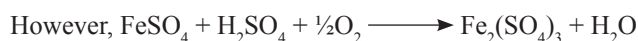
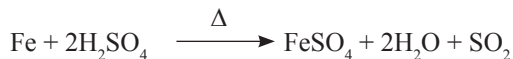


or,



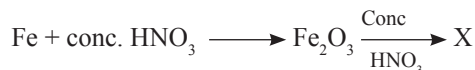
- (c) Conc. H_2SO_4

Hot conc. H_2SO_4 oxidizes Fe to FeSO_4 and itself reduced to SO_2 .



(d) Conc. HNO_3 (Passivity of Iron)

Conc. HNO_3 passivates iron. It is due to the formation of a thin film of oxide on the surface of iron.



Acidic dichromate ($\text{Cr}_2\text{O}_7^{2-} + \text{H}^+$), aquaregia etc. i.e., strong oxidizing medium also passivates iron.

Corrosion of Iron

Corrosion is the process in which a metal changes over to a compound in environment. In case of iron it is called rusting. It is a complex chemical process. Rust appears to be hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Iron does not rust in (i) dry air or (ii) air free water. It shows that water and oxygen both are required for rust formation. Rusting is speeded up by:

- (i) Acids
- (ii) Contact with less active metals.
- (iii) Presence of rust (autocatalysis).

To account for the above observations, the following chemical processes have been proposed for corrosion (the electrochemical, theory). The steps are:

- Conversion of Fe into Fe^{2+}
- $\text{Fe}_{(s)} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$
- Liberated electrons are taken up by H^+ from water or acid or by noble metal present in iron.
- $\text{H}^+ + \text{e}^- \longrightarrow \text{H}$
- In the third step H is converted into water
- $2\text{H} + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$
- Iron, thus becomes anode and noble metal, the cathode. Therefore, a small local electrochemical cell is formed on the surface.
- Fe^{2+} ultimately oxidized to Fe^{3+} forming hydrated $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (reddish brown).
- $2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + (2 + x)\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 4\text{H}^+$
- The H^+ is seen catalyst in the process of rusting. The above is called electrolytic theory of corrosion.

Prevention from rusting

- (i) To add protective coating over iron surface i.e., painting.
- (ii) Electroplating Fe with Sn, Cr, Ni etc.
- (iii) By developing a coating of Fe_3O_4 over surface by passing steam on red-hot iron.

Important compounds of iron**Table 7.10**

| Oxidation no. | Compound | Formula | Common name | Colour | Magnetism |
|-----------------------|---------------------|---|-------------|------------|--------------|
| Fe^0 | Iron pentacarbonyl | $\text{Fe}(\text{CO})_5$ | — | — | |
| $\text{Fe}^{+}(3d^7)$ | Brown ring compound | $[\text{Fe}(\text{H}_2\text{O}_5\text{NO})]^{+2}$ | — | Deep brown | Paramagnetic |

(Continued)

| Oxidation no. | Compound | Formula | Common name | Colour | Magnetism |
|--|---------------------------------------|---|---------------|-------------------|--------------------|
| Fe^{2+} (3d ⁶) (ferrous) | Ferrous oxide | FeO | — | Black | Anti ferromagnetic |
| | Ferrous sulphate heptahydrate | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | Green vitriol | Green | Paramagnetic |
| | Ferrous ammonium sulphate hexahydrate | $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | Mohr's salt | Greenish | Paramagnetic |
| | Potferrocyanide | $\text{K}_4[\text{Fe}(\text{CN})_6]$ | — | Greenish | Diamagnetic |
| | Sod. nitroprusside | $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ | — | Brown red crystal | Diamagnetic |
| Fe^{3+} (3d ⁵) (ferric) | Ferric potassium sulphate hydrate | $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ | Alum | Brown | Paramagnetic |
| | Pot ferricyanide | $\text{K}_3[\text{Fe}(\text{CN})_6]$ | — | Yellowish | Paramagnetic |
| $\text{Fe}^{2+}/\text{Fe}^{3+}$ | Ferri ferro oxide | Fe_3O_4 ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) | Magnetite | Brown | Ferromagnetic |

Note:

- (i) Fe_3O_4 has inverse spinel structure. That is, all Fe^{2+} ions are in octahedral voids and half of the Fe^{3+} ions in Td and half in octahedral voids of a cubic close-packed oxide ions.
- (ii) FeO is used in the manufacture of green glass.
- (iii) Fe_3O_4 is used in computers due to magnetic property.
- (iv) Mohr's salt is a double salt. It is water soluble. Aq. solution contains NH_4^+ , Fe^{2+} , and SO_4^{2-} ions. Therefore, Mohr's salt gives the following tests.
 - (a) Forms blue ppt. or colouration with $\text{K}_3[\text{Fe}(\text{CN})_6]$.
 - (b) Gives NH_3 when heated with NaOH solution, i.e., gives test of NH_4^+ ion.
 - (c) Forms white ppt. with BaCl_2 solution i.e., gives test of SO_4^{2-} ions.
 - (d) Mohr's salt solution decolourizes acidic MnO_4^{2-} (pink) and forms green solution with acidic $\text{Cr}_2\text{O}_7^{2-}$ (orange). It is due to reduction of Fe^{2+} in Mohr's salt.
 - (e) Mohr's salt aq. solution is not oxidized to $\text{Fe}_2(\text{SO}_4)_3$ in air. Therefore, standard solution of Mohr's salt is primary standard and is used in titration.
- (v) Pot. ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6]$ is a reagent in salt analysis. It forms
 - (a) Blue ppt. or colouration with Fe^{3+} ion

$$4\text{Fe}^{3+} + 3[\text{Fe}(\text{CN})_6]^{4-} \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6] \text{ (Prussian blue)}$$
 - (b) Brown ppt. with Cu^{2+} .

$$2\text{Cu}^{2+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \text{ (Brown ppt.)}$$
 - (c) White ppt. with Zn^{+2}

$$2\text{Zn}^{2+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow \text{Zn}_2[\text{Fe}(\text{CN})_6] \text{ (White ppt.)}$$

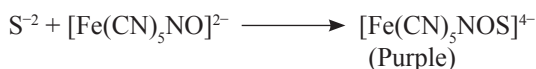
- (vi) Pot. ferricyanide $K_3[Fe(CN)_6]$, forms a dark blue ppt. or colouration, (Turnbull's blue), with Fe^{2+} ion. The reaction is



Now it has been proved that Prussian blue and Turnbull's blue have the same formula,



- (vii) Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, is a reagent for S^{2-} ion. It forms purple coloration with S^{2-} ion.



Solution of H_2S or the free gas does not give purple colour. However, filter paper moistened with sodium nitroprusside, if made alkaline with $NaOH$ or NH_4OH , forms purple spot with H_2S gas.

- (viii) Brown ring compound, in the test of NO_3^- ion, is $[Fe(H_2O)_5NO]^{2+}$. It is coloured due to charge transfer and formal oxidation state of iron in the compound is +1.

Test to distinguish Fe^{2+} and Fe^{3+} ions

Table 7.11

| Reagent | Fe^{2+} ion | Fe^{3+} ion |
|--------------------------|----------------------------------|---------------------------------|
| NH_4SCN solution | X | Blood red colour $Fe(SCN)_3$ |
| $K_4[Fe(CN)_6]$ solution | White ppt $K_2Fe[Fe(CN)_6]$. | Blue ppt. $Fe_4[Fe(CN)_6]_3$ |
| $K_3[Fe(CN)_6]$ solution | Blue ppt. $Fe_4[Fe(CN)_6]_3$ | Brown ppt. $Fe[Fe(CN)_6]$ |

Copper (Cu)

Copper has been known since about 4000BC. The Cu age is well described in history. It is widely distributed in nature in trace amounts, in rocks, soils, mineral water, sea etc. Living organisms requires minor quantities of Cu. Cu deficiency in human's causes a major problem, the Parkinson's disease.

Ores

Table 7.12

| Chalco pyrite | $CuFeS_2$ (copper coloured) |
|-----------------------------------|---------------------------------|
| Copper glance or Chalcocite | Cu_2S (dark grey) |
| Cuprite | Cu_2O (ruby red) |
| Malachite | $CuCO_3 \cdot Cu(OH)_2$ (green) |

(Continued)

| Chalco pyrite | CuFeS ₂ (copper coloured) |
|------------------------------|--|
| Azurite | 2CuCO ₃ ·Cu(OH) ₂ |
| Bornite or Peacock ore | Cu ₅ FeS ₄ (color like peacock feathers, blue, brown, purple, red) |
| Turquoise | CuAl ₆ (PO ₄) ₄ (OH) ₈ ·4H ₂ O (blue, gemstone). |

Chalcopryite or copper pyrite is major source of copper.

Some important points

- (i) Copper has very high affinity for S.
- (ii) Solong as FeS is present in the ore Cu remains mostly as Cu₂S. (Cu₂O + FeS → Cu₂S + FeO)
- (iii) Cu is isolated by self reduction process.

Stages in extraction

- (i) Copper pyrite is concentrated by froth floatation process.

(ii) Roasting

Concentrated ore is roasted in a current of air in reverberatory furnance → Sulphur, As, Sb etc are removed as oxide. Some Cu₂O and FeO are formed

→ Some Cu₂O and FeO are formed

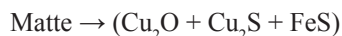


(iii) Smelting

Roasted ore is mixed with sand and heated strongly (1400 – 1450°C) in a blast furnance. Most of the FeS is converted into Fe – oxide and is removed as slag, FeSiO₃.



Thus, most of the iron is removed as slag. There remains a solid mixture, Cu₂O, Cu₂S and a little FeS. It is called 'Matte' i.e.,



(iv) Bessimerization

Molten matte and Sand are transferred to a bessimer converter and air is blown. The reactions are





Solid Cu obtained is known as blister Cu. It is because surface of the solid is blistered due to removal of SO_2 . The product is about 98 – 99% Cu.

Purification

Copper is mainly refined by electrolytic process.

Anode \longrightarrow blister Cu

Cathode \longrightarrow pure Cu

Electrolyte \longrightarrow CuSO_4 + a little H_2SO_4

Anode reaction $\text{Cu}_{(\text{s})} \longrightarrow \text{Cu}_{(\text{aq})}^{+2} + 2\text{e}$

Cathode reaction $\text{Cu}_{(\text{aq})}^{+2} + 2\text{e} \longrightarrow \text{Cu}_{(\text{s})}$

Thus, anode dissolves and Cu deposits at cathode. This Cu is about 99.9% pure. Impurities of less active metals like Ag and Au do not dissolve but settle at bottom of the cell. It is called 'anode mud'. These are recovered from anode mud.

Uses

Important uses are:

- (i) In electrical industry, wire, cable, generators etc.
- (ii) In utensils
- (iii) Coins
- (iv) Electroplating
- (v) In alloy formation

Alloys of copper

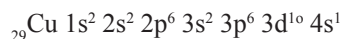
Copper forms a number of important alloys.

Table 7.13

| Alloy | Composition | Uses |
|------------------|---------------------|--|
| Brass | Cu (60%) + Zn (40%) | Utensils, condenser tube |
| Bronze | Cu (75%) + Sn (25%) | Coins, statues, bells, utensils |
| Bell metal | Cu (80%) + Zn (20%) | Bell |
| Monel metal | Cu + Ni + Mn + Fe | Electrolytic cell used in the production of F_2 alkali industry |
| Gun metal | Cu + Sn | For making gun barrels. |
| Phosphor Bronze | Cu + Sn + P | Bearing valves, galvanometer |
| German silver | Cu + Zn + Ni | Plates, ornaments |
| Constantan | Cu + Ni | Electrical apparatus. |
| Aluminium bronze | Cu + Al + Sn | Cheap ornaments golden plate, coins |

Brief chemistry of Cu

Copper is an element of Group – 11
 Period – 4
 At. No. – 29

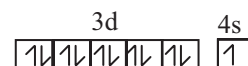


This configuration is due to greater stability of fulfilled ($3d^{10}$) and half filled ($4s^1$) orbitals.

The metal

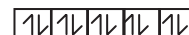
- Copper is ductile, soft and tough reddish metal.
- It is second only to silver in thermal and electrical conductivities.
- Copper has ccp lattice structure.
- Lattice contains Cu^{2+} ions, i.e., a $3d^9$ system.
- The d – electrons are also involved in metallic bonding, making lattice more stable. So, Cu has high mp (1083°C).

(i) Valence orbitals and electrons ($3d^{10}4s^1$)



(ii) Oxidation states

Cu^+ (cuprous)



Cu^{2+} (cupric)

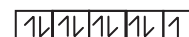


Figure 7.7

(iii) Core electrons

$\text{Cu}^+(18)$

$\text{Cu}^{2+}(17)$

(iv) Ionization Energy

Cu^+

7.72 eV

Cu^{2+}

20.3 eV

(v) Electronegativity

1.9

(v) Atomic radius

1.17\AA

(vi) Ionic radii

r_{Cu^+}

0.93\AA

$r_{\text{Cu}^{2+}}$

0.72\AA

(vii) mp

1083°C

(viii) bp

2325°C

(ix) $E^\circ \text{Cu}^+ + e \longrightarrow$

Cu

+0.52V

$\text{Cu}^{2+} + 2e \longrightarrow$

Cu

+0.34V

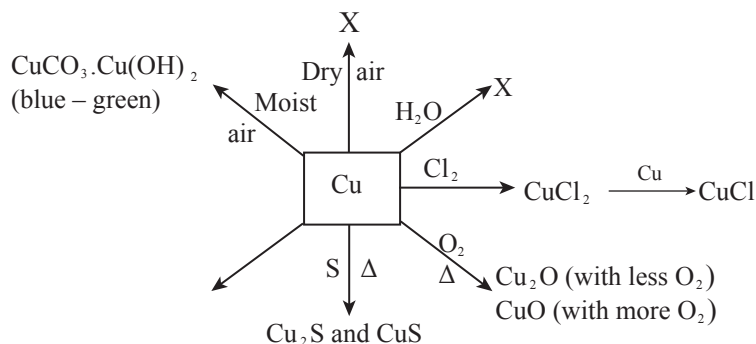
$\text{Cu}^{2+} + e \longrightarrow$

Cu^+

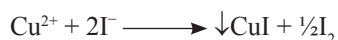
+0.15V

Note:

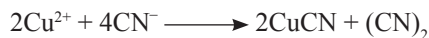
- Electrode potential values show that Cu is uncreative.
- Cu(I) is an oxidizing agent, capable of oxidizing itself to Cu(II) . Thus Cu(I) disproportionates in a q. solution.
- $2\text{Cu}_{(\text{aq})}^+ \longrightarrow \text{Cu}_{(\text{s})} + \text{Cu}_{(\text{aq})}^+$
- Cu(I) is stable only in insoluble salts and in Cu(I) complexes.
- Cu(I) i.e., cuprous ($3d^{10}$) compounds are diamagnetic but Cu(II) , cupric ($3d^9$) compounds are paramagnetic.

Chemical reactions**Figure 7.8**

- (a) Cupric iodide (CuI_2) is not stable. It is due to the fact that Cu^{2+} oxidizes I^- and iodide reduces Cu^{2+} .



Cupric cyanide is also unstable due to the same reason (CN^- , pseudo halide)



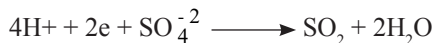
- (b) Dry air and water do not react with Cu.
 (c) Moist air reacts with Cu and a bluish green crust, basic copper carbonate, is formed at the surface.



- (d) Acids

(i) Dil. HCl and H_2SO_4 have no action on Cu.

(ii) Conc. H_2SO_4 reacts with Cu, when heated.



Thus, solution becomes bluish due to the presence of $\text{Cu}_{(\text{aq})}^{+2}$ in solution.

(iii) HNO_3 reacts with Cu. Product depends upon acid concentration and temperature.

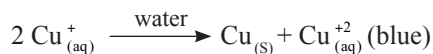
Table 7.14

| Acid conc. | Temperature | Products |
|------------|-------------|---|
| Dil. | Normal | $\text{Cu}(\text{NO}_3)_2$ and N_2O |
| 50% | Normal | $\text{Cu}(\text{NO}_3)_2$ and NO |
| Conc. | Hot | $\text{Cu}(\text{NO}_3)_2$ and NO_2 |
| Acid vap | Hot | CuO and N_2 |

- (e) Cu dissolves in a solution of CuCl_2 but CuCl ppts when the reaction mixture is poured in water.



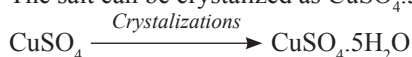
- (f) Cu_2O dissolves in dil. H_2SO_4 to form a blue solution which contains $\text{Cu}_{(\text{aq})}^{+2}$. It is due to disproportionation of soluble cuprous sulphate.



- (g) The most common salt of copper is CuSO_4 . It may be prepared as,



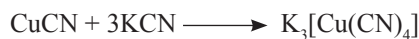
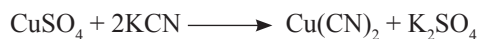
The salt can be crystallized as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (blue). It is called blue vitriol.



The actual constitution of the crystal is $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$. It has the following structure.

That is, four H_2O are coordinated to Cu^{2+} and fifth one is H – bonded with SO_4^{2-} and coordinated water. Thus, the surrounding of Cu^{2+} is octahedral.

- (h) Cu^{2+} is reduced by CN^- to Cu^+ , and cyanogens gas, $(\text{CN})_2$, is formed. But with excess CN^- ions Cu^+ forms a cyanocomplex.



Or,

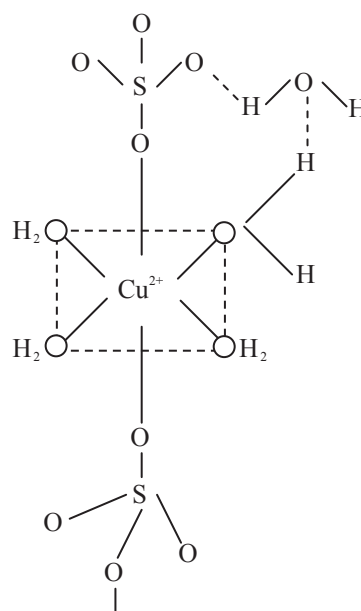


Figure 7.9

Important compounds and complexes

Table 7.15

| Compound | Formula | Common name | Colour | Magnetism |
|------------------------------|---|--------------|--------|--------------|
| Co (II) oxide | CuO | — | Black | Paramagnetic |
| Cu(I) oxide | Cu_2O | — | Red | Diamagnetic |
| Cu(II) sulphate pentahydrate | $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | Blue vitriol | Blue | Paramagnetic |

(Continued)

| Compound | Formula | Common name | Colour | Magnetism |
|------------------------|---|-------------|---------------|--------------|
| Basic Cu(II) carbonate | $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ | — | Bluish green | Paramagnetic |
| Basic Cu(II) acetate | $\text{Cu(CH}_3\text{COO)}_2 \cdot \text{Cu(OH)}_2$ | Verdigris | Greenish blue | Paramagnetic |

Complexes

Table 7.16

| Complexes | Formula | Hybrid nature of the metal | Structure |
|-----------------------|----------------------------|----------------------------|-------------|
| Tetrammine Cu(II)ion | $[\text{Cu(NH}_3)_4]^{2+}$ | sp^2d | Sq. planar |
| Hexammine Cu(II) ion | $[\text{Cu(NH}_3)_6]^{2+}$ | Sp^3d^2 | Octahedral |
| Dicyanocuprate (I) | $[\text{Cu(CN)}_2]^-$ | sp | Linear |
| Tetracyanocuprate (I) | $[\text{Cu(CN)}_4]^{3-}$ | sp^3 | Tetrahedral |

Zinc (Zn)

Zinc was known in India around 8th century AD. It is believed to be prepared first by Nagarjuna (8th – 9th century AD) from calamine.

Ores

It is widely distributed in nature. It is also found in trace amount in snake's venom.

| | |
|-------------|--|
| Zinc blende | |
| Or | ZnS |
| Sphalerite | |
| Calamine | ZnCO_3 |
| Zincite | ZnO |
| Franklinite | $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ |
| Willemite | Zn_2SiO_4 |

Zinc blende is used for extraction of Zn.

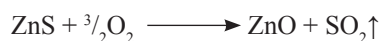
Stages

(i) Concentration

Ore is concentrated by froth floatation process.

(ii) Roasting

Concentrated ore is roasted in a furnace around 900°C .





(iii) Smelting

Roasted ore is heated with carbon in a furnace. Metallic Zn distills over



This reaction is reversible when carbon is present in small quantities. Therefore, carbon is maintained in high concentration.

Purification

Zinc recovered by the above method is impure and is known as spelter. It may be refined by

- (a) Distillation
- (b) Electrolytic method

Distillation

Spelter contains Pb, Cd, Fe etc., as impurities. These metals differ widely in bp with Zn.

| | Zn | Cd | Fe | Pb |
|-----|-------|-------|--------|--------|
| bp. | 907°C | 766°C | 2735°C | 1750°C |

On distillation, Zn and Cd vaporize. They also differ in boiling points. Thus, Cd comes out first leaving behind Zn.

Electrolytic process

| | |
|-------------|----------------------------|
| Cathode | – pure Zn |
| Anode | – spelter |
| Electrolyte | – ZnSO_4 solution |

On electrolysis anode dissolves and pure Zn deposit at cathode.



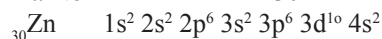
Uses

- (i) In galvanization of iron.
- (ii) In the manufacture of dry battery.
- (iii) In the extraction of Ag and Au.
- (iv) Zn dust as reducing agent in laboratory.
- (v) In many important alloys (given in Cu)

Brief chemistry of Zn

Zinc is an element of group – 12

Period – 4
At. No – 30




Zinc and its ion Zn^{+2} both have ten d – electrons ($3d^{10}$). Thus, it is not a true transition metal but is a d – block elements.

The metal

Zn is a white lustrous tarnishable metal. It has hcp (i.e., hexagonal close packed) structure. It has filled 3d orbitals ($3d^{10}$). The d – orbitals have lesser contribution towards metallic bonding. So, lattice is not very strong and Zn has relatively low melting point (419°C).

General physical properties

| | | |
|------------------------------------|--|---|
| (i) Valence orbitals and electrons | ($4s^2$) |  |
| (ii) Oxidation state | Zn^{+2} | $4s^0$ |
| (iii) Core electrons | Zn^{+2} | 18 |
| (iv) Ionization energy | Zn^+ | 9.4 eV |
| | Zn^{+2} | 17.95 eV |
| (v) Electronegativity | 1.65 | |
| (vi) Atomic radius | | 1.25 \AA |
| (vii) Ionic radius | Zn^{+2} | 0.72 \AA |
| (viii) mp | | 419°C |
| (ix) bp | | 907°C |
| (x) E° | $\text{Zn}^{+2}_{(\text{aq})} + 2e \rightarrow \text{Zn}_{(\text{s})}$ | -0.76V |

Note:

- Electrode potential shows that Zn is a reactive metal and will liberate H_2 from dil. acids (but not with dil. HNO_3 , because even dil HNO_3 oxidizes liberated H to H^+).
- Zn is reducing metal.
- Zn compounds are colourless and diamagnetic as 3d orbitals are full filled, $3d^{10}$.

Chemical reactions

Zn is amphoteric metal

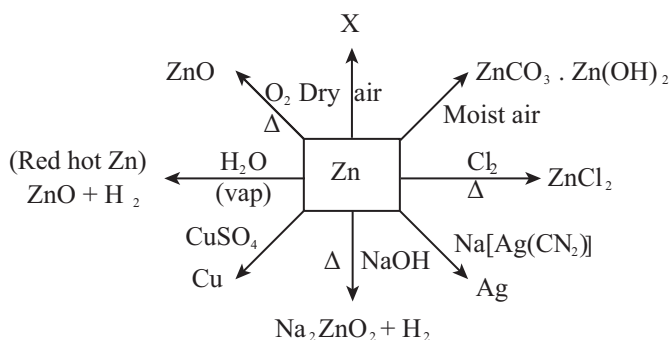


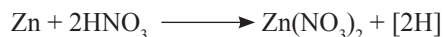
Figure 7.10

Reaction of Zn with acids

Table 7.17

| Acid | Very dil. | 50% | Conc. |
|--------------------------------|--|------------------------------------|---|
| HNO ₃ | Zn(NO ₃) and NH ₄ NO ₃ | Zn(NO ₃) and NO | Zn(NO ₃) ₂ and NO ₂ |
| HCl | ZnCl ₂ + H ₂ | ZnCl ₂ + H ₂ | ZnCl ₂ + H ₂ |
| H ₂ SO ₄ | ZnSO ₄ + H ₂ | ZnSO ₄ + H ₂ | ZnSO ₄ + SO ₂ |

- (i) Very dil. HNO₃ forms NH₄NO₃ with Zn. It is because liberated nascent H reduces nitrate to NH₃ (very dil. HNO₃ is not capable of oxidizing H to H⁺).



- (ii) Reaction in moist air takes place as,



Important compounds

Table 7.18

| Compound | Formula | Common name |
|----------------|--------------------------------------|---|
| Zinc oxide | ZnO | Chinese white or philosopher's wool or pompholyx. Hot ZnO is yellow due to lattice defect. |
| Zinc carbonate | ZnCO ₃ | Calamine |
| Zinc sulphate | ZnSO ₄ ·7H ₂ O | White vitriol |
| Zinc sulphide | ZnS | Natural ZnS Zinc blende. Zns is phosphorescent. |

Mercury (Hg)(Hydrargyrum)

Ore

Cinnabar HgS

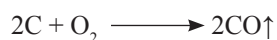
Stages in the metallurgy of Hg

(i) Concentration

The ore is concentrated by froth floatation process.

(ii) Roasting

Concentrated ore is mixed with coke, and heated in a shaft furnace, fitted with a cup and cone arrangement. The Coke burns, and generates heat, HgS is roasted to HgO which decomposes to produce Hg–vapour. It is condensed and then collected.





Purification

Mercury contains suspended and Cu, Zn, Pb etc, as impurities. The following steps are used for purification:

- Hg is filtered through canvas leather. It removes suspended impurities.
- Filtered Hg is mixed with $\text{Hg}(\text{NO}_3)_2$ and run several times through dil. HNO_3 . It removes dissolved metals.



- Hg is dried, and subjected to vacuum distillation.

Uses

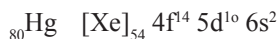
- Hg is thermometer and barometer liquid.
- Used in Hg – vapour lamp.
- In mirrors (Hg-Sn).
- In the formation of amalgam (Na – Hg).
- In the filling of cavities of teeth (Cd – Hg, Au – Hg, Zn – Hg).
- In the extraction of Ag and Au.
- In the manufacture of caustic soda (NaOH).

Brief chemistry of Hg

Hg is an element of Group – 12

Period – 6

At. No. – 80

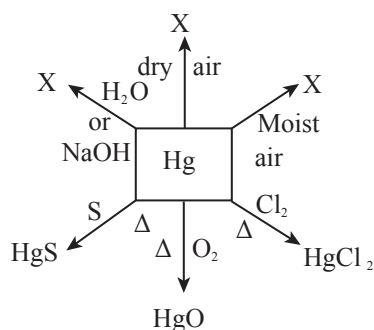


Hg and its ions (+1 and +2 both) both have ten d – electrons ($5d^{10}$). Thus, Hg is not a true transition metal but is a d – block elements.

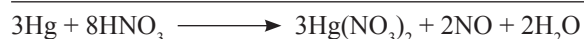
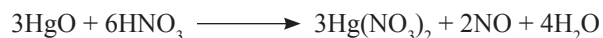
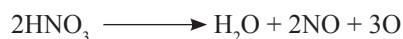
General physical properties

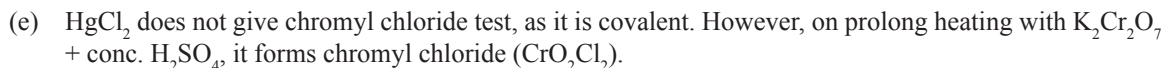
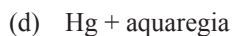
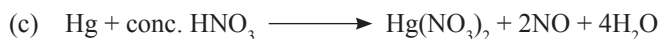
| | | | |
|------------------------------------|-----------------|--|----------|
| (i) Valence orbitals and electrons | | | $6s^2$ |
| (ii) Oxidation states | +1 | Hg_2^{2+} (there is Hg – Hg bond) | |
| | +2 | Hg^{+2} (Mercuric) | $6s^0$ |
| (iii) Ionization energy | $(\text{IE})_1$ | | 10.43 eV |
| | $(\text{IE})_2$ | | 18.65 eV |
| (iv) Electronegativity | | | 1.44 |
| (v) Atomic radius | | Hg | 1.44 Å |
| (vi) Ionic radius | | Hg^{2+} | 1.02 Å |

| | | |
|--|--|----------|
| (vii) mp | | -39°C |
| (viii) bp | | 357°C |
| (ix) E° | $\text{Hg}^{2+} + 2e \rightleftharpoons \text{Hg}$ | +0.85 eV |
| E° value shows that Hg is anoble metal. | | |

Chemical reactions**Figure 7.11****Table 7.19**

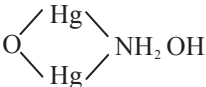
| Acids | Dil. | Conc. |
|---|--|---|
| HCL | X | X |
| H ₂ SO ₄ | X | HgSO ₄ + SO ₂ |
| HNO ₃ | Hg ₂ (NO ₃) ₂ + NO | Hg(NO ₃) ₂ + NO ₂ |
| AQUAREGIA (3HCL + HNO ₃) | HgCl ₂ + NOCl | |

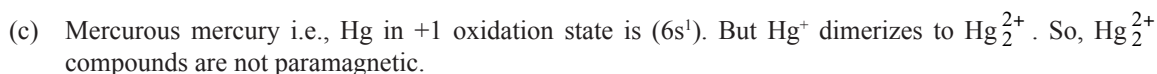
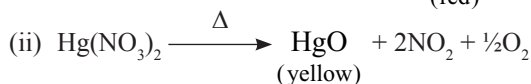
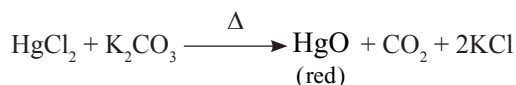
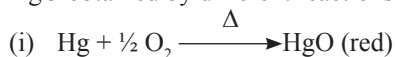
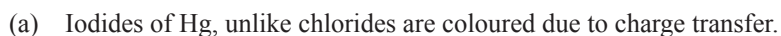




Important compounds

Table 7.20

| Compound | Formula | Common name | Colour |
|--------------------|---|--|----------------|
| Mercuric oxide | HgO | — | Red and yellow |
| Mercuric chloride | HgCl ₂ | Corrosive sublimate | Colourless |
| Mercuric sulphide | HgS | Vermilion | Red and black |
| Mercuric iodide | HgI ₂ | — | Red |
| Mercurous chloride | Hg ₂ Cl ₂ | Calomel | Colourless |
| Mercurous iodide | Hg ₂ I ₂ | — | Green |
| Nessler's reagent | K ₂ [HgI ₂] + KOH | (Used in the test of NH ₄ ⁺ or NH ₃) | |
| Millon's base |  | | |
| Mercury fulminate | 2Hg(CNO) ₂ .H ₂ O | (Explosive) | |



Distinction between Hg_2^{2+} (Mercurous) and Hg^{+2} (Mercuric)**Table 7.21**

| Reagent | Hg^{2+} | Hg_2^{2+} |
|------------------------|---|---|
| NH_4OH | White ppt of HgNH_2Cl $\text{HgCl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{NH}_4\text{Cl} + \text{Hg}(\text{NH}_2)\text{Cl} + 2\text{H}_2\text{O}$ | Black ppt. $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Hg} + \text{Hg}(\text{NH}_2)\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$ |
| KI solution | Red ppt. $\text{Hg}(\text{NO}_3)_2 + 2\text{KI} \rightarrow \text{HgI}_2 + 2\text{KNO}_3$ | Green ppt. $\text{Hg}_2(\text{NO}_3)_2 + 2\text{KI} \rightarrow \text{Hg}_2\text{I}_2 + 2\text{KNO}_3$ |
| Dil. HCl | White ppt. $\text{Hg}_2(\text{NO}_3)_2 + 2\text{HCl} \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{HNO}_3$ | — |

Tin – Sn (stannum)

Tin is known in the form of bronze, its alloy since 300 B.C. in Egypt, India and China.

Ores

Cassiterite or tinstone – SnO_2

Metallurgy**(i) Concentration the ore**

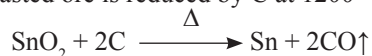
Powdered ore is concentrated by gravity separation method.

(ii) Roasting

Concentrated ore is roasted in inclined revolving furnace. Sulphur, As are removed as oxides, SO_2 and As_2O_3 .

(iii) Reduction

Roasted ore is reduced by C at $1200 - 1300^\circ\text{C}$.

**Purification**

Sn contains Cu, iron, W as impurities. It is refined by

- (a) Liquation method
- (b) Electrolytic method

Liquation method

Sn has low mp (232°C). The metal is melted on the sloping bed of a furnace. Tin melts flows out leaving behind the impurities of Cu, Fe, W.

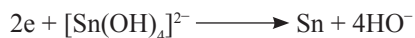
Electrolytic method

| | |
|-------------|------------------------|
| Anode | impure Sn |
| Cathode | pure Sn |
| Electrolyte | a bath of dil. alkali. |

Tin from impure sample dissolves at anode and forms stannite, $[\text{Sn}(\text{OH})_4]^{2-}$ in solution.



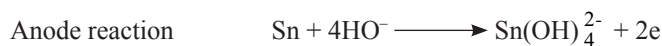
Sn is then deposited at cathode. The reaction is



Tin is above H in electro chemical series, but it deposit due to H – over voltage.

Isolation of Sn from scrap tin

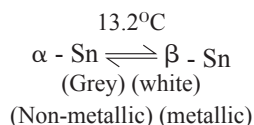
Clean scrap tin is compressed in bundles. It is used as the anode. A sheet of pure tin is made cathode. Electrolytic cell is a bath of dil. alkali. Tin from scrap tin passes into solution at anode as stannite. From this solution, Sn deposits at cathode.

**Uses**

- For electroplating of iron.
- For alloys, bronze, solder and type metal.
- For making tin plates.
- For making containers.
- $\text{Sn} + \text{HCl}$ and SnCl_2 as reducing agent.

Allotropic forms

Tin exists in two allotropic forms, the α - tin and β - Sn. They form an equilibrium



Grey tin is non metallic and has diamond structure while white tin is metallic and has BCC tetragonal structure. If tin is heated above 161°C it becomes brittle. It has rhombic structure ($a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$).

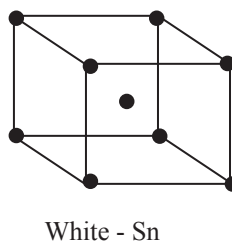
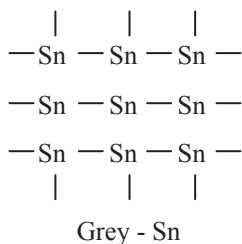


Figure 7.12

When tin is cooled below 13.2°C, its structure changes from metallic to non-metallic i.e., Bcc type to diamond type. This change is followed with a crackling sound which is known as 'tin cry'.

Physical properties

| | | |
|------------------------------------|------------------------------------|---------------------------------|
| (i) Valence orbitals and electrons | | 5s ² 5p ² |
| (ii) Oxidation states +2 and +4 | | |
| (iii) Ionization Energy (ev) | I | 14.5 |
| | II | 39.4 |
| (iv) Electronegativity | | 1.7 |
| (v) Atomic radius (Å) | | 1.4 |
| (vi) Ionic radius (Å) | Sn ⁺⁴ | 0.71 |
| (vii) mp(°C) | | 232.0 |
| (viii) bp(°C) | | 2360.0 |
| (ix) E°(V) | Sn ⁺² /Sn | -0.136 |
| | Sn ⁺⁴ /Sn ⁺² | 0.15 |

As radii of tin is not large and core electrons (18 or 18 + 2) are more, tin compounds have covalent nature.

Chemical reactions

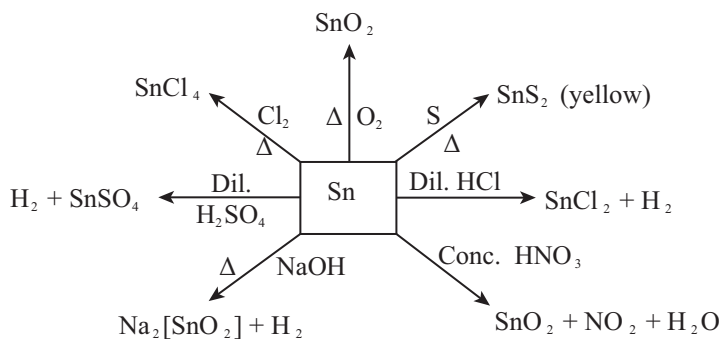
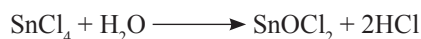
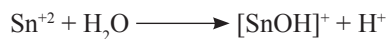


Figure 7.13

- (i) Tin in +2 and +4 oxidation states are amphoteric. Therefore, SnO, Sn(OH)₂, SnCl₂, SnCl₄ etc., dissolve in sodium hydroxide solution.



- (ii) Due to high charge/radius ratio for Sn⁺² or Sn⁺⁴, presence of empty orbitals and coordination unsaturation, tin compounds are hydrolyzed making aq. solution slightly acidic. They also behave as Lewis acids.

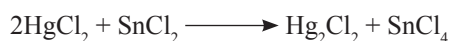


(iii) Tin sulphides SnS and SnS_2 are colored due to charge transfer.



Figure 7.14

(iv) SnCl_2 is a very common reducing agent.



$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ Stannic chloride pentahydrate, is called 'butter of tin'.

Lead (Pb) [Plumbum]

This metal is known since the Vedic period in India. It is widely distributed in nature and is the end product of all natural radioactive series.

Ores

Galena – Pbs

Extraction

1. Concentration

The powdered ore is concentrated by froth floatation process

2. Roasting

The concentrated ore is roasted. The reactions are



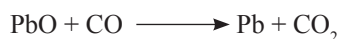
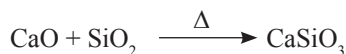
Now the supply of air is cut off more ore is added and then heated. Lead is obtained by self-reduction.



Lead is also extracted by carbon reduction method. It is employed for the ore which is low in lead.

The roasted ore is heated with C and lime in a blast furnace. Lime removes silica (SiO_2), the impurity.

The reactions are

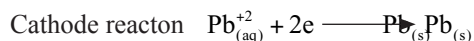
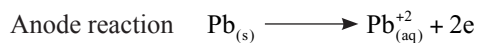


Purification

The extracted lead contains Cu, Ag, Sn, Sb as impurities. It is purified by electrolytic method.

| | |
|-------------|--------------|
| Anode | Impure lead |
| Cathode | Pure lead |
| Electrolyte | Lead acetate |

Reaction



Uses

- Pb is resistant to acid at low temperature and to atmospheric corrosion. Therefore, it is used for cable sheathing and in chemical plants.
- Pb compounds are used in making pigments.
- For alloys:

Type metal – Pb + Sb + Sn
 Solder – Pb + Sn
- In lead storage batteries
- In making bullets.
- Lead containers used to keep radioactive material

The metals

Pure lead is silver white. It has ccp structure. It is soft and can mark paper.

Physical Properties

| | | |
|-------------------------------------|---|--|
| (i) Atomic number | 82 | $_{54}\text{[Xe]}4f^{14}5d^{10}6s^26p^2$ |
| (ii) Valence orbitals and electrons | | $6s^26p^2$ |
| (iii) Oxidation states | | +2 and +4 |
| (iv) Ionization Energy (ev) | IE_2 | 15.03 |
| | | IE_4 42.3 |
| (v) Electronegativity | | 1.8 |
| (vi) Atomic radius (Å) | | 1.54 |
| (vii) Ionic radius (Å) | Pb^{+2} | 1.19 |
| | Pb^{+4} | 0.78 |
| (viii) mp(°C) | | 327.5 |
| (ix) bp(°C) | | 1744.0 |
| (x) E° (V) | $\text{Pb}^{+2} + 2e \longrightarrow \text{Pb}$ | -0.13 |

Note

- The +2 oxidation state is due to inert pair effect. It is more stable. The +4 oxidation state is strongly oxidizing (PbO_2 S.O.A.).

2. The E° shows Pb more reactive (it is above H in electrochemical series) but it is not like that. One of the reasons is insoluble surface coating (PbCl_2 , PbSO_4 etc insoluble).

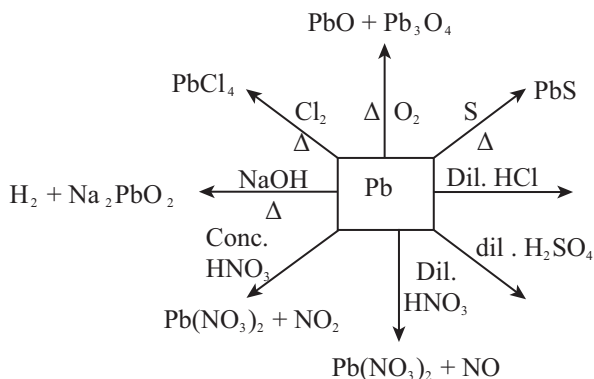


Figure 7.15

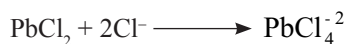
- $\text{Pb}_3\text{O}_4 \equiv 2\text{PbO} \cdot \text{PbO}_2$ i.e., a mixture of Pb^{+2} and Pb^{+4} oxides. It is actually $\text{Pb}_2^{+2}[\text{PbO}_4]$ i.e., plumbus plumbate.
- In spite of having $E^\circ = -0.13\text{V}$ Pb does not react with dil. HCl and $\text{dil. H}_2\text{SO}_4$ due to the formation of insoluble coatings of PbCl_2 and PbSO_4 . However, a powder of Pb (or on heating) reacts with these acids forming H_2 .



- Pb is amphoteric so forms H_2 when heated with NaOH solution.



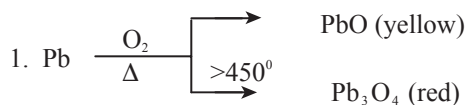
- PbCl_2 is soluble in high conc. of Cl^- ions due to the formation of PbCl_4^{-2} .



Important compounds

Table 7.22

| Compounds | Formula | Common name | Colour | Application |
|------------------------------|--|---------------|--------|--|
| Pb (II)oxide | PbO | Litharge | – | Paint, varnishes, glazing pottery |
| Pb (IV) oxide | PbO_2 | Black lead | Black | Storage batteries |
| Pb (II) + Pb(IV) oxide | Pb_3O_4 | Red lead | Red | Oxidant In anticorrosion paints, in glass and pottery |
| Basic carbonate | 2PbCO_3 + Pb(OH)_2 | White lead | White | Paint pigment |
| Lead chromate | PbCrO_4 | Chrome yellow | Yellow | Pigment |
| Basic lead chromate | $\text{PbCrO}_4 \cdot \text{PbO}$ | Chrome red | Red | Pigment |

Some important reaction

2. When Pb_3O_4 is warmed with HNO_3 the color changes from red to brown (PbO_2).



3. PbO_2 is a strong oxidizing agent with conc. HCl it forms Cl_2 and PbCl_2 .

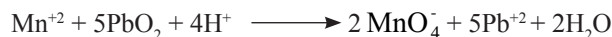


(Cl^- is oxidized to Cl_2).

MnO_2 behaves in the same way.



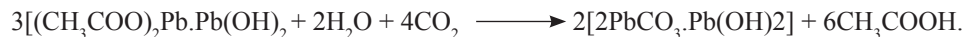
4. Red lead, Pb_3O_4 (or PbO_2) oxidizes Mn^{+2} to MnO_4^- in acid medium (conc. HNO_3)



5. PbSO_4 dissolves in conc. solution of $\text{NH}_4\text{OOCCH}_3$. It is due to the formation of tetraacetato plumbate



6. White lead i.e., basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ is used as a paint pigment. It is prepared in large scale by the action of acetic acid and CO_2 on Pb .

**PRACTICE QUESTIONS****A. Fill in the blanks**

(a) _____ and _____ are obtained by _____ method.

(b) _____ and _____ are found in _____ state.

(c) _____ and _____ form stag.

(d) The chemical methods of ore concentration are _____ and _____.

(e) Iron is not extracted from _____ ore.

(a) Lead is mainly obtained by _____.

(b) When ferric oxide is matrix in alumina it is concentrated _____ by and _____.

(c) The mineral $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ is called _____.

(d) The composition of magnetite is _____.

(e) The composition of malachite is _____.

(f) Horn silver goes in solution by _____ with _____.

- (g) Magnesium and Al are obtained by _____.
- (h) The carbon content of pig iron is _____ among other forms.
- (i) The chemical composition of azurite is _____.
- (j) Sulphides ores are concentrated by _____ which is a _____.
- (k) The carbon content of wrought iron is _____ steel.
- (l) The main reducing agent in blast furnace in the metallurgy of iron is _____.
- (m) In the metallurgy of Zn partial fusion of ZnO with coke is called _____ and reduction of the ore to the molten metal is called _____.
- (n) The most abundant element in the universe is _____.
- (o) Steel is obtained by _____ to wrought iron.
- (p) Tin has _____ and _____ structures both.

B. True or False

- (a) When matrix is present is removed by physical methods.
- (b) Sodium can be obtained by electrolysis of brine.
- (c) Zn can not be refined by distillation method.
- (d) A sodium-potassium alloy has melting point less than zero degree centigrade.
- (e) The composition of ruby copper is Cu_2S .
- (f) Wrought iron has least carbon content.
- (g) Steel can be prepared by adding carbon to pig iron.
- (h) Mg can be obtained by the Dow process from sea water.
- (i) The reduction of a transition metal chloride by Mg to metal is known as Van Arkel method.
- (j) In the metallurgy of Fe, CaCO_3 is added to increase the concentration of reducing agent.
- (k) In the reduction of ZnO by C to Zn, the amount of C is maintained high.
- (l) Magnesite and cuprite are sulphides.

OBJECTIVE-TYPE QUESTIONS

- The process of removing matrix by fusing with flux is known as
 - Calcination
 - Roasting
 - Smelting
 - Sintering
- In the electrolysis of alumina cryolite is added to
 - Increase the electrical conductivity.
 - Minimize the anode effect.
 - Lower the melting a point of alumina.
 - Remove impurities from alumina.
- Which of the following is obtained by aluminothermic reduction?

| | |
|--------|--------|
| (a) Cr | (b) Pb |
| (c) Hg | (d) Ag |
- In the commercial electrochemical process for Al extraction, the electrolyte used is
 - An aqueous solution of $\text{Al}_2(\text{SO}_4)_3$.
 - A molten mixture of Al_2O_3 and Na_3AlF_6 .
 - A molten mixture of $\text{Al}(\text{OH})_3$ and Al_2O_3 .
 - A molten mixture of NaOH and $\text{Al}(\text{OH})_3$.
- The following reaction which represents refining of the metal is known as

$$\text{Ni} + 4\text{CO} \xrightarrow{-60^\circ\text{C}} \text{Ni}(\text{CO})_4 \xrightarrow{-200^\circ\text{C}} \text{Ni} + 4\text{CO}$$
 - Kroll process
 - Mond's process
 - Van Arkel method
 - Zone refining
- The chemical process in the production of steel from haematite ore involve
 - Reduction
 - Oxidation
 - Reduction followed by oxidation
 - Oxidation followed by reduction
- Which of the following order represents correct carbon content?
 - Steel < Wrought iron < Pig iron
 - Wrought iron < Steel < Pig iron
 - Steel < Pig iron < Wrought iron
 - Steel < Cast iron < Wrought iron

8. The metal which is obtained by carbon reduction process is
(a) Mg (b) Ca
(c) Al (d) Zn
9. The compound formed by the combination of the impurities in the ore and the foreign substance added is known as
(a) Flux (b) Gangue
(c) Slag (d) Alloy
10. Pig iron is obtained by reduction of Fe_2O_3
(a) In the presence of C and O_2
(b) In the presence of C and CaCO_3
(c) In the presence of C, O_2 and CaCO_3
(d) In the presence of C only
11. 'Matte' in the extraction of Cu has the composition
(a) Cu_2O , Cu_2S , FeS
(b) Cu_2O , FeO, Cu_2S
(c) Cu_2O , FeO
(d) Cu_2S , FeO, FeS
12. The ore of Zn, calamine is a
(a) Carbonate (b) Sulphide
(c) Oxide (d) Sulphate
13. Siderite is a
(a) Sulphate (b) Carbonate
(c) Oxide (d) Sulphide
14. The composition of cuprite is
(a) CuFeS_2
(b) Cu_2S
(c) Cu_2O
(d) $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
15. Thomas slag is a byproduct of steel industry. It is used as fertilizer and has the composition
(a) $\text{CaSiO}_3 + \text{CaHPO}_4$
(b) $\text{Ca}(\text{HPO}_4)_2 + \text{CaSiO}_3$
(c) $\text{CaSiO}_3 + \text{Mn}_3(\text{PO}_4)_2$
(d) $\text{CaSiO}_3 + \text{Ca}_3(\text{PO}_4)_2$
16. The electrolytic reduction method is used to obtain
(a) Transition metals
(b) Metalloids
(c) Highly electropositive metals
(d) Highly electronegative element
17. Which of the following is not concentrated by froth floatation process?
(a) Zinc blende (b) Pyrolusite
(c) Copperpyrite (d) Pentlandite
18. When a red hot steel is quickly cooled in water, the process is called
(a) Quenching (b) Tampering
(c) Annealing (d) Nitriding
19. Impurities of Pb in silver are removed by
(a) Solvay process
(b) Cyanide process
(c) Parkes process
(d) Kroll process
20. Silver is refined by cupellation process. It removes the impurity of
(a) Pb (b) Cu
(c) Au (d) Zn
21. Spelter is
(a) Pure – Zn (b) Impure – Zn
(c) Zn – Hg (d) ZnO

ANSWERS

1. (c) 2. (a, c) 3. (a) 4. (b) 5. (b) 6. (c) 7. (b) 8. (d) 9. (c) 10. (c) 11. (a) 12. (a)
13. (b) 14. (c) 15. (d) 16. (c) 17. (b) 18. (a) 19. (c) 20. (a) 21. (b).

8

Important Chemical Compounds

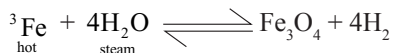
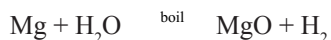


METAL COMPOUNDS

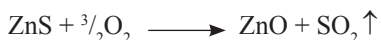
General methods of preparation and their properties.

Oxides

1. By the action of water (or steam) on hot metal



2. By heating metals or metal sulphides in O_2

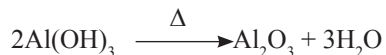


(Formation constant, ΔH_f of Al_2O_3 is most negative of all metals).

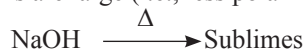
3. By heating hydroxides, nitrates, carbonates, sulphates etc.

Hydroxides

Hydroxides of relatively small metal ions are weak bases. They dehydrate to metal oxides (M^{n+} polarizing and polarize O – H bond).

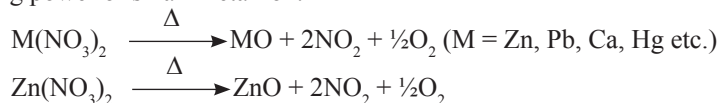


The hydroxides, NaOH, KOH, CsOH etc do not dehydrate, rather sublime on heating. It is because metal ions are large (i.e., less polarizing)



Nitrates

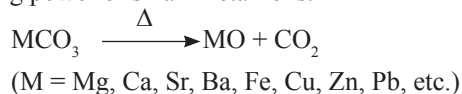
Di and trivalent (i.e., M^{+2} and M^{+3}) metal nitrates decompose on heating to metal oxide. The reason is polarizing power of small metal ion.



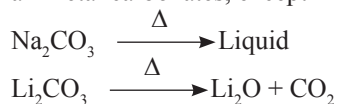
Reason of above reaction is polarizing power of small metal ion Monovalent (i.e., M^+) metal nitrates, except $LiNO_3$ do not decompose on heating to metal oxide. It is because M^+ are large, less polarizing.

Carbonates

Di and trivalent (i.e., M^{+2} and M^{+3}) metal carbonates decompose on heating to metal oxide. The reason is polarizing power of small metal ions.



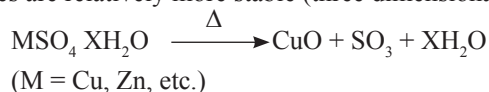
Alkali metal carbonates, except Li_2CO_3 , do not decompose rather melt on heating.



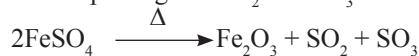
This reaction takes place, as Li^+ is small and polarizing.

Sulphates

Sulphates are relatively more stable (three dimensional anion) and decompose on heating to metal oxide.



Ferrous sulphate gives SO_2 and SO_3 both.



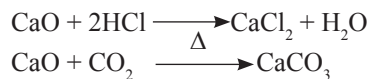
Properties

1. Oxides are basic. The base strength depends on size of the metal ion.

Large $M^{n+} \longrightarrow$ Oxide more basic

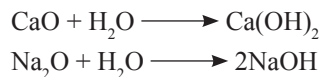
Small $M^{n+} \longrightarrow$ Oxide less basic

2. They form salt with acids and acidic oxides.



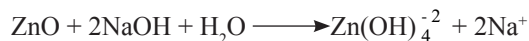
Stability of such salts depends on the gap of acidic and basic nature of the oxides.

3. Many oxides (Ca, Sr, Ba and Group-1) dissolve in water to form hydroxides.



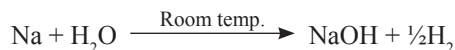
Transition metal (Fe, Cu, Cr, V etc.) and p-block metal (Al, Sn, Pb etc) oxides do not dissolve in water.

4. Amphoteric oxides dissolve in hydroxide bases.



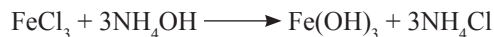
Hydroxides

- Some oxides dissolve in water to give hydroxides. (Reaction are given in oxides)
- Reactive metals (Na, K, Rb, Cs etc) react with water to give hydroxides.



(it is an explosive reaction, due to its high exothermicity)

- Water insoluble hydroxides [$\text{Fe}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$ etc.] are obtained by reaction between soluble salt of the metal and NH_4OH (aq, NH_3).



Properties

- Metal hydroxides in general are basic. Their basic strength depends on the radius of the metal ion. Large M^{n+} hydroxides are more basic and small M^{n+} hydroxides are less basic.



- Some metal hydroxides are amphoteric. They react with acids as well as bases.



That is, amphoteric hydroxides dissolve in strong bases like NaOH, KOH etc.



Those hydroxides are amphoteric in which M – OH and O – H bonds are almost equal in reactivity (See Chapter on Chemical Reactions.)

Sodium Hydroxide NaOH (Caustic Soda)

Sodium hydroxide is an important substance used in industry, and as laboratory reagent. Therefore, it is produced in tones.

Methods of Manufacturing of NaOH

1. Castner – Kellner process

In this method NaOH is produced by electrolysis of brine (saturated solution of NaCl).

| | | |
|-------------------|---|----------|
| Electrolytic cell | : | Iron |
| Electrolyte | : | Brine |
| Anode | : | Graphite |
| Cathode | : | Hg |

Electrolysis produces Cl_2 at anode and Na at cathode. It combines with Hg and forms sodium amalgam (Na – Hg).

Sodium amalgam reacts with water to form NaOH and H_2 .

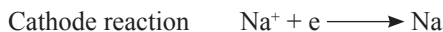


Note: Na or Na – Hg does not react with brine.

2. Nelson cell process

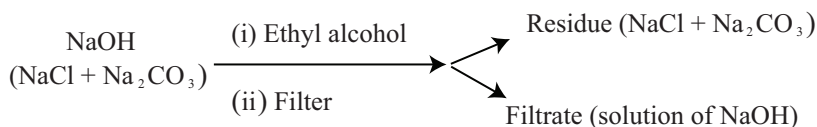
Brine on electrolysis produces NaOH, H_2 and Cl_2 . Cathode and anode are separated by asbestos. Therefore, Cl_2 and NaOH do not react.

| | | |
|-------------------|---|--------------------------|
| Electrolyte | : | Brine |
| Cathode | : | Nicket (perforated tube) |
| Anode | : | Graphite |
| Electrolytic cell | : | Iron |



Pure NaOH

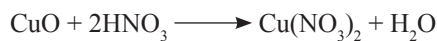
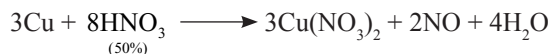
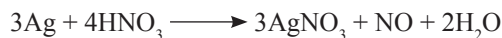
Manufactured NaOH contains NaCl, Na_2CO_3 etc as impurities. Sodium hydroxide is soluble in ethyl alcohol while NaCl and Na_2CO_3 are insoluble in alcohol.



The filtrate is distilled when alcohol distills off leaving behind pure NaOH.

Nitrates

Metal, metal oxide, metal hydroxide and metal carbonate on reaction with HNO_3 form metal nitrates.



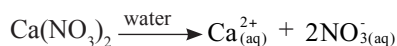
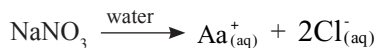
NaNO_3 : Chile Saltpetre

KNO_3 : Saltpetre

AgNO_3 : Lunar caustic

Properties

1. All nitrates are soluble in water.

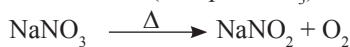


2. Effect of heat on Nitrates

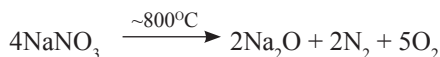
(i) The nitrates of M^{+2} and M^{+3} decompose on heating to give brown fumes of NO_2 .



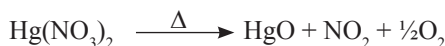
(ii) Alkali metal nitrates (except LiNO_3) decompose to metal nitrite and O_2 .



However, at high temperature they decompose to metal oxide, N_2 and O_2 .

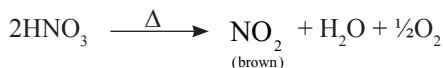


(iii) AgNO_3 and $\text{Hg}(\text{NO}_3)_2$ on heating decompose ultimately to metal.



3. Nitrates + conc H_2SO_4

All nitrates when heated with conc. H_2SO_4 forms brown fumes of NO_2 .



Nitrates are tested as brown ring compound (details in analytical chemistry). The brown ring compound is $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^+$.

4. Nitrates are reduced to NH_3 when heated with Al powder (or Devard's alloy – Al/Zn/Cu) and NaOH solution, NO_3^- is reduced to NH_3 .



Nascent hydrogen produced in the above reaction reduces NO_3^- to NH_3 .



Uses

1. AgNO_3 as laboratory reagent (for tests of halide ions, in silver mirror test for aldehydes).
2. KNO_3 in the manufacture of explosives (nitrates are oxidizing agent). NaNO_3 is hygroscopic. Therefore, it is not used in the manufacture of explosives.

Carbonates

Preparation

1. By neutralizing metal hydroxides by CO_2 .



Excess CO_2 forms soluble CaHCO_3 .

2. By thermal decomposition of bicarbonates (i.e., hydrogen carbonates).



3. By the action of Na_2CO_3 on soluble metal salts.

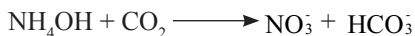


However, soluble salts of Mg^{+2} , Fe^{3+} , Cu^{+2} , Zn^{+2} , Hg^{+2} , Pb^{+2} etc. form basic carbonates with Na_2CO_3 . It is due to hydrolysis of CO_3^{2-} (conjugate base of the weak carbonic acid, H_2CO_3).

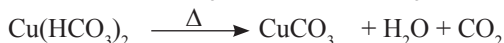


Carbonates of these metals are obtained as:

- (i) Metal salt solution is saturated with aq NH_3 and CO_2 is passed in it. It produces bicarbonate. When this solution is heated metal carbonates precipitate.



- (ii) Alternatively soluble salt of the metal when heated with NaHCO_3 , metal carbonate precipitates.



Sodium Carbonate (Na_2CO_3)

(Washing soda $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)

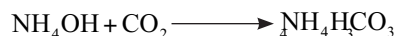
It is of wide commercial application. Therefore, it is manufactured in large amounts.

Manufacture of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

1. Solvay Ammonia Soda Process

This method uses brine (saturated solution of NaCl) for Na_2CO_3 .

Brine is saturated with NH_3 and CO_2 is passed in it. It produces NH_4Cl and NaHCO_3 . The solution on cooling and crystallization gives crystals of NaHCO_3 as it is less soluble than NH_4Cl . Sodium hydrogen carbonate on heating gives Na_2CO_3 .

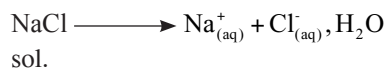


Note

Like NaHCO_3 , potassium bicarbonate (KHCO_3) cannot be produced by Solvay process as it is much more soluble than NaHCO_3 .

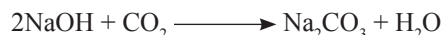
2. Electrolytic method

Brine on electrolysis gives NaOH . When CO_2 is passed into NaOH , sodium carbonate is formed.



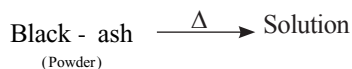
Anode reaction

Cathode reaction



3. Le-Blanc method

When salt cake (Na_2SO_4), lime stone (CaCO_3) and coke (C) are heated strongly, it produces a mixture ($\text{Na}_2\text{CO}_3 + \text{CaS}$) which is known as black ash. Powdered black ash is thoroughly mixed with water and filtered. The filtrate on evaporation gives crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

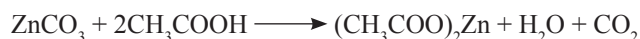


Note

(i) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is called Washing Soda.

Properties

1. Most of the carbonates are insoluble in water.
2. Only Gr 1 carbonates, M_2CO_3 ($\text{M} = \text{Li}$ to Cs) and $(\text{NH}_4)_2\text{CO}_3$ are soluble in water.
3. All carbonates are decomposed by even dil. acids to CO_2 .



Even H_2O_2 can decompose Na_2CO_3

**4. Thermal effect**

(a) Except Li_2CO_3 , other alkali metal carbonates are thermally stable. Melt on heating before decomposition.



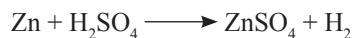
(b) Carbonates of M^{+2} and M^{+3} , decompose on heating to M – oxide and CO_2 .



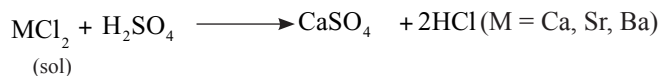
(c) Carbonates of Hg^{2+} and Ag^+ decompose to Hg and Ag on heating.

**Sulphates****Preparation**

1. Metal, metal oxide, metal hydroxide, carbonates, nitrates and chlorides on reaction with H_2SO_4 form sulphates.



2. Insoluble sulphates CaSO_4 , SrCO_4 , BaSO_4 and PbSO_4 can easily be precipitated from their soluble salt solution.



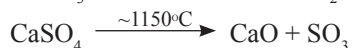
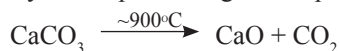
Properties

- (i) Most of the sulphates are soluble in water.

Insoluble sulphates CaSO_4 , SrSO_4 , BaSO_4 , PbSO_4

- (ii) Sulphates (tetrahedral ion) are relatively more stable compared to carbonates and nitrates (planar ions)

They decompose at higher temperature.



Ferrous sulphate decomposes to form SO_3 and SO_2 both.



- (iii) Sulphates generally crystallize with water molecules.

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ White Vitriol

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ Green Vitriol

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Blue Vitriol

- (iv) Sulphates are reduced by C (or Na) to metal sulphides on strong heating.

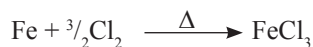
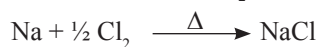


Chlorides

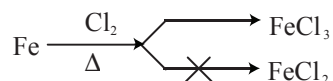
Preparation

Chlorides can be prepared:

- (i) By heating metal and Cl_2

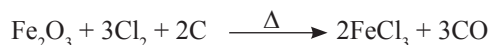


Metals which show variable oxidation states form their chloride in higher oxidation state.



- (ii) By heating metal oxide, C and Cl_2





(iii) By the action of HCl on metal, metal oxide metal hydroxide and metal carbonate.



(HCl forms chloride in lower oxidation state with metals which show variable oxidation state).



Most important is NaCl. It is called common salt or table salt. Pure NaCl is not hygroscopic. But common salt is because of the presence of MgCl_2 in it (Mg^{+2} ion is small).

Properties

(i) Most of the chlorides are soluble in water

Insoluble chlorides: AgCl , PbCl_2 , Hg_2Cl_2

(ii) Most of the chlorides are hygroscopic.

(iii) With conc. H_2SO_4 , chlorides form HCl on heating.



(iv) Ionic chlorides when heated with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 form deep red vapours of chromyl chloride CrO_2Cl_2 .



(Details of this reaction will be found in the Chapter, Analytical Chemistry).

Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

When chromite [$\text{Fe}(\text{CrO}_2)_2$] is fused with Na_2CO_3 in air (or NaNO_3) sodium chromate Na_2CrO_4 , is formed.



The fused mass is extracted with water and filtered. The filtrate is concentrated and acidified with H_2SO_4 . It produces $\text{Na}_2\text{Cr}_2\text{O}_7$.



This solution is concentrated and then saturated with KCl. Orange crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ separates out.

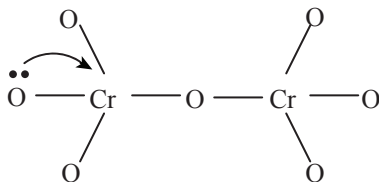


Sodium dichromate is hygroscopic but not the $\text{K}_2\text{Cr}_2\text{O}_7$. Therefore, $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{Na}_2\text{Cr}_2\text{O}_7$.



Properties

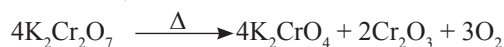
- (i) It is orange crystalline solid. Soluble in water, colour is due to charge transfer.

**Figure 8.1**

- (ii) With alkali (i.e., $\text{pH} > 7$) it turns yellow due to the formation of chromate.



- (iii) When $\text{K}_2\text{Cr}_2\text{O}_7$ is heated it gives O_2 .



But $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating gives N_2 .



(Orange) (Green)

- (iv) Solid $\text{K}_2\text{Cr}_2\text{O}_7$ with conc. H_2SO_4 forms a red solution. The red is dichromic acid.



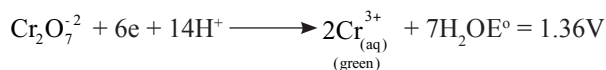
When the solution is concentrated bright orange (or red) crystals of CrO_3 are formed.



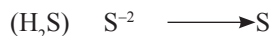
That is $\text{K}_2\text{Cr}_2\text{O}_7$ is dehydrated by conc. H_2SO_4 to bright orange solid CrO_3 . The $(\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4)$ mixture is used for cleaning glassware as it is highly oxidizing.

(v) $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidizing agent

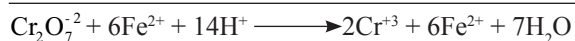
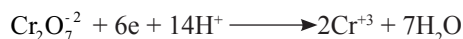
$\text{K}_2\text{Cr}_2\text{O}_7$ is a good oxidizing agent in acid medium and reacts as



It oxidizes:



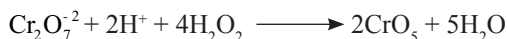
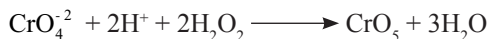
Reactions



Thus SO_2 and H_2S turn orange solution of $\text{K}_2\text{Cr}_2\text{O}_7$ (acidic) to green due to the reduction of $\text{Cr}_2\text{O}_7^{2-}$ ion to $\text{Cr}^{+3}_{(\text{aq})}$.

(vi) **$\text{K}_2\text{Cr}_2\text{O}_7$ as qualitative reagent**

- (a) Chromyl chloride test: Details is given in analytical chemistry chapter (i.e., salt analysis).
 (b) To test H_2O_2 : $\text{K}_2\text{Cr}_2\text{O}_7$ (or K_2CrO_4) in acid solution + amyl alcohol, when treated with H_2O_2 , CrO_5 is formed. It dissolves in amyl alcohol making deep blue solution.



CrO_5 is not stable in aq. medium and decomposes to Cr^{+3} and O_2 .



(vii) **$\text{K}_2\text{Cr}_2\text{O}_7$ as quantitative reagent**

The acidic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is an oxidizing agent. The solution is a primary standard as:

- (a) $\text{K}_2\text{Cr}_2\text{O}_7$ prepared very pure.
 (b) Solution of $\text{K}_2\text{Cr}_2\text{O}_7$ stable.
 (c) The solution is much less readily reduced by organic substances.
 (d) Not affected by light.

The standard solution is used with redox indicator (i.e., internal indicator) to determine end point. Sodium or barium diphenylamine sulphonate is common indicator (0.2% aq. solution). It is generally used to estimate Fe in a sample (Mohr salt or Haematite etc.).

Structure of $\text{Cr}_2\text{O}_7^{2-}$

The structure involves two tetrahedral joined through O – atom. Cr is sp^3 in $\text{Cr}_2\text{O}_7^{2-}$. The structure is

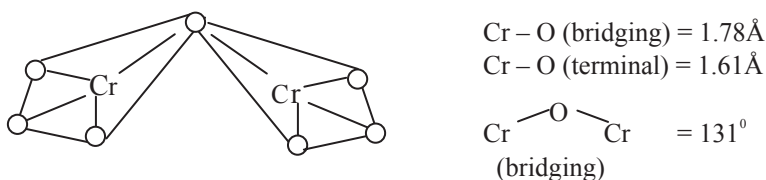
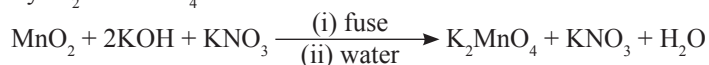


Figure 8.2

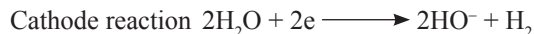
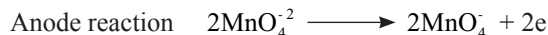
The Cr – O bonds have multiple bond nature due to (d – p) interaction.

Potassium permanganate (KMnO_4)

When MnO_2 (Pyrolusite) is fused with KOH and KNO_3 (O.A.) K_2MnO_4 (green) is formed. It (K_2MnO_4) is oxidized by Cl_2 to KMnO_4 .



Oxidation of K_2MnO_4 may be caused electrolytically (better).



Oxidized solution on concentration gives violet (deep purple) crystals of KMnO_4 (The crystals however, appear almost black).

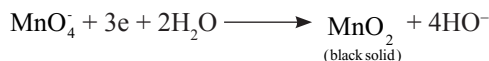
Properties

- (i) Violet solid colour is due to charge transfer.
- (ii) KMnO_4 is soluble in water and the solution is red violet.
- (iii) KMnO_4 is widely used as a laboratory oxidizing agent. It is oxidant in neutral, acid and basic solutions. The reaction are:

(a) In acid medium



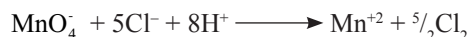
(b) Neutral or dil. alkali



(c) conc. alkali



Hydrochloric acid (HCl) is not used to create acid medium as MnO_4^- oxidizes Cl^- to Cl_2 ($\text{Cl}^- \rightarrow \text{Cl}_2$, $E^\circ = 1.34\text{V}$).



In acid medium MnO_4^- oxidizes,



and itself is reduced to Mn^{+2} . Therefore, pink solution of KMnO_4 is decolourized in all of the above reactions. In the case of S^{-2} , white S precipitates.

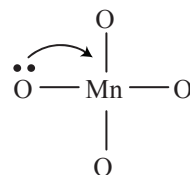
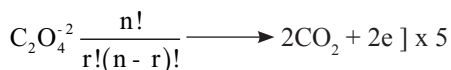
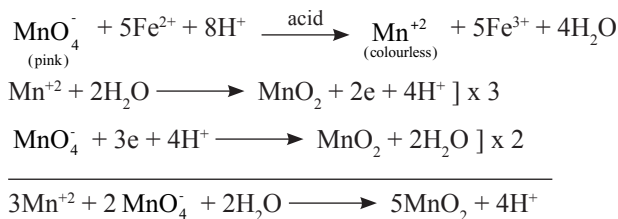


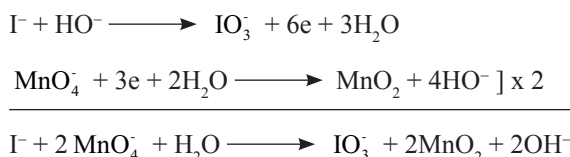
Figure 8.3

Other reactions can be written in the same way.

FeSO_4 solution (light green) decolourizes MnO_4^- solution in acid medium. But if excess MnO_4^- is added a black ppt. is formed. It is due to oxidation of Mn^{+2} to MnO_2 .



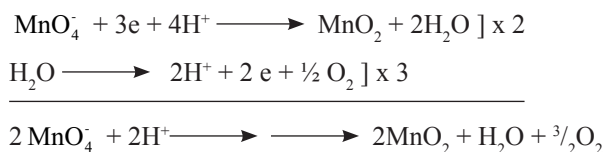
In alkaline solution iodide (I^-) is oxidized by MnO_4^- to iodate (IO_3^-)



(iv) KMnO_4 as volumetric reagent

Standard acidic solution of KMnO_4 is oxidizing agent and is used as a volumetric reagent. But it is a secondary standard (not a primary standard like $\text{K}_2\text{Cr}_2\text{O}_7$), because KMnO_4 converts to MnO_2 in water and oxidizes H_2O to O_2 . The reaction is, however, very slow.

($\text{H}_2\text{O}/\text{O}$ $E^0 = -1.23\text{V}$, $\text{MnO}_4^-/\text{MnO}_2$, $E^0 = +1.70\text{V}$)



It is for the above reason; KMnO_4 solution in volumetric analysis is standardized before every use.

Titration with KMnO_4 solution does not require indicator. It acts as a self-indicator because even a drop of dil. KMnO_4 imparts pale pink colour to the solution.

It is used for the estimation of iron, H_2O_2 , NO_2^- , MnO_2 (in pyrolusite) etc.

Structure of MnO_4^-

This ion is tetrahedral. Mn is either sp^3 or sd^3 hybridized. The hybrid may be taken as a mixture of sp^3 and sd^3 .

Uses

- As oxidizing agent in volumetric analysis.
- As Bayer's reagent (1% alkaline solution of KMnO_4) to detect $\text{C}=\text{C}$.
- As bleaching agent (bleaches wool, silk, cotton etc.).
- As disinfectant for water.

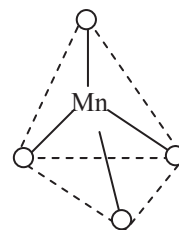


Figure 8.4

NON-METAL COMPOUNDS

Ozone (O_3) [Trioxygen]

Ozone is an allotrope of dioxygen (O_2). It is symmetrical, trigonal planar in structure and is V – Shaped (or bent). Central O – atom is sp^2 hybridized.

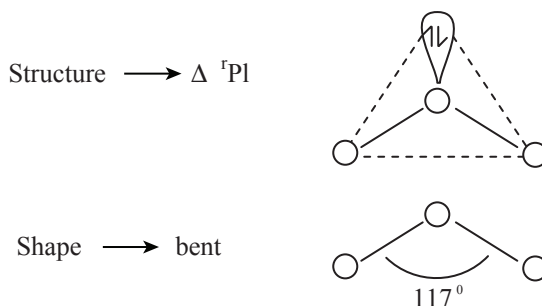


Figure 8.5

The O – O bond distance is 1.28\AA in O_3 . It is intermediate between O – O single bond distance (1.49\AA) and double bond distance (1.21\AA). Thus O_3 has considerable double bond nature and is best represented by a resonance structure,

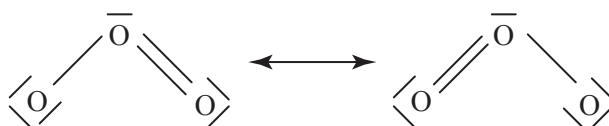


Figure 8.6

One O – O bond in O_3 is coordinate covalent bond

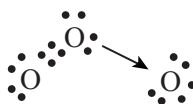


Figure 8.7

Due to the coordinate covalent bond and bent shape, O_3 molecule is polar (unlike for a homonuclear system) and has dipole moment.

Preparation

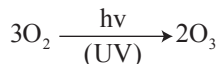
1. Ozone is produced when silent electric discharge is passed in O_2 .



The apparatus used is known as ozoniser.

Pure O_3 can be obtained by fractional liquefaction of $O_2 - O_3$ mix. It is a deep blue explosive liquid.

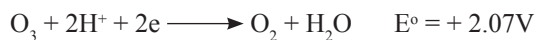
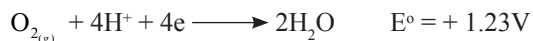
2. The action of ultraviolet light on O_2 produces O_3 in the upper atmosphere, a photochemical reaction.



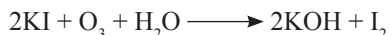
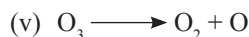
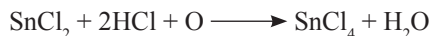
The maximum conc. of O_3 is at an altitude of ~ 25 km. It is known as said O_3 umbrella and protects earth's surface from harmful UV-radiation ($220 - 290$ nm).

Properties

1. O_3 is pale blue gas having fishy smelle.
2. It condenses to a deep blue liquid (bp 161.2k) and to a violet black solid (mp. 80.6k).
3. It is thermally and photochemically unstable $2O_3 \longrightarrow 3O_2$.
4. Ozone is a powerful oxidizing agent, stronger than O_2 . In acid solution oxidizing agents stronger than ozone are F_2 , atomic oxygen, HO radical and few others. It can be seen from reduction potentials.



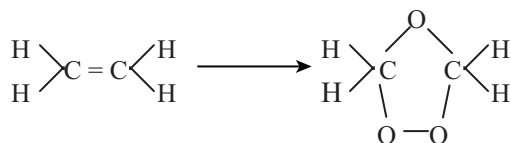
Thus among common oxidizing agents O_3 is second only to F_2 .

Ozone oxidizes**Reactions**

This reaction is quantitative. O_3 may be estimated quantitatively by liberation of I_2 (from thiosulphate titration).

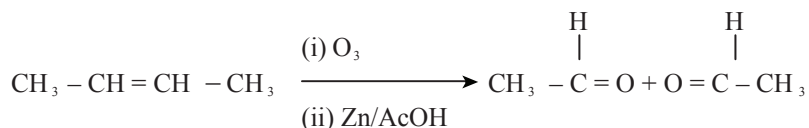
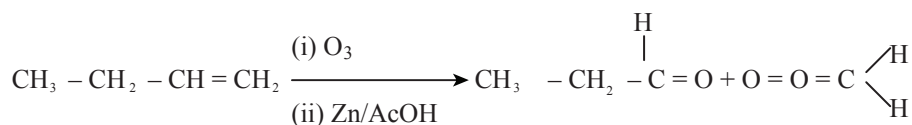
5. Addition reaction of ozone

O_3 adds to $>C=C<$ and $-C\equiv C-$. The product is called ozonide.



It can be used to determine number and position of double bonds.

Also, ozonides are decomposed by $Zn/AcOH$ etc., to give carbonyl compounds. The whole reaction is said ozonolysis. It may be used to locate the position of double bond in a carbon chain.



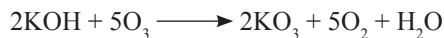
6. Ozone as bleaching agent

Ozone is a bleaching agent. Its bleaching action is due to oxidation. Bleaching is permanent.



Coloured substance + O \longrightarrow Colourless substance

7. Ozone reacts with KOH to produce potassium ozonide KO_3 .



KO_3 is an orange solid. It is paramagnetic due to the paramagnetic ion O_3^- (19 i.e., odd electrons in)

Uses

- (i) As an oxidizing agent.
- (ii) In counting the number of double bond and locating their position in a carbon chain.
- (iii) As bleaching agent.
- (iv) In sterilizing water.
- (v) For purifying air.

Hydrogen peroxide (H_2O_2)

The hydride of oxygen or oxide of hydrogen, H_2O_2 is named hydrogen peroxide (O – O bond is called peroxide bond).

Hydrogen peroxide has a structure similar to a open book i.e., both H-atoms are in different planes.

The O – O distance is 1.49\AA and O – H distance is 0.97\AA . In the crystal, the dihedral angle is reduced to 90.2° due to H – bonding. (The skew structure of H_2O_2 is due to repulsion between the OH moiety).

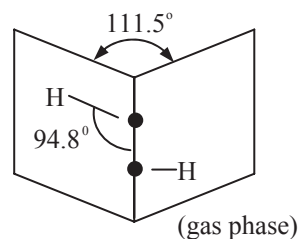


Figure 8.8

Preparation

1. Lab method

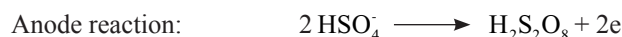
It is prepared by the action of cold dil. H_2SO_4 on Na_2O_2 or BaO_2 .



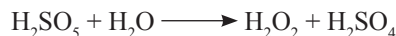
2. Large scale preparation

(a) From H_2SO_4 or (NH_4 – Sulphate + H_2SO_4) sol.

Electrolytic oxidation of H_2SO_4 produces peroxodisulphuric acid which is hydrolysed to H_2O_2 . It is old and expensive method.



Anode solution on reaction with H_2O gives H_2O_2



Fractional distillation of the hydrolyzed solution can give 90 – 98% H_2O_2 .

(b) From 2 – ethyl anthraquinol

The autooxidation of 2 – ethylanthraquinol produces H_2O_2 .

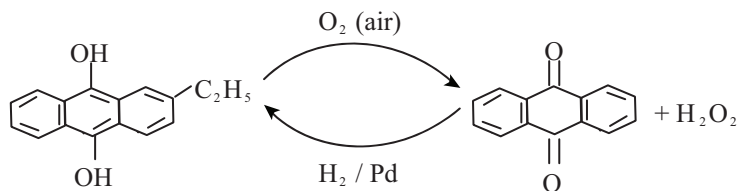


Figure 8.9

Thus the reaction is combination of H_2 and O_2 to form H_2O_2 which is extracted with water. It is concentrated by distillation under reduced pressure, a 30% H_2O_2 solution by weight.

Properties

1. Pale blue liquid, soluble in water.
2. Decomposes vigorously on heating $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ bp cannot be determined at atmospheric pressure. It is determined at reduced pressure (bp 423.2 K). The decomposition is catalysed by metal ions, Fe^{2+} , metal powders (Pt, Au) and MnO_2 etc.
3. H_2O_2 is highly, associated via H-bonding more so than H_2O and is found 40% denser than H_2O .
4. In aq. solution, H_2O_2 is more acidic than water, $\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^-$ $K_{20} = 1.5 \times 10^{-12}$. It forms salts like NaHO_2 and Na_2O_2 .



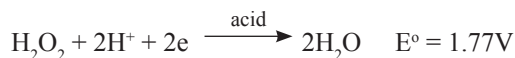
Its acidity is sufficient to decompose carbonates.



5. Redox chemistry

The oxidation state of oxygen in H_2O_2 is -1 . It can decrease (O^{-2}) and can increase also (O_2). Therefore, H_2O_2 is oxidizing as well as reducing agent in both acid and alkaline solution.

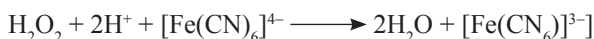
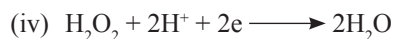
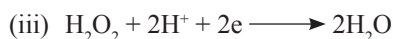
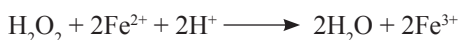
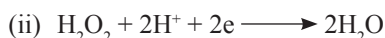
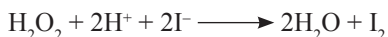
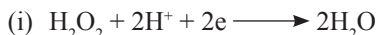
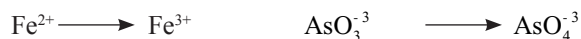
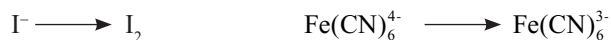
A. H_2O_2 as an oxidizing agent (or oxidant)

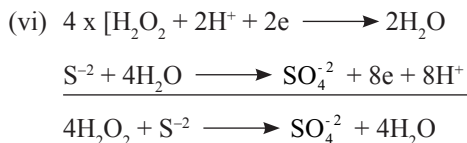
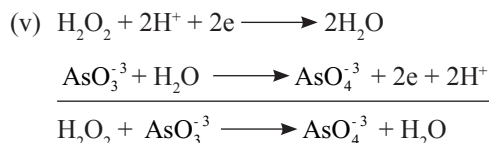
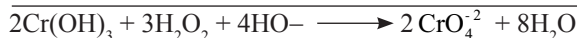
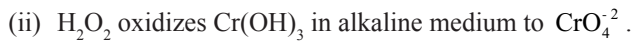
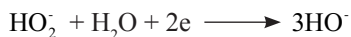
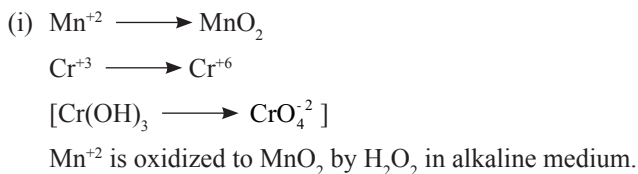


So, H_2O_2 is a strong oxidizing agent in acid medium (or alkaline medium).

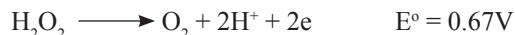
Oxidation in acid

In acid solution it oxidizes,



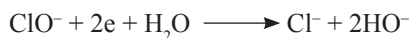
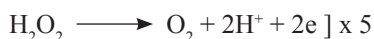
**Oxidation in alkaline medium****B. H₂O₂ as reducing agent**

H₂O₂ is a reducing agent and reacts as

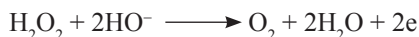


(Here O – atoms goes from –1 to zero oxidation state).

However, it is a reducing agent only for strong oxidizing agents such as MnO_4^- , ClO^- etc.

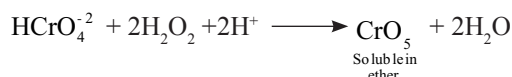


(iii) Ferricyanide ion is reduced to $\text{Fe}(\text{CN})_6^{4-}$ by H_2O_2 in alkaline medium.



Test for H_2O_2

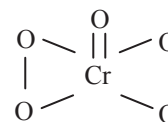
H_2O_2 forms a deep blue colour with acidified solution of CrO_4^{2-} or $(\text{Cr}_2\text{O}_7^{2-})$. The blue colour is due to the formation of CrO_5 (bis peroxochromium oxide). It is stable in ether or amyl alcohol but decomposes rapidly in aq. medium.



CrO_5 decomposes in acidic aq. medium to Cr^{+3} , so colour fades.



Thus CrO_5 has two peroxide groups.



Strength of H_2O_2

H_2O_2 is leveled as volume strength, e.g., 10V, 15V, 20V etc.

The volume strength means, volume of O_2 produced from 1cc H_2O_2 at NTP. Thus, 20V H_2O_2 means that 1cc of the sample produces 20cc O_2 at NTP.

H_2O_2 strength in different units

Table 8.1

| | Units | Equation |
|-------|---|----------------------------|
| (i) | g/l (i.e., conc.) | $\frac{68}{22.4} \times V$ |
| (ii) | % Strength | $\frac{68 \times V}{224}$ |
| (iii) | Normality ($= \frac{\text{conc.}}{\text{Eq. wt.}}$) | $\frac{V}{5.6}$ |
| (iv) | Molarity ($= \frac{\text{conc.}}{\text{Mol. wt.}}$) | $\frac{V}{11.2}$ |

Note V is volume strength of H_2O_2 .

Uses

1. As oxidizing and reducing agent.
2. As bleaching agent (especially in textiles, wood and paper pulp).
3. As disinfectant for cuts (dil. Solution).
4. Highly concentrate H_2O_2 is used as an oxidant for rocket fuel.
5. For the restoration of the colour of old painting. (White lead paint changes to black PbS by H_2S in the atmosphere. H_2O_2 oxidises PbS to White PbSO_4).

Sodium Thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)

Sodium thiosulphate is salt of thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$). The free acid is unstable at ordinary temperature. Decomposition is complicated,



Free acid can be made in the absence of water (e.g., in Et_2O),

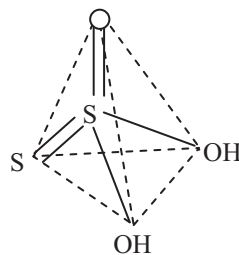
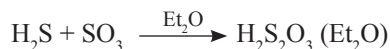
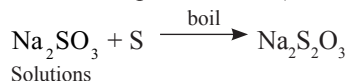


Figure 8.10

Preparation ($\text{Na}_2\text{S}_2\text{O}_3$)

1. When sodium sulphite neutral (or alkaline) solution is boiled with S, $\text{Na}_2\text{S}_2\text{O}_3$ is formed.



Na_2SO_3 on large scale is prepared as



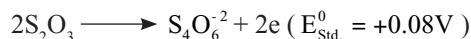
2. Pure $\text{Na}_2\text{S}_2\text{O}_3$ is obtained from a solution of ($\text{NaHS} + \text{NaHSO}_3$). From the mixture $\text{Na}_2\text{S}_2\text{O}_3$ crystallize out.



Sodium thiosulphate crystallize as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. It is called 'Hypo'.

Properties

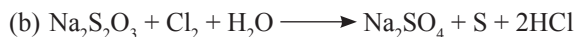
1. It is soluble in water.
2. Thiosulphates ($\text{Na}_2\text{S}_2\text{O}_3$) are decomposed by warming with dil. HCl to give S and SO_2 .
 $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \text{S}$. precipitation of S and liberation of SO_2 is an indication of $\text{S}_2\text{O}_3^{2-}$ ion (which is used in salt analysis).
3. The thiosulphate is a reducing agent of moderate strength.



It reduces,

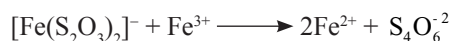


This reaction is basis of iodimetry in volumetric titration (estimation of Cu^{+2}).



As Cl_2 is stronger oxidizing agent than I_2 , sulphate is formed.

- (c) With Fe^{3+} pink ferric thiosulphate is formed. However, the colour rapidly vanishes due to redox reaction.



Important

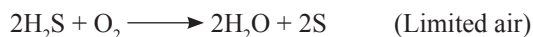


H_2S from Keep's apparatus.

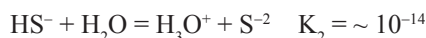
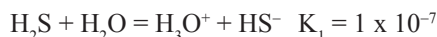
H_2S is an important lab reagent. It is prepared for this purpose in the Keep's apparatus.

Properties

- (i) It is gaseous at normal temperature and has an odour of rotten egg.
- (ii) It burns in air with a blue flame:



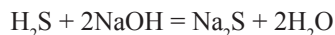
- (iii) It moderately dissolves in water and the solution is a weak acid,



Thus S^{-2} ions are present only in very alkaline solution ($> 8 \text{ M NaOH}$).

- (iv) As H_2S is a dibasic acid, it forms two series of salts.

- (a) Excess alkali



- (b) Limited alkali

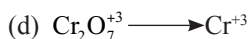
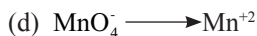
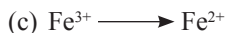
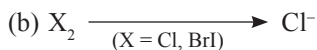
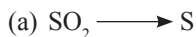


- (v) The I_A and II_A metals form ionic sulphides which are water soluble. However, S^{-2} extensively hydrolyze producing alkaline solution.



- (vi) H_2S as reducing agent

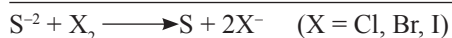
The oxidation state of S in H_2S is -2 , which is minimum for S. H_2S is only reducing agent. It reduces

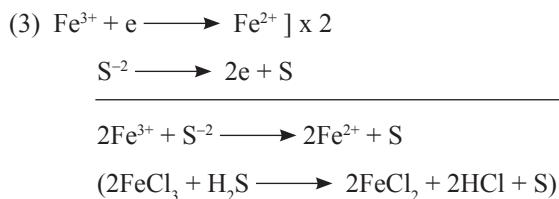


- (1) When SO_2 is passed in aq. Solution of H_2S , S ppts.

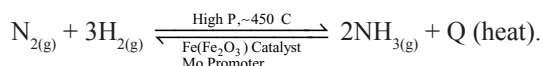


- (2) H_2S reduces Cl_2 , Br_2 , and I_2 to Cl^- , Br^- and I^- .



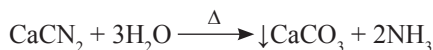
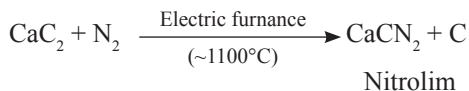
***NH₃ and its reactions***

- (1) Small scale preparation (see group 15)
- (2) Large scale preparation
 - (a) Haber's process



The reaction is exoergic but takes place at high temperature, because of its high activation energy (bond energy in N₂ and H₂ are high).

- (b) Cyanamide process



1. NH₃ is soluble in water. Solubility is through intramolecular H – bonding. The aqueous solution is basic but concentration of NH₄⁺ and HO[–] is very low (NH₄OH is a weak base).



Therefore, aqueous solution is better represented as NH₃(aq).

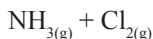
2. The concentrated aqueous solution of NH₃ is called liquor ammonia.
3. Liquefied ammonia is termed as liquid NH₃ i.e., NH_{3(l)}. It is a protic non-aqueous solvent which self ionizes as:



$$k_{-50^\circ} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}.$$

Its dielectric constant at –50° is 23 i.e., a low value. Thus, it is a better solvent for less polar solutes than water. For its reactions see group – I chemistry.

4. Reactions of aq – NH₃ and NH_{3(g)}



- (a) Products of this reaction depend on relative amounts of NH₃ and Cl₂.

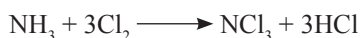
- (i) More NH₃ and less Cl₂.

In this condition products are N₂ and NH₄Cl



- (ii) Less NH₃ and more Cl₂

This reaction gives NCl₃ (an explosive).



(b) NH_3 is oxidized by sodium hypochlorite (NaOCl) to hydrazine (N_2H_4).



Hydrazine is important as alkylated hydrazines are used as potential rocket fuels.

(c) Reaction of aq. NH_3

It can be classified in three main groups.

(i) aq NH_3 as a metal – hydroxide precipitating agent. Except group – 1 and Ca, Sr and Ba, other metal hydroxides are insoluble in water. Therefore when a soluble salt of such metals are treated with aq —NH_3 , their hydroxides precipitates.



(ii) Aqueous NH_3 as a complexing agent.

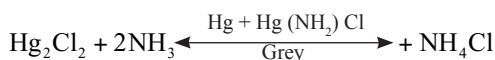
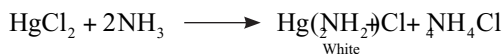
Hydroxides or soluble salts of metals like Cu^{2+} , Zn^{2+} and Ni^{2+} , however, form water soluble ammonia complexes (i.e., hydroxides dissolve in excess aq. NH_3).



Zn^{2+} forms $[\text{Zn}(\text{NH}_3)_4]^{2+}$ but Ni^{2+} gives $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

(iii) Aqueous NH_3 as a reagent for Hg^{2+} and Hg_2^{2+}

Ammonia forms white and black (or grey) precipitates with HgCl_2 and Hg_2Cl_2 respectively.



9

Hydrogen and its Chemistry



The H-atom is the first member of the Periodic Table. It is simplest of all atoms with a nucleus of only one proton (+1 charge) and a single electron in 1s orbital. It is found in more compounds than any other element, water is the most abundant compound of hydrogen. Coal, crude oil and natural gas all contain combined hydrogen, the hydrocarbons.

POSITION IN THE PERIODIC TABLE

Hydrogen is placed with alkali metals in group 1(I_A) and also with halogens in group 17(VII_A). It is due to the fact that H has similarity with Gr1 as well as Gr17 elements.

Table 9.1

| Alkali metals (Gr1) | Halogens (Gr 17) |
|---|---|
| One valence electron ($1s^1$) like Gr1 metals (ns^1) | One electron short than noble gas like halogens (ns^2np^5) |
| H forms halides H_x like M_x (M =alkalimetals, X =halogens). In which H has +1 oxidation state like M^+ ion. | H forms H^- like X^- with I_A and II_A metals. |
| From H_x , H is discharge at cathode like alkali metal ions M^+ | H^- (in MH or MH_2) is discharged at anode like X^- (MX) |

But H is a non-metal. Therefore, it is more logical to place H with – halogens. However, the unique properties of H require a separate place in the periodic table.

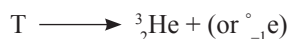
Isotopes of Hydrogen

Atoms having the same atomic number but different atomic mass are known as isotopes. Thus isotopes are due to difference in the number of neutrons. Three isotopes of hydrogen are known. They are protium, deuterium and tritium.

Table 9.2

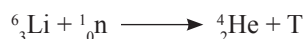
| Isotopes | Proton | Neutrons | Symbol | Abundance |
|---|--------|----------|----------------------|------------------------------|
| Ordinary hydrogen or Protium | 1 | X | H (^1_1H) | 99.984% |
| Heavy hydrogen or Deuterium (Urey 1931) | 1 | 1 | D (^2_1H) | 0.016% |
| Tritium | 1 | 2 | T (^3_1H) | One part T to 10^7 parts H |

Tritium is radioactive and is β – active with a half life of 12.26 yrs.



It is also produced in nuclear transformation such as:

(a) Nuclear reactors



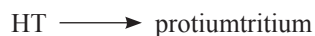
(b) In nature



The isotopes H and D differ appreciably in rates and equilibrium constants of their reactions. It is due to both the mass and nuclear effects.

Normal Physical State

Hydrogen exists at normal temperature and pressure (i.e., in standard state) as a diatomic molecule, H_2 . As there are three isotopes, H, D and T, natural hydrogen can exist as:



i.e., a total of six forms.

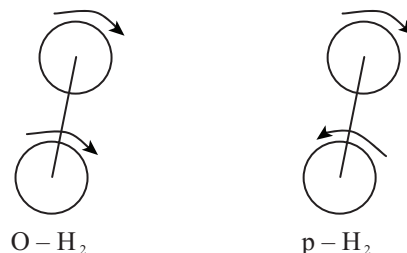
Molecular forms of diprotium (H_2)

Like electrons nuclear particles also have spin. Two protons in H_2 can have their spins parallel or anti-parallel. Thus H_2 can exist in two forms:

(a) ortho – H_2 (O – H_2) spins of both protons parallel

(b) para – H_2 (p – H_2) spins of both protons anti-parallel

Thus O – H_2 and p – H_2 are nuclear spin isomers.

**Figure 9.1**

Such forms are also found in symmetrical molecules having non-zero spin, e.g., D_2 , N_2 , F_2 etc., (i.e., diatomics which are made from atoms having odd atomic numbers).

At room temperature $O - H_2$ 25% is 75% and $-H_2$ 25%. But at lower temperature ($\sim 20K$) pure $p - H_2$ can be obtained.

The $O - H_2$ and $p - H_2$ differ in thermal conductivities, specific. Heat, vapour pressure, melting point and boiling point.

Oxidation States and Bonding

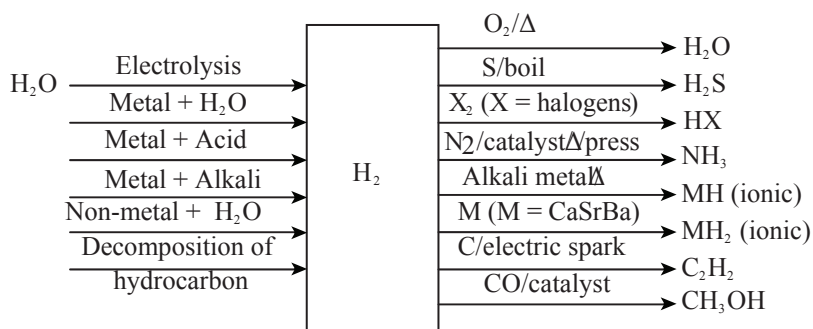
Hydrogen is the smallest atom having a single valence electrons ($1s^1$) and no core electrons. Thus, there is no shielding of the nuclear charge. It makes hydrogen unique in its chemical activity. Oxidation states and modes of bonding are given below:

Table 9.3

| Oxidation State | Comment |
|--|---|
| (a) Zero | It is present in H_2 |
| (b) +1 (H^+ , the hydrogen ion) | <p>It is produced by loss of $1s^1$ electron, i.e., H^+. It is very small, $r_H \sim 1.5 \times 10^{-13} \text{cm}$ (compared to $r_H \sim 10^{-8} \text{cm}$. Thus H^+ has enormously high charge to radius ratio (6.6×10^{12}). Therefore, H^+ never exists alone except in gaseous ions. It is always associated with the solvent.</p> <p>$H_2O + H^+ \rightarrow H_3O^+$</p> <p>The hydration energy being very high. 1091 KJmol^{-1}</p> <p>$HF + H^+ \rightarrow H_2F^+$ etc</p> |
| (c) -1 (H^-) hydride ion | <p>It is formed by gain of an electron to attain $1s^2$ structure of He. The formation of H^- from H_2 is, however, endothermic,</p> <p>$\frac{1}{2} H_2 + e \rightarrow H^-$</p> <p>$\Delta H = +36 \text{ kcal mol}^{-1}$</p> <p>Therefore, H^- exists only in crystalline hydrides of most electropositive metals, the alkali metals (Gr1) and Ca, Sr and Ba (Gr2),</p> <p>NaH, CaH_2 etc.</p> <p>The H^- ion is a very strong reducing agent in aq. medium $H^- + H_2O \rightarrow H_2 + OH^-$.</p> |
| (d) Electron – pair bond ($2c-2e$) | H is very small, has relatively high χ . Therefore, it is mostly covalent in its compounds example. H_2O , NH_3 , H_2O_2 , HF etc. |
| (e) H – bonding | <p>H can act as a bridge to join two electron rich centres, the so called H-bond, this unique behaviour of H is mainly due to absence of core electrons in H.</p> <div style="text-align: center;"> $\begin{array}{c} > N \cdots H-O \\ F \cdots H-F \\ > O \cdots H-O \end{array}$ </div> |
| (f) H-bridge bond or multicentre bonding | It is found in electron deficient compounds like boron-hydrides (B_2H_6) etc. |

Physical Properties of H

| | |
|------------------------------|--|
| (i) Valence electron | $1s^1$ (no core electron) |
| (ii) Atomic radius | 0.37\AA |
| (iii) Ionic radii H^+ | $1.5 \times 10^{-13}\text{cm}$ |
| (iv) Ionization Energy H^- | $2.8 \times 10^{-8}\text{cm}$ 13.6eV |
| (v) Electron affinity | 0.71ev (16.4 kcal) |
| (vi) Electronegativity | 2.1 |

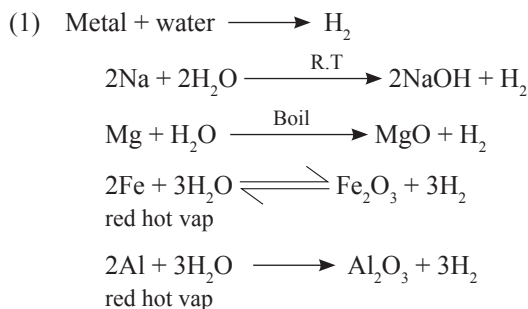
Preparation**Reactions****Figure 9.2****Preparation of H_2 (small scale)**

Hydrogen is prepared mainly by:

- Reducing protonic hydrogen present in water acids or base
- Decomposition of hydrocarbons

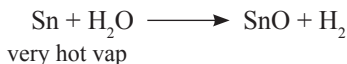
 H_2 by reduction

Elements which have positive oxidation potential (or negative std electrode potential) produce H_2 with water or acids. Those are the elements which are above H in electrochemical series (Na, Mg, K, Ca, Fe etc.).

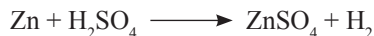


It is seen that the reaction temperature varies with reactivity of the metal (i.e., position of the metal in the activity series) and also on kinetics of the reaction (Al).

Metals below Fe in activity series react very slowly with water, example, Sn.



Metals above H in activity series produce H_2 with acids. Ease of this reaction decreases as the std electrode pot. becomes less negative.



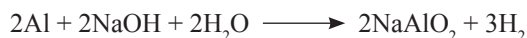
Pure Zn reacts very slowly with acids. It is due to hydrogen over voltage which develops due to deposition of H_2 on Zn. Commercial Zn contains Fe etc. as impurities. Presence of impurities restricts hydrogen over voltage. So, commercial Zn is used to produce H_2 .

Nitric acid is not used to prepare H_2 . It is due to the fact that HNO_3 is strong oxidizing agent and oxidizes hydrogen to H^+ .

However, very dilute HNO_3 forms H_2 with some metals. Example,

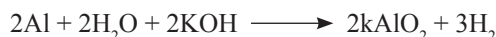


Conc. H_2SO_4 also is not used to prepare H_2 for the same reason.



Uyeno's reaction

Pure H_2 is produced by the action of KOH on scrap Al. This rk. is very fast.

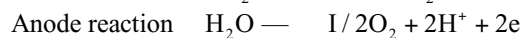
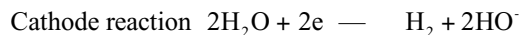
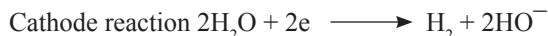


This reaction is used for military purposes.

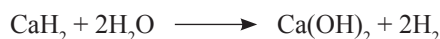


Very pure H_2 is obtained by electrolytic decomposition of water containing small amount of acid or base (water is a poor electrical conductor).

Reactions



Ionic hydrides (NaH , CaH_2 etc.) contain H^- which is a strong reducing agent.



Manufacture of H_2 **Bosch's Process (water gas reaction)**

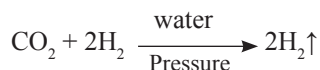
Steam is passed over very hot coke. The product is a mixture of CO and H_2 (water gas or synthesis gas).



Water gas is mixed with steam and is passed over a mixture of $Fe_2O_3 + Cr_2O_3$, the catalyst. Watergas reduces steam to H_2 .



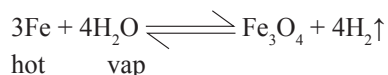
Carbon dioxide is absorbed in water under pressure



Traces of CO present in H_2 is removed by passing through ammoniacal CuCl (CuCl forms $CuCOCl$, thus CO is absorbed).

Lane's Process

Steam is passed over hot iron. The reaction is



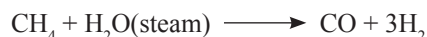
Iron is regenerated by reducing Fe_3O_4 with water gas ($CO + H_2$).

**From Natural gas (Hydrocarbons)**

It is modern method of H_2 manufacture. Diprotium (H_2) is obtained by:

(i) Partial oxidation of hydrocarbon

Natural gas is mixed with steam and passed over a Ni–Cr catalyst at about 700°C . The reactions are



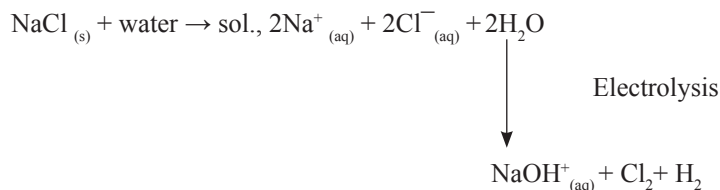
CO_2 and CO are removed from H_2 by passing the gaseous mixture through water at high pressure and ammoniacal CuCl respectively.

(ii) Cracking

H_2 can also be obtained by cracking.

 **H_2 as a by product***(i) In the manufacture of NaOH*

Sodium hydroxide is industrially prepared by the electrolysis of aq. NaCl. In this method H_2 is the by product. The reaction is



(ii) In the isolation of Na from fused NaOH (Castner's process)

H₂ is also obtained as a by product in the Castner's process of manufacture of Na by the electrolysis of fused NaOH.



H₂O produced is decomposed at cathode to form H₂.

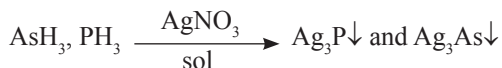
Laboratory Preparation of H₂

It is prepared in the laboratory by the action of dil H₂SO₄ on commercial Zn (not pure Zn, as explained above).

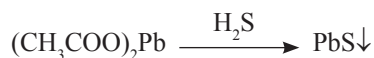


Diprotium (H₂) from the above method has PH₃, AsH₃, H₂S, SO₂ and water vap as impurities. They are removed by passing the gaseous mixture through:

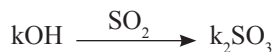
(a) AgNO sol. It removes PH₃ and AsH₃.



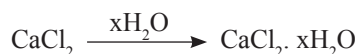
(b) (CH₃COO)₂Pb sol. It removes H₂S.



(c) KOH sol. It removes SO₂



(d) CaCl_{2(s)} (or P₂O₅). It removes water vapour



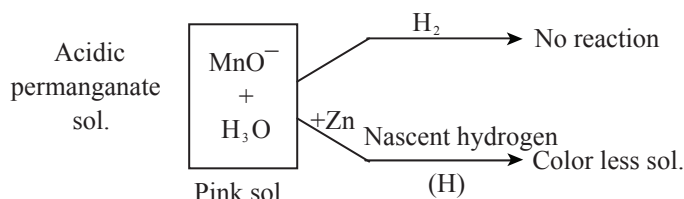
Finally dry H₂ is collected over Hg.

Nascent hydrogen

Atomic hydrogen produced by a chemical reaction in solution is known as "Nascent Hydrogen".



Nascent hydrogen is a stronger reducing agent than diprotium (H₂). It is seen in the following reaction:

**Figure 9.3**

The pink sol. is decolourized due to reduction of MnO_4^- to Mn^{+2} with nascent hydrogen (H) produced by the action of acid on Zn added.



Compounds of Protium (H)

Hydrides

Binary compounds of hydrogen (H) are known as Hydrides, NaH , B_2H_6 , NH_3 , AlH_3 , H_2O , CH_4 etc. They have diverse nature and properties depending on the other element. There are of four types.

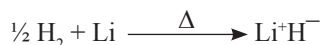
- Saline or ionic hydrides
- Covalent hydrides
- Transition metal hydrides.
- Boarder line hydrides

Ionic (or saline) hydrides

These contain the hydride ion (H^-). Formation of H^- from H_2 is endothermic,



Therefore, highly electropositive metals like Gr1 and Ca, Sr and Ba form ionic hydrides.



- Stability of ionic hydrides decreases with increase in the radius of the metal ion (M^{n+}).
Decreasing order of stability
 $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$ (L.E. effect)
- They have high mp
- Fused hydrides conduct electricity and form H_2 at anode. It shows that they contain H^- ion.
- The H^- ion is a strong reducing agent



- In aq. Medium H^- is strong reducing agent ($\text{H}_2/\text{H}^- = 2.25\text{V}$)

Covalent hydrides

These are made by Be, Mg and p-block elements. Covalent hydrides have polar covalent bond, and molecular lattice.

- (a) Covalent hydrides have low mp and bp
- (b) Gr13 (III_A) elements (B, Al etc.) form electron deficient hydrides (AlH₃, B₂H₆ etc.)
- (c) Gr15 (V_A) hydrides MH₃ are basic, (NH₃, PH₃ etc.)
- (d) Gr16 (VI_A) and Gr17 (VII_A) hydrides are acidic.



Transition metal hydrides

They are diverse in nature having M – H bonds. Some transition metal hydrides are non – stoichiometric, example.



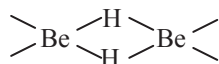
Many of the transition metal hydrides are interstitial. They act as catalyst, Ni/H₂, Pd/H₂ etc.

Pd is very special with respect to reaction with hydrogen. Red hot Pd absorbs (or occlude) large volume of hydrogen when cooled in H₂. This may be used to separate H₂ (or D₂) from He or other gases.

Border line hydrides

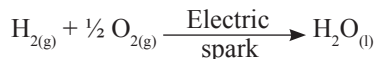
Hydrides of Gr11 (I_B) Cu, Ag, Au, Gr12 (II_B) Zn, Cd, Hg and In and Tl are neither ionic nor covalent. They are in between the two. They are termed as border line hydrides.

Such hydrides are electron deficient, e.g., BeH₂ like (AlH₃)_n. Thus BeH₂ has polymeric structure, having H – bridge.



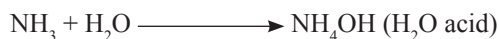
Water

Water (H₂O) is most important compound of hydrogen. It is present as sea water, river water, and rain water and also as ground water. It may be prepared as:



Properties

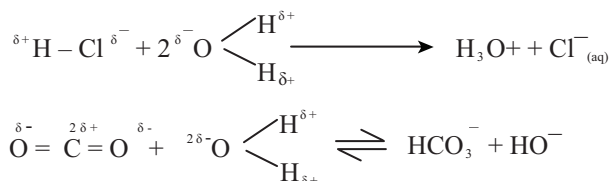
1. Liquid at room temperature and 1 atm.
2. mp of ice (solid water) – 0°C.
3. bp of water 100°C
4. Density at 4°C – maximum 1g/cc
5. Dielectric constant is 82
6. Amphoteric in nature



7. Water is most remarkable of all solvents. It has very high dielectric constant (~ 82), high dipole moment ($\mu = 1.85\text{D}$) and high ability to form H – bond. Therefore, variety of chemical substances (acids, bases, salts, covalent ones etc.) dissolve in water.

(a) Dissolution due to dipole – dipole interaction

Water is a polar molecule. Many polar covalent substances dissolve in water due to dipole – dipole interaction.



(b) Dissolution due to H – bonding

Substances capable of forming H – bond generally dissolve in water such as, alcohols, sugars, NH_3 etc.

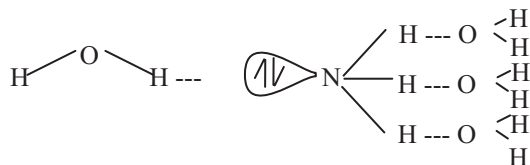
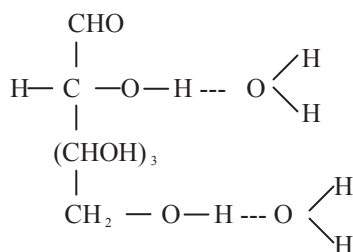


Figure 9.4



(c) Dissolution of Ionic comds (compounds)

Electrostatic interaction (attraction or repulsion) between two ions is given by,

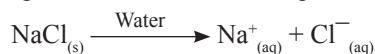
$$V = - \frac{Z_1 \cdot Z_2 \cdot e^2}{D \cdot r}$$

Where, Z_1, Z_2 = charges on the ions

r = distance between the ions

D = dielectric constant of the medium

In air, $D = 1$, so attraction is generally large, e.g., in NaCl , it is $-119 \text{ kcal mol}^{-1}$. But in water, the attractive energy is only $-1.5 \text{ kcal mol}^{-1}$. Therefore, in water solid NaCl does not exist. It dissolves in it. Also, water is a polar molecule. So, the separated ions (Na^+ and Cl^-) exist as hydrated ions, $\text{Na}^+_{(\text{aq})}$ and $\text{Cl}^-_{(\text{aq})}$.



Thus, it can be summarized that many ionic substances dissolve in water due to its high dielectric constant.

Another important factor is lattice energy. In general water solubility condition is

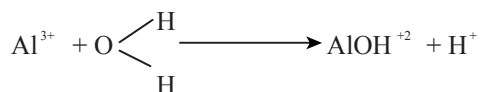
$$LE - HE = -\text{ive}$$

Hydrolysis

Many substances hydrolyze in water, cations as well as anions.

(a) Cation hydrolysis

Small cations (Be^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Cu^{+2} etc.) hydrolyse in water. It is due to high charge to radius ratio. Therefore, aq. Solution of such substances is slightly acidic



(b) Anion Hydrolysis

Conjugate bases of weak acids (N^{3-} , C^{4-} , S^{2-} , CO_3^{2-} , CH_3COO^- etc.) hydrolyse in water. It produces slightly basic solution.



Solution is basic due to higher concentration of HO^- produced in the reaction.

Hydrates

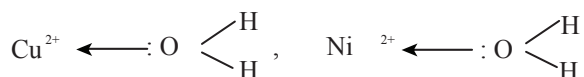
Solids that contain water molecules with molecules of a compound are called hydrates. They are mainly of two types:

- (a) Salt hydrates and
- (b) Water clathrates

Salt hydrates contain water molecules as:

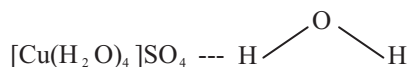
- (a) Coordinated water
- (b) Anion water and
- (c) Zeolite water

Water is a polar molecule, O – atom being the negative end. In addition to this, O – atom has lone pairs. Therefore, water is coordinated to M^{n+} through O – atom,



Such water molecules are called “Coordinated Water”.

The H – atoms in H_2O has δ^+ charge. Thus water is also bound to negative ions in the solid. They are called anion water. It is rare and is found in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. In this hydrate, four water molecules are coordinated water and the fifth one is anion water,



Generally, non-coordinated water molecules are known as water of crystallization.

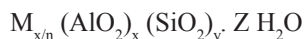
Table 9.4

| Salt hydrate | Coordinated water | Crystal water | Formulation |
|---|-------------------|---------------|---|
| $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | 6 | 1 | $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ | 6 | 1 | $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | X | 10 | It is called tectohydrate |

Salt hydrates are also formed by organic cations such as R_4N^+ , R_3S^+ etc. Such as $[(n - \text{C}_4\text{H}_9)_4\text{N}]^+ \text{C}_6\text{H}_5\text{COO}^- \cdot 39.5 \text{H}_2\text{O}$ and $[\text{Bu}_3\text{S}]^+ \text{F}^- \cdot 20\text{H}_2\text{O}$.

Zeolite water

Zeolites are frame work aluminosilicates. They have the composition



Where n = charge of the cations, Mn^+ (Na^+ , Ca^{2+} , K^+)

The open structures of zeolites have channels and cavities of different sizes (2 to 11 Å in diameter). Water molecules in zeolites are present in these cavities i.e., zeolite water. Thus zeolites can be dehydrated without much affecting the lattice.

Water clathrates

Clathrates are inclusion compounds (Latin, Clathratus meaning ‘enclosed’). They are formed when water is frozen in the presence of Ar, Kr, Cl_2 , SO_2 , CH_4 etc. These small molecules are trapped in the H-bonded structure of water molecules.

Liquid hydrates are also supposed to be formed. Relatively larger molecules like CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$ etc., form liquid hydrates. The anesthetic effect of CHCl_3 thought to be due to the formation of liquid hydrate crystals in brain tissue.

Hard and Soft water

Natural water is either hard or soft.

Water which forms less of lather with soap is known as It is due to dissolved salts, chlorides, sulphates and hydrogen carbonates of Mg^{2+} and Ca^{2+} (i.e., MCl_2 , MSO_4 and $\text{M}(\text{HCO}_3)_2$).

Water which forms enough lather with soap is called soft water.

Soap is Na or K salt of high molecular weight fatty acid such as stearic acid, i.e., $\text{RCOO}^- \text{Na}^+$ ($\text{R} = -\text{C}_{17}\text{H}_{35}$). Calcium and Mg stearates are insoluble in water. Therefore, presence of these ions (Mg^{2+} or Ca^{2+}) precipitates soap (scum) and so hard water does not form lather.

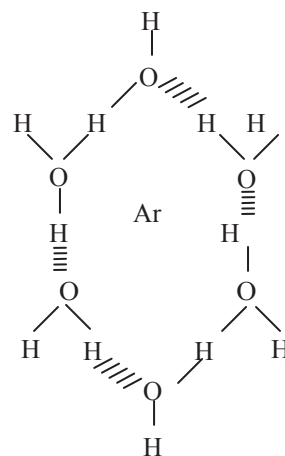
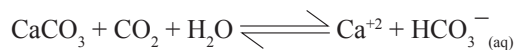


Figure 9.5

Hard water also forms scales (insoluble deposits) in water pipes, boilers etc. Formation of scales in industrial boilers is a great problem, because CaCO_3 is a poor heat conductor.

Causes of Hardness

Lime stone (CaCO_3), a nonsilicate rock is insoluble in water but dissolves in water containing CO_2 due to the formation HCO_3^- .



As atmosphere contains CO_2 ground water dissolves lime stone. Also chlorides and even sulphates dissolve in water making it hard.

Hardness of Water

Hardness of water is of two types.

Temporary hardness

It is due to the presence of hydrogencarbonates (HCO_3^-) of Mg^{2+} and Ca^{+2} [i.e., $\text{M}(\text{HCO}_3)_2$]. It is called temporary as it is removed simply by boiling water (i.e., a physical method).

Permanent hardness

It is due to dissolved chlorides and sulphates of Mg^{2+} and Ca^{+2} (i.e., MCl_2 and MSO_4). It is removed only by chemical methods.

Softening of hardness (Removing hardness of water)

Temporary hardness

It is removed by physical as well as chemical methods.

- (a) Physical method: By boiling hydrogencarbonates convert into insoluble carbonates and precipitates



- (b) Chemical method: By adding lime to hard water.

Lime [$\text{Ca}(\text{OH})_2$] precipitates out MCO_3 ($\text{M} = \text{Mg, Ca}$)



It is a neutralization reaction.

Permanent Hardness

It is due to dissolved chlorides and sulphates of Mg and Ca (MCl_2 or MSO_4). It is removed as follows:

- (i) By reacting hard water with Na_2CO_3 (soda). It (Na_2CO_3) precipitates insoluble MgCO_3 and CaCO_3 .



- (ii) Methods: Ion exchangers are giant molecules. They have ability to trap ions. Thus ions in water (Mg^{2+} , Ca^{+2} , Cl^- , SO_4^{2-}) are trapped in the exchangers.

(a) Inorganic Exchangers

(1) Permutite method

Sodium aluminium mixed silicate is known as “Zeolite”. It is represented as Na_2Z . (Where $\text{Z} = \text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$) and has mobile Na^+ ions in the structure. It exchanges Mg^{2+} and Ca^{+2} ions for Na^+ .



(Where $\text{M} = \text{Mg}, \text{Ca}$)

Thus, Mg^{2+} and Ca^{+2} are trapped in the zeolite, making water soft.

Zeolite is regenerated by treating used one with NaCl solution.



(2) Calgan method

Sodium polyphosphate such as sodium hexametaphosphate, $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ is called “Calgan”. It ties up Mg^{2+} and Ca^{+2} ions present in water. Thus calgan acts as a sequestering agent to form complex with Mg^{2+} and Ca^{+2} ions,

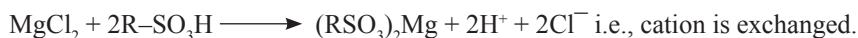


($\text{M} = \text{Ca}, \text{Mg}$)

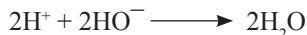
Thus, water is free from Mg^{2+} and Ca^{+2} ions and is soft.

(b) Organic exchangers

Large hydrocarbon frame work is called a resin. Resins containing acidic groups like $-\text{SO}_3\text{H}$, $-\text{COOH}$ works as cation exchangers whereas resins containing $-\text{NH}_3^+\text{HO}^-$ groups are anion exchangers. On passing hard water through exchangers successively ions are exchanged producing H^+ and HO^- .



The H^+ and HO^- ions produced in equivalent amounts react to form H_2O .



Thus soft water results. Such water is called “Deionized Water”.

Exchangers (cation and anion) are regenerated by passing acid and alkali solutions through resins respectively.

**Bad effects of hard water**

Hard water is not fit for:

1. Washing with soap and
2. Use as boiler water.

Hard water forms scum with soap and thus reduces effectiveness of soap.

Hard water in boilers forms scales of CaCO_3 .

It is thermal insulator. Therefore, boilers need large amount of heat and ultimately they may crack. However, hard water is fit for

1. Drinking
2. Washing with detergents

Structure of Water and Ice

Water is very important as much of chemistry including the chemistry of life takes place in water medium. It has many unusual properties, although has low molecular mass; such as

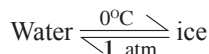
- (i) High boiling point
- (ii) High heat of vaporization
- (iii) High specific Heat

In addition to the above,

- (i) Liquid water has higher density than its solid, the ice, and
- (ii) It has high dissolving power for variety of substances.

The structure of liquid water explains all the above properties. Water is a polar molecule O-atom is partially negative and H-atoms are partially positive. It has an extensive network of H-bonds. The H-bonded structure is loosely bound lattice of H_2O molecules, a pseudo crystalline form. This model has been determined by X-ray scattering studies.

Actually the structure of ice (solid water) reveals structure of water (liquid).



The X-ray examination shows that in ice each H_2O is tetrahedrally surrounded by 4 O-atoms of four H_2O molecules. The H-atoms are in between (two near and the other two at a larger distance).

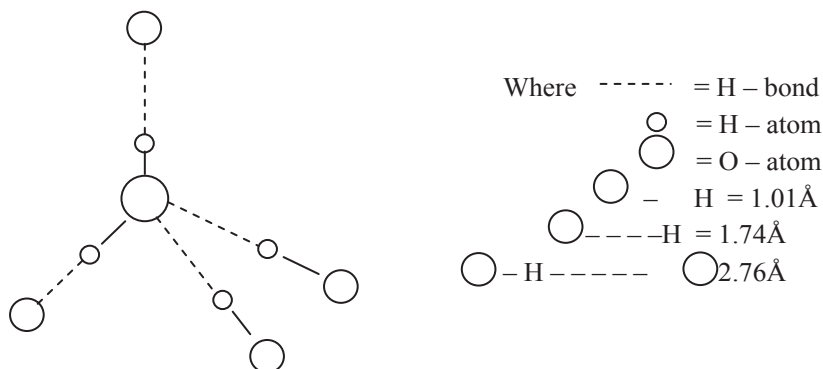


Figure 9.6

Such a bonding continues in all the three dimensions and a structure containing rings result,

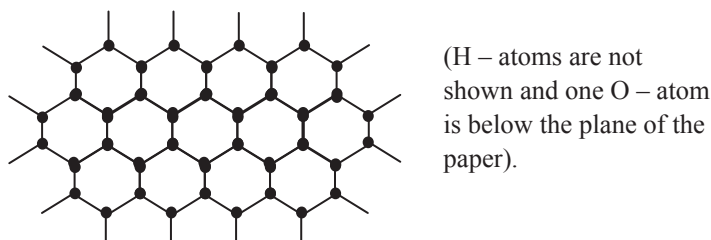


Figure 9.7

The structure is thus a very open structure, having large empty space. The structure of liquid water compares with ice.

Density of Water and Ice

Ice has a very open structure having empty spaces. When ice melts H – bonds break, many of the water molecules get free. They pack in the empty spaces. It leads to decrease in volume and so there is increase in density. Thus, due to more empty space, ice has lower density than water. (Ice floats on water).

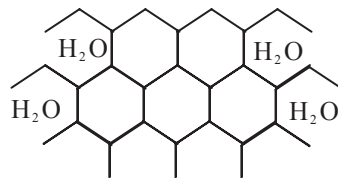


Figure 9.8

Density of water at 4°C (Maximum density)

The density of water at 4°C is maximum (1g/cm³). When ice melts H – bonds break progressively and with rise in temperature there is freedom of movement of H₂O molecules. As the liquid water warms, the density is affected by:

- The breaking of H – bonds resulting into closer packed structure
- The thermal expansion

At 4°C these two effects balance each other and water is at its maximum density. But above 4°C, thermal expansion dominates and density continues to decrease, the normal behavior of a liquid.

However, still there exists H – bonded structure. Even at high temperature (~ 90°C) only a few per cent of the water molecules appear not to be H – bonded.

Heavy water

Water contains oxygen and hydrogen. Both H and O have stable isotopes,

| | |
|----------|---|
| Oxygen | ¹⁶ O, ¹⁷ O, ¹⁸ O |
| Hydrogen | H and D (² H) |

Therefore, natural water is expected to contain H₂O¹⁶, H₂O¹⁷, H₂O¹⁸, D₂O¹⁶, D₂O¹⁷, D₂O¹⁸, HDO¹⁶ etc. However the isotopic abundance of D, ¹⁷O, ¹⁸O are very small and ¹⁷O much less than ¹⁸O. Thus natural water is mainly H₂O¹⁶, D₂O¹⁶ and H₂O¹⁸, which are named as:

| | |
|--------------------------------|---|
| H ₂ O ¹⁶ | Ordinary water |
| H ₂ O ¹⁸ | Enriched water (O ¹⁸ enriched) |
| D ₂ O ¹⁶ | Heavy water |

Heavy water was discovered by Urey, an American chemist (1932)

Production of Heavy water (D₂O)

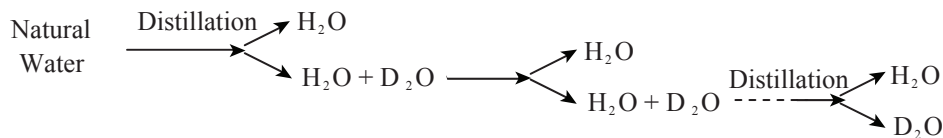
Heavy water is produced from natural water either by

- Continuous distillation or,
- Continuous electrolysis.

Ordinary water (H₂O) and Heavy water (D₂O) differ in boiling points.

| | | |
|------------------|----|----------|
| H ₂ O | bp | 100°C |
| D ₂ O | bp | 101.42°C |

It forms the basis of separation. As the H_2O has low bp it distills first and then D_2O . Distillation is carried out in a long fractionating column ($\sim 13\text{m}$). The distillation process is repeated several times, which ultimately gives water richer in D_2O .

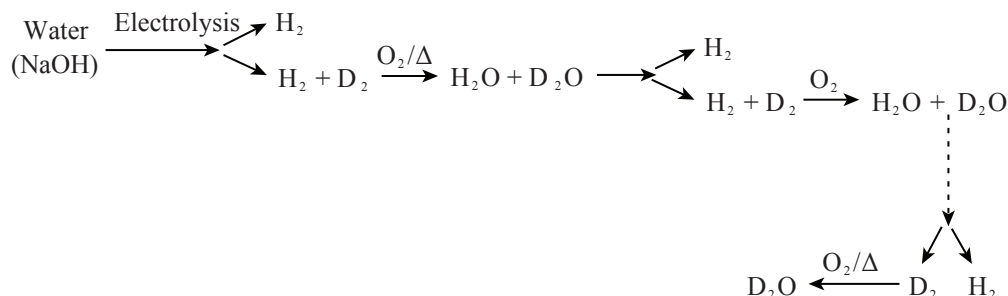


Electrolytic method

This method is based upon the fact that during electrolysis of water, H_2 is liberated faster than D_2 . It is because:

- (i) H^+ is discharge quicker than D^+
- (ii) H combines faster to form H_2 than do D to form D_2 . (H is lighter, so the above effects).

A multistep continuous electrolysis of water containing some NaOH and burning of the product is carried out. Ultimately pure deuterium



(D) Is produced which is burnt in pure oxygen to form D_2O (~100% pure).

This method is main source of D₂O. In India D₂O is manufactured at Nagal in Punjab and at BARC (Bhabha Atomic Research Centre) at Tromby (Mumbai, Maharashtra).

The electrolytic cell used in electrolysis is shown below:

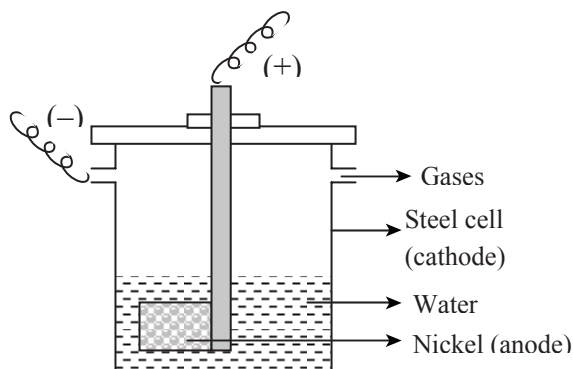


Figure 9.9

Physical properties

The physical properties of D₂O differ slightly from those of H₂O.

Table 9.5

| Properties | D ₂ O | H ₂ O |
|---|-----------------------|-----------------------|
| Freezing point (0°C) | 3.8 | 0 |
| Boiling point (0°C) | 101.42 | 100 |
| Density g/cm ³ (20°C) | 1.106 | 0.998 |
| Temp. of max. density g/cm ³ (0°C) | 11.6 | 4 |
| Ionic product (K _w) at 25°C | 3.0x10 ⁻¹⁵ | 1.0x10 ⁻¹⁴ |
| Dielectric constant (20°C) | 80.5 | 82 |
| Enthalpy of formation (KJmol ⁻¹) | -294.6 | -285.9 |
| Enthalpy of vaporization (KJmol ⁻¹) | 41.61 | 40.66 |
| Solubility of NaCl (g/100 g water) | 30.9 | 35.9 |

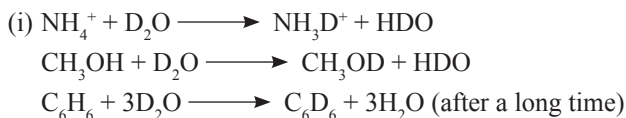
Note

- (a) The difference in physical properties is due to larger mass of D₂O
 (b) As dielectric constant of D₂O is smaller than H₂O, it (D₂O) is a poor solvent for ionic compounds, (see solubility of NaCl).

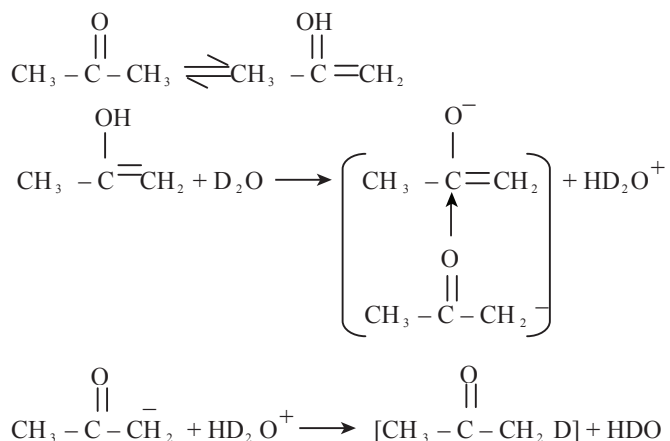
Chemical properties

The chemical reactions of D₂O and H₂O are similar. The most important reactions are isotope exchange reactions.

- (a) $\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2\text{HDO}$
 (b) D₂O exchanges D with compounds having H.



- (ii) The H atoms of an alkyl groups do not exchange directly. But it can happen when there are keto – enol tautomers.



(iii) Deuterated compounds are prepared using D_2O .



(iv) Chemical reactions in D_2O are slow. So, D_2O is toxic (biochemical reactions get slowed down).

Uses

- (a) As moderator in nuclear reactors (because reduces energies of fast fission neutrons without reducing neutron flux).
- (b) In the study of reaction mechanism.
- (c) For preparing deuterated compounds
- (d) As insecticide

PRACTICE QUESTIONS

1. Explain the following in short:
 - (a) Ortho – H_2 and para – H_2 . Are they isotopes of H_2 ?
 - (b) What type of molecules can exhibit ortho and para-forms? Give examples.
 - (c) Sodium, Mg and Fe produce H_2 on reaction with water but in different conditions.
 - (d) Pure Zn is not used for preparation of H_2 , why?
 - (e) Bond energy in H_2 is high.
 - (f) Density of ice is lesser than liquid water.
2. Write balanced chemical equations for the following.
 - (a) Water vapour is passed over red hot Fe.
 - (b) Zinc is placed in an acidic sol. of $KMnO_4$.
 - (c) Al is boiled with NaOH.
 - (d) Water vapour is passed over red hot coke.
 - (e) Water is added in Calcium hydride.
 - (f) H_2 gas is passed in boiling S.
- (g) Electric spark is passed in a mixture of H_2 and coke.
- (h) $K_2S_2O_8$ is mixed with D_2O .
- (i) H_2 is passed over hot CuO.
- (j) Water is electrolyzed using Pt – electrodes.
- (k) To show that water is oxidizing and reducing both.
3.
 - (a) What is hardness of water?
 - (b) What are temporary and permanent hardness?
 - (c) What is calgan, write its chemical formula?
 - (d) More of soap is consumed in hard water, why?
 - (e) Aq. solutions of $AlCl_3$ and Na_2CO_3 are slightly acidic and basic respectively, why?
 - (f) What is heavy water? Write principles to prepare it.

OBJECTIVE-TYPE QUESTIONS

1. In which of the following, H has zero oxidation number?
 - (a) CaH_2
 - (b) NaH
 - (c) PdH_2
 - (d) NH_3
2. Which of the following is a salt like hydride?
 - (a) PdH_2
 - (b) NH_3
 - (c) NaH
 - (d) B_2H_6

3. The ionization energy of H is
 - (a) 1.36 eV (b) 13.6 eV
 - (c) 136 eV (d) 0.136 eV
4. When H_2 and O_2 combine to form H_2O
 - (a) H_2 is oxidized
 - (b) H_2 is reduced
 - (c) H_2 is reduced and O_2 is oxidized
 - (d) H_2 is oxidized and O_2 is reduced
5. Ortho and para hydrogen differ in
 - (a) atomic mass
 - (b) sp in of protons
 - (c) atomic number
 - (d) number of neutrons
6. D_2O is used in nuclear reactors as
 - (a) source of neutron
 - (b) moderator
 - (c) fuel
 - (d) neutron absorber
7. Match the following;

| | |
|-----------------------------|----------------------------|
| (a) Heavy water | (i) Bosch's process |
| (b) Ionic hydride | (ii) An artificial zeolite |
| (c) Hard water | (iii) Oxide of deuterium |
| (d) Manufacture of hydrogen | (iv) Hydrolith |
| (e) Permutit | (v) Scale in boilers |
8. Which of the following gaseous mixture is used in Bosch's process for the manufacture of dihydrogen?
 - (a) Coal gas (b) Producer gas
 - (c) Water gas (d) Natural gas
9. Dihydrogen is evolved by the action of cold dil HNO_3 on
 - (a) Fe (b) Mg
 - (c) Al (d) Cu
10. Tritium is radioactive and decays giving
 - (a) γ – rays (b) α – particles
 - (c) Neutrons (d) β – particles
11. When two ice cubes are pressed over each other they unite to form one big cube. Which of the following forces is responsible to hold them together?
 - (a) Van der Waal's forces
 - (b) Covalent force
 - (c) Hydrogen bond formations
 - (d) Dipole – dipole attraction
12. Out of the following metals, which will give H_2 on heating with NaOH?
 - (I) Zn
 - (II) Mg
 - (III) Be
 - (IV) Al
 - (a) I, II, III, IV (b) II, IV
 - (c) I, II (d) I, III, IV
13. One gram of which of the following hydrides will give maximum H_2 ?
 - (a) LiH (b) NaH
 - (c) KH (d) RbH
14. Manufacture of H_2 by Bosch's process uses the catalyst
 - (a) Ni – Cr (b) $Fe_2O_3 - Cr_2O_3$
 - (c) CaO (d) FeO – MnO
15. Temporary and permanent hardness of water can be removed by reacting water with
 - (a) Na_2CO_3
 - (b) $Ca(OH)_2$
 - (c) $Na_2CO_3 + Ca(OH)_2$
 - (d) $Na_2CO_3 + NaOH$
16. Heavy water is insecticide because
 - (a) Rate of reaction in D_2O is fast,
 - (b) Rate of reaction in D_2O is slow,
 - (c) Boiling point of D_2O is high,
 - (d) Dielectric constant of D_2O is low.
17. Which of the following diatomic will not show ortho – para forms?
 - (a) D_2 (b) N_2
 - (c) O_2 (d) F_2
18. The exhausted permutit is regenerated by percolating through it a solution of
 - (a) Sodium chloride
 - (b) Aluminium chloride
 - (c) Magnesium chloride
 - (d) Calcium chloride
19. Mark the correct statement for permutit.
 - (a) It can exchange Mg^{2+} and Ca^{+2} from hard water,
 - (b) It is an artificial zeolite,
 - (c) It is a Ca – Al orthosilicate,
 - (d) (a) and (b) both.

20. The H – bond is strongest in

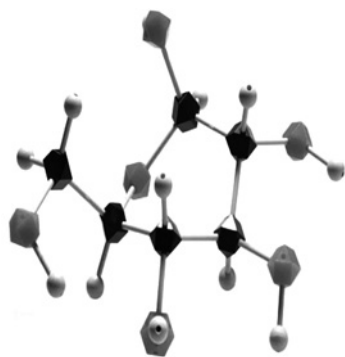
- (a) S – H – – – O
- (b) O – H – – – S
- (c) F – H – – – O
- (d) F – H – – – H

21. Which of the following is a boarder line hydride?

- | | |
|------------------|--------------------|
| (a) NaH | (b) CaH_2 |
| (c) TlH | (d) BeH_2 |

ANSWERS

- | | | | | | | | | | | |
|---------|---------|---------|----------|---------|---------|--|--------|--------|---------|--|
| 1. (c) | 2. (c) | 3. (b) | 4. (d) | 5. (d) | 6. (b) | 7. a – iii, b – iv, c – v, d – i, e – ii | | | | |
| 8. (c) | 9. (b) | 10. (d) | 11. (d) | 12. (d) | 13. (a) | 14. (b) | 5. (c) | 16.(b) | 17. (c) | |
| 18. (a) | 19. (d) | 20. (d) | 21. (c). | | | | | | | |



10

Group 1 (I_A) The alkali metals

Alkaline metals are Li, Na, K, Rb, Ss and Fr. General properties of alkali metals are given below:

Table 10.1

| Property | Li | Na | K | Rb | Cs | Fr |
|--|-----------|-----------|-----------|-----------|-----------|----|
| Atomic No. | 3 | 11 | 19 | 37 | 55 | |
| Electron configurations | He $2s^1$ | Ne $3s^1$ | Ar $4s^1$ | Kr $5s^1$ | Xe $6s^1$ | |
| Atomic mass | 6.94 | 22.99 | 39.1 | 85.47 | 132.90 | |
| Isotopes | 6, 7 | 22,23 | 39,40,41 | 85,87 | 133 | |
| Atomic radii (Å) | 1.23 | 1.57 | 2.03 | 2.16 | 2.35 | |
| Ionic radii (Å) | 0.6 | 0.95 | 1.33 | 1.48 | 1.69 | |
| Ionization energy I (ev) | 5.4 | 5.14 | 4.34 | 4.18 | 3.9 | |
| Electronegativity | 1.0 | 0.9 | 0.8 | 0.8 | 0.7 | |
| Effective nuclear charge (Z^*) | 1.3 | 2.2 | 2.2 | 2.2 | 2.2 | |
| mp ($^{\circ}\text{C}$) | 1337 | 880 | 758 | 700 | 670 | |
| bp ($^{\circ}\text{C}$) | 3.04 | 2.71 | 2.92 | 2.99 | 3.02 | |
| $E^{\circ} (M^+ + e \rightarrow M)$ | 3.4 | 2.76 | 2.28 | 2.28 | 2.28 | |
| Hydrated radii (Å) | 33.5 | 43.5 | 67.5 | 67.5 | 68.0 | |
| Ionic mobility (at infinite dilution, 18°C) | | | | | | |

All the metals crystallize with body centered cubic (BCC) lattice, i.e., coordination number is eight. This structure is adopted due to large atomic radius.

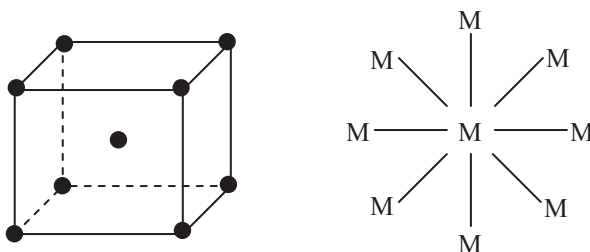


Figure 10.1

It is not the closest packed structure.

As there is only one valence electron per atom, the binding energy in the metal lattice is relatively weak. The metals are, thus, very soft and have low melting points. (A Na – K alloy with 77.2% K has a melting point of -12.3°C). Gaseous metals are diatomic, M_2 , covalently bonded.

Lithium, Na, K and Rb (Silvery White), Cs (Golden – yellow) appearance.

Comments on the Above Table

- (i) Valence – electron — only one (ns^1)[AU].
- (ii) All the metals form unipositive, M^+ ions only. Due to the spherical nature and low polarizability, the chemistry of these elements is principally ionic. However, Li^+ has high charge–radius ratio. Therefore, lithium compounds have some covalent nature also.
- (iii) Core electrons Li^+ 2–electrons, others M^+ 8–electrons.
- (iv) Largest gap in mp and bp is seen between Li and Na. it is due to –
 - (a) Larger radius and
 - (b) More core electrons (8) in Na than Li

As Na has larger radius (than Li) metallic bond strength in Na is weaker (than Li). Also more core electrons in Na results into larger repulsive energy between lattice points. Thus, total cohesive energy in Na is smaller than in Li. Therefore, gap between melting points and boiling points are large.
- (v) Many of the properties vary regularly in this group

(a) *Properties which decrease down the group are*

Table 10.2

| Property | Li | Na | K | Rb | Cs |
|---|----|----|---|----|----|
| Melting point | | | | | |
| Boiling point | | | | | |
| Heat of atomization $\text{M}_{(\text{s})} \rightarrow \text{M}_{(\text{atom})}$ | | | | | |
| Ionisation energy | | | | | |
| Electronegativity | | | | | |
| Hydrated radii | | | | | |
| Hydration energy $\text{M}^+ + \text{aq} \rightarrow \text{M}_{(\text{aq})}^+ + \Delta\text{H}$ | | | | | |
| Strength of covalent bond in M_2 | | | | | |
| Ease of thermal decomposition of MNO_3 and M_2CO_3 | | | | | |
| Heats of formation (ΔH_f) of MF, MH | | | | | |
| Oxides and carbides | | | | | |
| Ease of reaction with N_2 | | | | | |
| Stability of MF and MH | | | | | |
| Solubility of MClO_4 | | | | | |

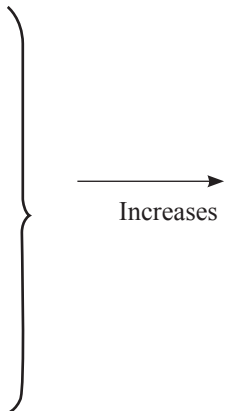
Decreases

(lattice energy effect)

(lattice energy effect)

(b) Properties which increase down the group are

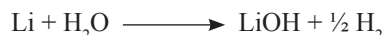
Table 10.3

| Property | Li | Na | K | Rb | Cs |
|--|---|----|---|----|----|
| Metallic character Atomic radii Ionic radii Ionic mobilities Temperature of thermal decomposition of MNO_3 and M_2CO_3 Stability of peroxide (O_2^{2-}) and super oxides (O_2^{-2}) Stability of sulphides (S^{2-}) M_2S Stability of MOH Chemical reactivity towards all reagents (except N_2) Base strength of oxides and hydroxides |  | | | | |

Chemical reactions

Metals of this group are highly electropositive that is, have high E° (red pot) values. Therefore, they are strong reducing agents.

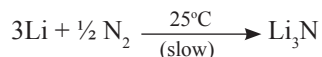
(1) All of these metals reduce H^+ in aqueous. solution.



Li does not react with alkynes.

(2) Reaction with N_2

Only Li reacts with N_2 at room temperature. The product is a ruby red crystalline nitride Li_3N



However around 400°C the reaction is fast. No any other alkali metal forms nitride (lattice energy effect).

(3) Reaction with O_2

Reaction products with O_2 differ.



Super oxides are paramagnetic (O_2^- has odd number of electrons, 17) and coloured.

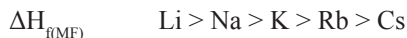




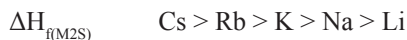
The increasing stability of peroxide and superoxides with increasing size of M^+ ion is a typical example of the stabilization of the larger anions by larger cations.

There are many such examples:

(a) ΔH_f of fluorides (F^- small)



(b) ΔH_f of sulphides (S^{2-} large)



(c) Per chlorates MClO_4

Larger M^+ form more stable lattice with large ClO_4^- ion. It is seen in solubility of perchlorates.

| | | | | |
|------------------|------------------|-----------------|------------------|------------------|
| LiClO_4 | NaClO_4 | KClO_4 | RbClO_4 | CsClO_4 |
| I | II | III | IV | V |

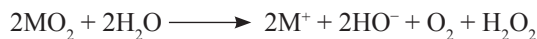
I is 10 times more soluble than II. It is mainly due to extensive solvation of smaller Li^+ ion. III, IV and V are much less soluble than II (10^{-3} times less). That is, solubility of MClO_4 decreases down the group. It is used in qualitative and quantitative chemistry of alkali metals.

Potassium is tested in salt analysis by sodium cobaltinitrite solution.



The K^+ salt is insoluble because K^+ is larger than Na^+ and forms more stable lattice with large anion, the $[\text{CO}(\text{ONO})_6]^{3-}$ ion.

The various oxides differ in reaction with water. It is due to highly electropositive nature of the metals.



The MOH are white crystalline solids. Their aq. solutions are strong bases and base strength increases down the group (Li to Cs).

The hydroxides are stable to heat and sublime unchanged on heating at $350\text{--}400^\circ\text{C}$. The vapours are found to contain dimmers, $(\text{MOH})_2$.

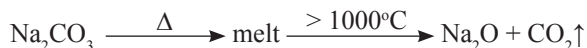
OXO salts

The oxosalts are carbonates (M_2CO_3), nitrates (MNO_3), sulphates (M_2SO_4), perchlorates (MClO_4) etc.

The oxosalts are remarkably stable. In general oxosalts of larger metal ions are more stable. Alkali metal ions, M^+ are large. Therefore, oxosalts of alkali metals ions are most stable.

(i) Carbonates and bicarbonates (or H – carbonates)

Carbonates of alkali metals are highly stable and melt before decomposition over 1000°C .



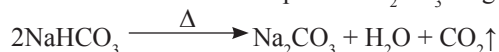
Li_2CO_3 decomposes like MgCO_3 , as Li^+ , small and highly polarizing



Larger metal ions only form solid bicarbonates (LiHCO_3 solid unknown) i.e., Na, K etc.

Ammonium bicarbonate (NH_4HCO_3) is also known in solid state as NH_4^+ ion compares in size to K^+ . Solid bicarbonates of metals of other groups are not known that is, M^{+2} or M^{+3} ions do not form solid bicarbonates).

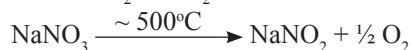
All solid bicarbonates decompose to M_2CO_3 on gentle heating.



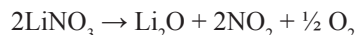
(ii) Nitrates MNO_3

Except LiNO_3 , nitrates of other alkali metals are most stable nitrates.

At around 500°C they decompose to MNO_2 and O_2 . But around 800°C the decomposition products are M – oxides, N_2 and O_2 .



Li differs due to its small size. The Li^+ ion is highly polarizing, so LiNO_3 decomposes easily.



Halides

Alkali metals react with X_2 directly and vigorously to form ionic halides MX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). These ionic substances are crystalline having high mp and bp.

Except LiF , all other halides are water soluble. The low solubility of LiF is due to high lattice energy which results from the combination of small Li^+ ion with F^- anion.

General properties of halides are given below:

(a) ΔH_f , Heat of formation (KJmol^{-1})

Table 10.4

| Metal | MF | MCl | MBr | MI |
|-------|-----|-----|-----|-----|
| Li | 612 | 398 | 350 | 271 |
| Na | 569 | 400 | 360 | 288 |
| K | 563 | 428 | 392 | 328 |
| Rb | 549 | 423 | 389 | 329 |
| Cs | 531 | 424 | 395 | 337 |

Observations on the above table

(i) ΔH_f decreases as $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ for any given metal. Thus MF most and MI least stable.

(ii) ΔH_f of MF decreases down the group (lattice energy effect)

Stability, MF $\xrightarrow{\text{Li to Cs}}$ decreases

(iii) ΔH_f of MI (alkali iodides) increases down the group (stabilization of large cation by large anion).

Stability, MI $\xrightarrow{\text{Li to Cs}}$ increases

(iv) ΔH_f of MCl and MBr do not change regularly.



(No concrete explanation is found for the above anomaly)

The stability follows the same order as ΔH_f .

(b) Lattice energies and mp (KCal mol^{-1} and $^{\circ}\text{C}$)

Table 10.5

| Alkali metal | MF | | MCl | | MBr | | MI | |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|
| | LE | Mp | LE | Mp | LE | Mp | LE | mp |
| Li | 244 | 870 | 202 | 614 | 191 | 552 | 178 | 440 |
| Na | 215 | 992 | 184 | 800 | 175 | 747 | 163 | 662 |
| K | 190 | 857 | 167 | 700 | 160 | 742 | 149 | 682 |
| Rb | 182 | 833 | 161 | 717 | 154 | 677 | 145 | 638 |
| Cs | 172 | 715 | 155 | 642 | 149 | 636 | 140 | 621 |

Comments

- (i) LE of LiX (X = F, Cl, Br, I) is highest.
- (ii) mp of LiX is lower (due to covalent nature in LiX) compared to NaX.
- (iii) LE of MX (X = F, Cl, Br, I) decreases down the group.
- (iv) mp of NaX (X = F, Cl, Br, I) is greater than LiX (due to increase in ionic nature of NaX).
- (v) mp of KI is highest among alkali metal iodides.
- (c) Solubility of CsX (X = F, Cl, Br, I)

Table 10.6

| Property | CsF | CsCl | CsBr | CsI |
|--------------------------------------|------|------|------|------|
| LE (KCal mol^{-1}) | 172 | 155 | 149 | 140 |
| HE of CsX (KCal mol^{-1}) | -181 | -151 | -143 | -132 |
| LE + HE | -9 | +4 | +6 | +8 |
| Solubility g/100 g water | 370 | 186 | 108 | 79 |

Observations

- (i) CsF is most soluble (due to high HE of small F^- ion).
- (ii) Solubility decreases from CsF to CsI.
- (iii) CsI least soluble. It is due to low HE of large Cs^+ and I^- ions.
- (d) Solubility of some alkali metal halides

Table 10.7

| Property | LiF | NaCl | NaI | RbCl |
|----------------------------------|------|------|------|------|
| LE (KCalmol^{-1}) | 247 | 186 | 166 | 162 |
| HE (KCalmol^{-1}) | -240 | -185 | -168 | -159 |
| LE + HE | +7 | +1 | -2 | +3 |
| Solubility mol lit^{-1} | 0.11 | 6.1 | 11.0 | 7.5 |

Observations

- (i) Solubility of LiF least (as LE + HE, most positive). LiF least soluble due to high lattice energy of LiF which results from combination of small F^- and Li^+ ions.
- (ii) Solubility of NaI highest (as LE + HE, most negative).

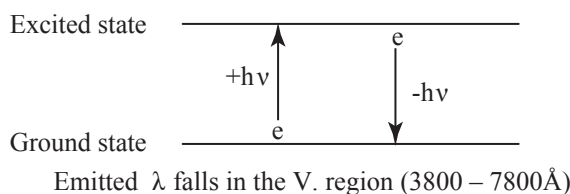
Flame colour of Alkali metals (and compounds)

Alkali metals and many of their compounds produce coloured flame when heated in a burner. Colours produced by alkali metals are:

| | | |
|----|---|-------------------|
| Li | → | Crimson |
| Na | → | Golden yellow |
| K | → | Violet (or Lilac) |
| Rb | → | Red |
| Cs | → | Blue |

The flame colour is due to emission of radiation in the visible region.

When heated loosely bound electron (ns^1) in alkali metals is excited to higher energy levels. When the excited electron returns to the ground state, radiation in the visible region is emitted producing colour.

**Figure 10.2**

The energy gap between ground and excited levels differ from one metal to the other. Thus each metal produce its unique colour (Li → Crimson, Cs → Blue) to the flame.

Alkali metals + Liquid NH_3

Alkali metals (and to a lesser extent Ca, Sr, Ba, Eu and Yb) are soluble in liquid NH_3 .

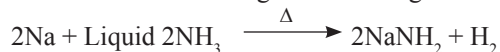
The solution of Na in liquid NH_3 is

- (i) Blue
- (ii) Paramagnetic
- (iii) Strongly reducing
- (iv) Conducting (electrolytically)

These properties are due to free solvated electrons in the solution.



When heated or on standing the solution gives NaNH_2 (sodium amide) and H_2 .



The concentrated solution of alkali metals in liquid NH_3 is copper coloured. This solution has very high electrical conductance similar to metals. It is supposed a metal cluster.

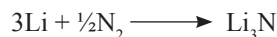
The coloured solution when evaporated leaves behind the alkali metal unchanged.

Anomalous behaviour of Li

Unlike other alkali metal ions, M^+ , lithium ion (Li^+) is very small. So, it has high charge to radius ratio (1.67) resulting into greater polarizing power than any other M^+ ions. Lithium compounds, therefore, have greater covalent nature. The properties of many Li-compounds are anomalous with respect to other alkali metal compounds. The size of Li^+ (0.6 Å) is very near to Mg^{2+} (0.65 Å). So, both have many properties in common. It is known as diagonal relationship.

Points of Similarity

- (i) Li and Mg both form nitride



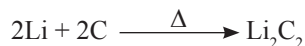
- (ii) Li_2CO_3 , LiNO_3 and LiOH like MgCO_3 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Mg}(\text{OH})_2$ form oxide on gentle heating.



Other alkali metals do not behave like Li.

- (iii) Like Mg, salts Li_2CO_3 , LiF , LiPO_4 are insoluble and LiOH is sparingly soluble like $\text{Mg}(\text{OH})_2$

- (iv) Li like II_A metals (and unlike other I_A metals) reacts directly with C to form an acetylide.



- (v) Li – halides (LiX) like Mg – halides (MX_2) are soluble in organic solvents (covalent nature factor).
 (vi) Hydration of Li^+ like Mg^{2+} is extensive (high charge to radius ratio factor).

PRACTICE QUESTIONS

- Explain the following:
 - Alkali metals crystallize with BCC lattice.
 - Alkali metals have low melting point.
 - The melting point gap between Li and Na is maximum.
 - Although Li has highest IE among the alkali metals, it is a strong reducing agent?
 - LiF is insoluble in water.
 - Among CsX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), CsI is least soluble.

- (g) Li resembles Mg.
 (h) LiCl is soluble, not only in water, but in acetone also.
 (i) Softness of alkali metals increases down the group.
 (j) LiI has covalent character.
 (k) Alkali metals are not isolated by electrolysis of their aq. salt solution.
- (l) Stability of MOH ($M = \text{Li, Na, K etc}$) increases down the group.
2. Complete the equations giving reasons for the same.
- (a) $\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O} \longrightarrow$
 (b) $\text{Cs} + \text{O}_2 \rightarrow \text{CsO}_2 \longrightarrow$
 (a) $\text{KNO}_3 + \text{K} \xrightarrow{\Delta}$
 (b) $\text{Na}_{(s)} + \text{NH}_{3(l)} \xrightarrow{\Delta}$

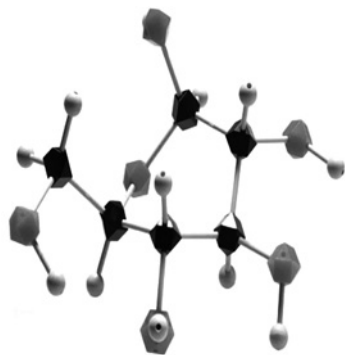
OBJECTIVE-TYPE QUESTIONS

1. In which of the following is oxidation state of oxygen the maximum?
 (a) MnO_2 (b) BaO_2
 (c) KO_2 (d) PbO_2
2. Sodium is heated with air or O_2 . The product is
 (a) Na_2O (b) Na_2O_2
 (c) Na_2O (d) NaO_2
3. Which of the following represents correct order of decreasing
 $E^\circ [\text{M}^+_{(\text{aq})} + e \rightarrow \text{M}_{(\text{s})}]$?
 (a) $\text{Li} > \text{Na} > \text{K} > \text{Rb}$
 (b) $\text{Rb} > \text{K} > \text{Na} > \text{Li}$
 (c) $\text{Li} > \text{Rb} > \text{K} > \text{Na}$
 (d) $\text{Rb} > \text{Li} > \text{Na} > \text{K}$
4. Sodium nitrate is heated above 800°C , the products are
 (a) Na_2O_2 and N_2
 (b) Na_2O , O_2 and NO_2
 (c) Na_2O , O_2 and N_2
 (d) Na_2O_2 , O_2 and N_2
5. The correct order of reducing power of alkali metals is
 (a) $\text{Li} > \text{Na} > \text{K} > \text{Cs}$
 (b) $\text{Cs} > \text{Li} > \text{Na} > \text{K}$
 (c) $\text{Li} > \text{Cs} > \text{K} > \text{Na}$
 (d) $\text{Na} > \text{K} > \text{Li} > \text{Cs}$
6. Consider the following statements:
 I Cs^+ is highly hydrated.
 II Among Li, Na, K and Rb, Li has highest mp.
 III Among the alkali metals only Li forms a nitride,
- Of these statements
 (a) I, II and III are correct
 (b) I and II are correct
 (c) II and III are correct
 (d) I and III are correct
7. The correct order of conductance of the given fused salts is
 (a) $\text{RbCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$
 (b) $\text{NaCl} < \text{LiCl} < \text{KCl} < \text{RbCl}$
 (c) $\text{LiCl} < \text{NaCl} < \text{KCl} < \text{RbCl}$
 (d) $\text{KCl} < \text{LiCl} < \text{RbCl} < \text{NaCl}$
8. Which of the following can be used as a source of O_2 at high altitudes or in submarines or in breathing masks?
 (a) BaO_2 (b) MnO_2
 (c) Na_2O_2 (d) KO_2
9. The lattice energy order of Li – halides is
 (a) $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$
 (b) $\text{LiCl} > \text{LiF} > \text{LiI} > \text{LiBr}$
 (c) $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$
 (d) $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
10. KNO_3 is heated with K metal. Nitrogen is converted into
 (a) N_2O (b) NO_2
 (c) N_2 (d) NO
11. Alkali metals form sulphides of the type M_2S ($M = \text{Li, Na, K}$). The ΔH_f decreases in the order
 (a) $\text{Li}_2\text{S} > \text{Na}_2\text{S} > \text{K}_2\text{S}$
 (b) $\text{K}_2\text{S} > \text{Na}_2\text{S} > \text{Li}_2\text{S}$
 (c) $\text{Na}_2\text{S} > \text{Li}_2\text{S} > \text{K}_2\text{S}$
 (d) $\text{K}_2\text{S} > \text{Li}_2\text{S} > \text{Na}_2\text{S}$
12. The solubility of MClO_4 ($M = \text{Li, Na, K, Rb}$) increases in the order

- (a) $\text{LiClO}_4 < \text{NaClO}_4 < \text{KClO}_4 < \text{RbClO}_4$
 (b) $\text{RbClO}_4 < \text{KClO}_4 < \text{NaClO}_4 < \text{LiClO}_4$
 (c) $\text{NaClO}_4 < \text{RbClO}_4 < \text{LiClO}_4 < \text{KClO}_4$
 (d) $\text{KClO}_4 < \text{LiClO}_4 < \text{NaClO}_4 < \text{RbClO}_4$
13. An alkali metal M reacts with N_2 to form a white powder 'A'. The compound 'A' gives a pungent gas 'B' with water. Which is correct for M, 'A' and 'B' respectively?
 (a) Na, Na_3N , NO_2
 (b) Li, Li_3N , NO_2
 (c) Li, Li_3N , NH_3
 (d) K, K_3N , NH_3
14. In the manufacture of caustic soda by Kellner Solvay cell electrolyte and cathode respectively are
 (a) Brine, Ni
 (b) Brine, Pt
 (c) brine, graphite
 (d) Brine, Hg
15. Which of the following is not found in solid state?
 (a) NaHCO_3
 (b) LiHCO_3
 (c) NH_4HCO_3
 (d) KHCO_3
16. Ionic mobility of M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$) follows the order:
 (a) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$
 (b) $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 (c) $\text{Li}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$
 (d) $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+$
17. Which of the following are true for a dilute solution of Na in liquid NH_3 ?
 (a) It is blue
 (b) The solution shows electrical conductance
 (c) The solution is diamagnetic
 (d) The solution is paramagnetic
18. Which of the following are true for a concentrated solution of Na in liquid NH_3 ?
 (a) It is deep blue
 (b) It is copper coloured
 (c) Solution is non-conducting
 (d) Conductivities of the solution is very high
19. Electro metallurgy is applicable to which one
 (a) Fe (b) Pb
 (c) Na (d) Ag
20. The fresh aq. solution of a white solid A turns red litmus colourless. The solid A is
 (a) Na_2O (b) Na_2O_2
 (c) NaOH (d) NaHCO_3
21. The stability of MOH ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$) follow the order
 (a) $\text{LiOH} > \text{NaOH} > \text{KOH} > \text{RbOH}$
 (b) $\text{RbOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$
 (c) $\text{KOH} > \text{RbOH} > \text{LiOH} > \text{NaOH}$
 (d) $\text{RbOH} > \text{NaOH} > \text{LiOH} > \text{KOH}$
22. Thermal stability of MNO_3 ($\text{M} = \text{alkali metals}$)
 (a) Decreases down the group
 (b) Increases down the group
 (c) Does not follow regular order
 (d) Remains almost similar

ANSWERS

1. (c) 2. (b) 3. (c) 4. (c) 5. (c) 6. (c) 7. (c) 8. (d) 9. (a) 10. (c)
 11. (b) 12. (b) 13. (c) 14. (d) 15. (b) 16. (b) 17. (a, b, d) 18. (b, d) 19. (c)
 20. (b) 21. (b) 22. (b)



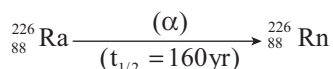
11

Group – 2 (II_A) [Be, Mg, Ca, Sr, Ba, Ra]

The group 2 elements are called alkaline earth metals. All are solids and have crystal structure. But unlike group 1 metals, crystal structures are not similar.

The valence shell of the metals is ns^2 . The metallic bond strength in these metals are stronger (2 valence electrons) than alkali metals (one valence electron). The metals are, therefore, harder than alkali metals (Be is hard enough to scratch glass). But the hardness decreases with increasing atomic size.

Beryllium compounds are toxic and affect lung tissue. All isotopes of radium are radio active,



that is, $226 - \text{Ra}$ is α active.

Radium was first isolated by Pierre and Marie Curie from the uranium ore pitchblende.

Table 11.1

| Be Mg | Hcp |
|----------|------------------------|
| Ca | ccp and Bcc |
| Sr | ccp, hcp and Bcc |
| Ba | Bcc |
| hcp | Hexagonal close packed |
| ccp | Cubic close packed |
| Bcc | Body centred cubic |

Electronic configuration of the elements and other properties

Table 11.2

| Property | Be | Mg | Ca | Sr | Ba | Ra |
|------------------------------|-------------|--------------|--------------|----------------------|----------------------|------------------------------|
| Atomic No. | 4 | 12 | 20 | 38 | 56 | 88 |
| Electronic configuration | $1s^2 2s^2$ | $-2p^6 3s^2$ | $-3p^6 3s^2$ | $-3d^{10} 4p^6 5s^2$ | $-4d^{10} 5p^6 6s^2$ | $-4f^{14} 5d^{10} 6p^6 7s^2$ |
| Atomic radius (Å) | 0.90 | 1.3 | 1.74 | 1.91 | 1.98 | — |
| Ionic radius (M^{+2} , Å) | 0.31 | 0.72 | 0.99 | 1.13 | 1.35 | 1.40 |
| Metallic radius (Å) | 1.12 | 1.60 | 1.97 | 2.16 | 2.22 | — |
| Ionization energy (ev) I | 9.32 | 7.64 | 6.11 | 5.69 | 5.21 | — |

(Continued)

| Property | Be | Mg | Ca | Sr | Ba | Ra |
|--|--------|-------|-------|-------|--------|--------|
| Ionization energy (ev) II | 18.21 | 15.03 | 11.69 | 11.00 | 10.00 | – |
| ΔH atom (25°C, Kcal/mol 1atom.) | 78.2 | 35.1 | 42.3 | 39.0 | 42.0 | – |
| Electronegativity | 1.5 | 1.2 | 1.0 | 1.0 | 0.9 | – |
| Charge/radius ratio | 6.5 | 3.1 | 2.0 | 1.8 | 1.5 | – |
| mp(°C) | 1278 | 651 | 851 | 800 | 850 | 700 |
| bp (°C) | (2500) | 1105 | 1494 | 1381 | (1850) | (1700) |
| $E^\circ [M^{+2}_{(aq)} + 2e \rightarrow M]$ | –1.85 | –2.37 | –2.87 | –2.89 | –2.90 | – |
| $\Delta H_{H_{yd}^2} M^{+2} (KJmol^{-1})$ | –2494 | –1921 | –1577 | –1305 | –1305 | – |

(Boiling points in brackets are approximate)

Many of the properties, stability and solubility of compounds vary regularly. Some decrease and some increase down the group. However, heat of atomization, mp and bp do not vary regularly.

mp order $Be > Mg < Ca > Sr < Ba$

It is due to the fact that metallic bond strength variation is irregular.

Let us consider valence orbitals of the elements

Mg $3s^2 3d^0$
Ca $4s^2 3d^0$
Sr $5s^2 4d^{10}$
Ba $4f^0 5d^0 6s^2$

It is argued that due to participation of 3d in Ca and 4f orbitals in Ba, metallic bond strength increases. Therefore, Ca and Ba show deviation in mp. As $4d^0$ in Sr has large size, d – d overlap is not so effective as it is in the case of Ca (3d small size). Therefore, Sr has lower mp than Ba.

Properties which decrease down the group

Table 11.3

| Property | Be | Mg | Ca | Sr | Ba | |
|--|----|----|----|----|----|-----------|
| Ionization energy | → | | | | | Decreases |
| Electron affinity | → | | | | | Do |
| Electronegativity | → | | | | | Do |
| Charge /radius | → | | | | | Do |
| ΔH_{Hyd} of M^{+2} | → | | | | | Do |
| Solubility of MCO_3 (M = Be to Ba) | → | | | | | Do |
| Solubility of MSO_4 (M = Be to Ba) | → | | | | | Do |
| Solubility of MCl_2 (M = Ca, Sr, Ba) | → | | | | | Do |

Properties which increase down the group**Table 11.4**

| Property | Be | Mg | Ca | Sr | Ba |
|--|----|----|----|----|-----------|
| Atomic radius | → | → | → | → | Increases |
| Ionic radius | → | → | → | → | do |
| Metallic radius | → | → | → | → | do |
| Electropositive nature | → | → | → | → | do |
| E° | → | → | → | → | do |
| Reducing power | → | → | → | → | do |
| Ionic nature of binary compounds | → | → | → | → | do |
| Rate of reaction with H_2 | → | → | → | → | do |
| Thermal stability of MCO_3 , MSO_4 , $\text{M}(\text{NO}_3)_2$, MO_2 | → | → | → | → | do |
| Basic nature of MO , $\text{M}(\text{OH})_2$ | → | → | → | → | do |
| Solubility of MO , $\text{M}(\text{OH})_2$ | → | → | → | → | do |
| MF_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) | → | → | → | → | do |

Oxidation states and nature of bond

Valence electrons of group 2 elements are ns^2 . The elements are all metals and are relatively large in size. The +2 oxidation state is stable and common to all. However, it is not achieved from direct ionisation. It is due to the fact that second IE is very high,



The +2 state is formed from disproportionation (self oxd–red) of M^+ ion. The energy for disproportionation comes either through lattice energy (M^{+2} forms more stable lattice) or from hydration energy (M^{+2} ion heavily hydrated).



But the case of Be is different. It is very small ($r_{\text{Be}^{+2}} \sim 0.3 \text{ \AA}$) and has highest charge/radius ratio (~ 6.5) among the metals. Therefore, Be^{2+} is highly polarizing and Be–compounds have appreciable covalent nature. It compares to a large extent with Al rather than other group members (the diagonal relationship). Magnesium in +2 state is also small (0.65 \AA) and so polarising. Therefore, Mg compounds also have some covalent nature. Calcium, Sr and Ba are large, form ionic compounds and resemble closely.

Hydrides

All the elements except Be react directly with H_2 to form hydrides of the type MH_2 .



BeH_2 is prepared by reducing BeCl_2 with LiAlH_4



BeH_2 and MgH_2 are covalent but others are ionic and have lattice structure. Lattice contains M^{+2} and H^- ions.

General properties of Hydrides

Table 11.5

| Property | BeH_2 | MgH_2 | CaH_2 | SrH_2 | BaH_2 |
|----------------|---|-----------------|----------------|-------------------|----------------|
| Bond nature | Covalent | Covalent | Ionic | Ionic | Ionic |
| Stability | Less | ← More stable → | | | → |
| mp | → Increases → | | | → | |
| Reducing power | → Increases → | | | → | |
| Structure | Polymeric (H – bridge structure) ← → | | | ← Ionic lattice → | |

Beryllium hydride is polymeric and has H – bridge structure,

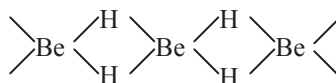
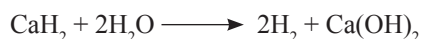


Figure 11.1

The bridge Be–H–Be has a three centre – two electron (3c – 2e) bond like B_2H_6 . Hydrides are hydrolyzed by water and acids to H_2

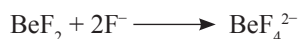


Halides

Group – 2 metals react with halogens directly and vigorously to form halides of the type MX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)



Beryllium halides have covalent nature because Be^{2+} is very small, has high charge/radius ratio and consequently is highly polarizing. BeF_2 , BeCl_2 are electron deficient and act as Lewis acids.



The structure of BeCl_2 (BeF_2 also) depends on its physical state:

- (i) In vapour state it is BeCl_2 and is linear having sp – hybridized Be,



- (ii) At lower temperature it is a dimer Be_2Cl_4 . It has a Cl – bridge structure

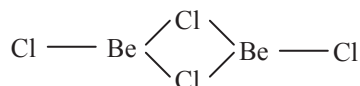
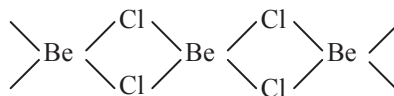


Figure 11.2

(iii) In solid state it is polymeric, $(\text{BeCl}_2)_x$. the structure contain Cl – bridge and Be sp^3 – hybridized.

**Figure 11.3**

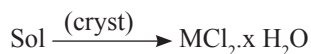
Other halides have ionic lattice.

General properties of Chlorides, MCl_2

Table 11.6

| Property | BeCl_2 | MgCl_2 | CaCl_2 | SrCl_2 | BaCl_2 |
|--------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ionic nature | | | | | Increases |
| mp | | | | | Increases |
| Conductivity of fused MCl_2 | | | | | Increases |
| Solubility of MCl_2 | | | | | Decreases |

Hydrated chlorides, $\text{MCl}_2 \cdot x \text{H}_2\text{O}$ can be crystallized from an aq solution of chlorides. They can be prepared by the action of HCl acid on the metals or M – oxides or M – hydroxides or M – carbonates.

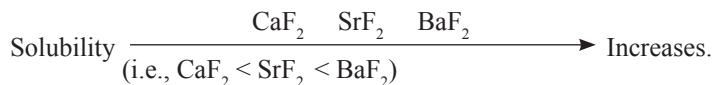


Magnesium, Ca and Sr form hexahydrates $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$ whereas Ba forms a dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. This change in hydration number is due to more efficient packing in BaCl_2 . Both Ba^{2+} and Cl^- are large, pack more efficiently in the lattice, leaving less vacant space. Therefore, hydration number for BaCl_2 is lower, two only ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). Also Ba^{2+} has lower ionic potential and so does not attract H_2O strongly.

It is very difficult to crystallize BeCl_2 . It is because covalent BeCl_2 hydrolyze easily to form $\text{Be}(\text{OH})_2$ and HCl instead of a hydrated salt



Bromides and iodides are similar to chlorides. However, fluorides differ in their nature, especially solubility. The solubility of fluorides MF_2 (M = Ca, Sr, Ba) is opposite to chlorides.

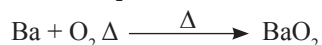


Calcium fluoride (CaF_2) is used for prism in spectrometers and also for making opal glass.

Calcium chloride (CaCl_2) is used as a laboratory-drying agent. It is also used for treating ice on roads to remove it (ice). It is because a 30% eutectic mixture of $\text{CaCl}_2/\text{H}_2\text{O}$ freezes at a very low temperature (-55°C).

Oxides and Hydroxides

Oxides of alkaline earth metals are formed by burning the metal. All, except Ba form oxide of the type MO (a normal oxide). As Barium is very large, ($r_{\text{Ba}^{+2}}$ 1.35) it forms a peroxide, BaO_2 .



The oxides are very stable solids, refractory in nature (ΔG high negative) and are used for brick linings in furnaces. The oxides can also be produced by the thermal decomposition of their carbonated, hydroxides or nitrates.



(M = Be, Mg, Ca, Sr, Ba)

General properties

Table 11.7

| Property | BeO | MgO | CaO | SrO | BaO |
|------------------|------------------|----------------------------|----------------------|-----|-----------|
| Bond nature | Largely covalent | ←———— Ionic —————→ | | | |
| Structure | Polymeric | ←———— Ionic lattice —————→ | | | |
| Water solubility | Insoluble | Insoluble | ←———— Soluble —————→ | | |
| Acid–base nature | Amphoteric | ←———— basic —————→ | | | |
| Base strength | —————→ | | | | Increases |

Beryllium oxide is largely covalent. It is because Be^{+2} has high polarizing effect on the oxide ion (O^{2-}). The high polarization effect of Be^{2+} is due to its very high charge to radius ratio (6.5).

BeO is amphoteric and reacts with acids and strong bases.

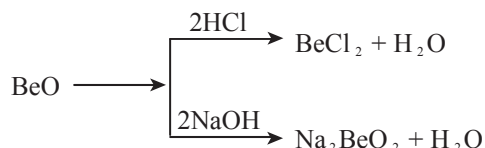


Figure 4

Or,

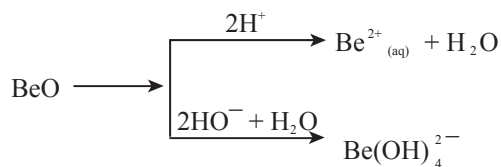
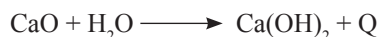


Figure 5

The oxides CaO, SrO and BaO react with water to form hydroxides. The reaction being highly exothermic.



This reaction is known as slaking of lime. Mg(OH)₂ is weakly basic and is used to treat acid indigestion.

The aq. solution of Ca(OH)₂ is called lime water and that of Ba(OH)₂ is baryta water.

Table 11.8

| Property | Be(OH) ₂ | Mg(OH) ₂ | Ca(OH) ₂ | Sr(OH) ₂ | Ba(OH) ₂ |
|------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Water solubility | —————→ | | | | Increases |
| Acid-base nature | Amphoteric | Weakly basic | ← | Strong bases | → |
| Base strength | —————→ | | | | Increases |

Lime water (or baryta water) are used to detect CO₂. It forms white turbidity with lime water. It is due to the formation of insoluble CaCO₃.



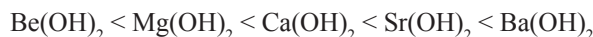
But in excess CO₂ turbidity vanishes due to the formation of soluble bicarbonate.



This reaction takes place due to acidic medium produced by excess CO₂.

Solubility of Hydroxides

Water solubility of hydroxides increases from Be (OH)₂ to Ba(OH)₂. It depends on lattice and hydration energies. Lattice energy decreases down the group due to increase in radius of M⁺². So also is the case for hydration energy. But decrease in LE is more compared to HE. Therefore, the difference LE – HE becomes more and more negative down the group. Thus solubility increases from Be(OH)₂ to Ba(OH)₂.



Nitrides

The group 2 elements burn in N₂ to form nitrides of the type M₃N₂



As bond energy in N₂ is very high (945KJmol⁻¹), the reaction requires a large amount of energy to convert N₂ into the nitride ion (N⁻³). This energy comes from high lattice energy as the lattice is made of highly charged ions, M⁺² and N⁻³.

Beryllium nitride is appreciably covalent and is volatile. Others are ionic crystalline solids.

The nitrides react with water to form NH₃.



Oxo salts

Carbonates, sulphates, nitrates etc., are oxosalts.

Carbonates

The alkaline earth metals form carbonates of the type, MCO_3 . They can be prepared in different ways:

- (a) By passing less of CO_2 in M(OH)_2



It is a neutralization reaction.

- (b) By treating a soluble salt with Na_2CO_3



However, a solution of MgCl_2 on reaction with Na_2CO_3 form a basic carbonate, $\text{Mg(OH)}_2 \cdot \text{MgCO}_3$. It is due to hydrolysis of Mg^{+2} ions. It can be made by the reaction



The carbonates are water insoluble and solubility decreases down the group.

They are thermally unstable and stability increases down the group.

Table 11.9

| | BeCO_3 | MgCO_3 | CaCO_3 | SrCO_3 | BaCO_3 |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|
| Decomposition temp. ($^\circ\text{C}$) | < 100 | 540 | 900 | 1290 | 1360 |
| Water solubility | —————→ | | | | Decreases |

Thermal stability depends on size of the metal ion:

- Large metal ions form more stable carbonate.
- Small metal ions form less stable carbonate.

Large metal ions have low charge to radius ratio whereas small metal ions have high charge to radius ratio.

Metal ions having high charge to radius ratio distort electron cloud of planar CO_3^{-2} ion very effectively.

Therefore, they easily decompose on heating. In addition to this small ion like Be^{+2} , polarizes oxide ion to a large degree. It results into covalent nature in BeO_2 , a further stabilization effect. Therefore, the decomposition temperature of BeCO_3 is relatively very low ($< 100^\circ\text{C}$).

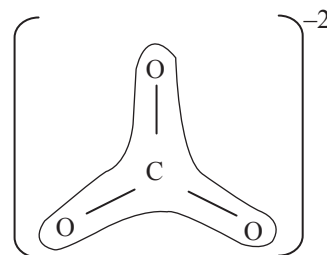
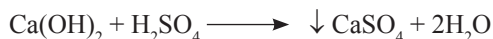
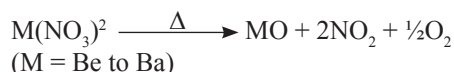


Figure 11.6

Sulphates

These metals form sulphates of the type MSO_4 . They can be prepared by the action of dil. H_2SO_4 on oxides, hydroxides or carbonates.





Solubility of Ca, Sr and Ba(M) compounds

It can be summarized as:

- MCl_2 , MBr_2 , MI_2 , $M(NO_2)_2$, $M(ClO_3)_2$, $M(ClO_4)_2$, $M(CH_3COO)_2$ are very soluble.
- Hydroxides, fluorides, BrO_3 are moderately soluble CaF_2 is insoluble.
- Sparingly soluble or insoluble compounds are carbonates, sulphates, iodates, oxalates.

Flame colouration by Ca, Sr and Ba

Beryllium and Mg chlorides do not impart colour to the Bunsen flame as excitation energy for electrons is high. Calcium, Sr and Ba chlorides imparts specific colour to the flame as excitation energy of electrons for these metals is low.

Table 11.12

| Metals | Flame colour |
|--------|----------------------------|
| Ca | Brick red |
| Sr | Crimson |
| Ba | Grass green or apple green |

PRACTICE QUESTIONS

1. Explain in brief:

- $BaSO_4$ is insoluble but $BeSO_4$ is soluble.
- $Be(OH)_2$ is insoluble but $Ba(OH)_2$ is soluble.
- Conductivity of fused chlorides follows the order:
 $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$.
- Melting point of Ca is greater than Mg, although Ca is larger in size.
- Sodium ion (Na^+) and calcium ion (Ca^{+2}) have very similar ionic radii ($\sim 0.9\text{\AA}$). But hydration enthalpy of Ca^{+2} is four times that of Na^+ .
- Mg does not impart colour to the flame.
- The decomposition temperature of $BeCO_3$ is much lower ($< 100^\circ C$) than that of $MgCO_3$ ($\sim 500^\circ C$).
- $BaSO_4$ and not $BeSO_4$ is used in the diagnosis of stomach ulcer.
- $BeCl_2$ solid is polymeric.
- The E° of Be is low but it is a good reducing agent.
- $BaCl_2$ forms a dihydrate whereas $CaCl_2$ forms a hexahydrates.

- The second ionization energy of Mg is high ($\sim 15\text{ev}$) but it forms compounds in +2 oxidation state only.
- Anhydrous $MgCl_2$ can not be prepared by heating $MgCl_2 \cdot 6H_2O$.
- Reaction of Na_2CO_3 with $MgCl_2$ solution produces a basic carbonate of Mg.
- Ca is not prepared by the electrolysis of fused CaO.

2. True or False

- $MgCl_2 \cdot 6H_2O$ on heating gives anhydrous $MgCl_2$.
- The bicarbonates (or hydrogen carbonates) of Mg and Ca are not stable in the crystalline salt.
- The carbonates of Mg and Ca are thermally unstable and decompose below their melting points.
- The solubility of chlorides of Gr 2 metals increases down the group.
- The solubility of fluorides of Gr 2 metals decreases down the group.
- The thermal stability of $ZnCO_3$ and $BaCO_3$ are similar.
- $Be(OH)_2$ is soluble in NaOH solution.

- (h) When plaster of paris is heated it forms gypsum.
 (i) When Mg is heated with air it forms MgO only.
 (j) Electrical conductance of molten BeCl₂ and BaCl₂ are similar.

3. Fill in the blanks

- (a) Calcium chloride crystallize with the molecular formula _____.
 (b) All oxides of Gr 2 metals are basic except _____ which is _____.
 (c) Plaster of paris is _____.
 (d) The solubility of sulphates of Gr 2 metals _____ down the group.

- (e) The thermal stability of Gr 2 carbonates _____ down the group.
 (f) When MgO is heated with Co(NO₃)₂ a _____ coloured mass is formed.
 (g) Calcium carbide, obtained by reduction of CaO with carbon is a _____.
 (h) Magnesium perchlorate is used as a _____ agent.
 (i) When CaC₂ is heated with N₂ at high temperature _____ is formed which is used as a _____.
 (j) Gypsum is added to cement to _____ its rate of setting.

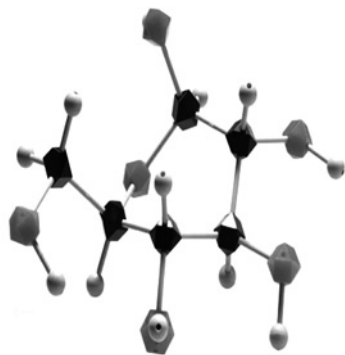
OBJECTIVE-TYPE QUESTIONS

- The compound insoluble in acetic acid is
 (a) CaO (b) CaCO₃
 (c) CaC₂O₄ (d) Ca(OH)₂
- Which of the following hydrated salts will give anhydrous salt on heating?
 (a) AlCl₃·6H₂O (b) MgCl₂·6H₂O
 (c) SnCl₂·2H₂O (d) CaCl₂·6H₂O
- The set which represents correct order of first ionization energy is
 (a) B > C > N (b) K > Na > Li
 (c) Be > Mg > Ca (d) Ge > Si > C
- The correct mp order gr Gr 2 metals is
 (a) Be > Mg > Ca > Sr
 (b) Be > Mg > Sr > Ca
 (c) Sr > Ca > Mg > Be
 (d) Be > Ca > Sr > Mg
- Bleaching power has the composition
 (a) CaCl₂·Ca(OH)₂
 (b) Ca(OCl)₂·CaCl₂·Ca(OH)₂·2H₂O
 (c) Ca(OCl)₂·H₂O
 (d) Ca(OH)₂·CaCl₂·2H₂O
- The formula of calcium cyanamide is
 (a) Ca(N₃)₂ (b) CaCN₂
 (c) CaC₂N (d) CaCHNH₂
- Which of the following sulphates will decompose at highest temperature?
 (a) MgSO₄ (b) SrSO₄
 (c) CaSO₄ (d) BeSO₄
- Ammonia is dried over
 (a) Slaked lime (b) Quick lime
 (c) CaCl₂ (d) P₄O₁₀
- The compound Mg₂C₃ reacts with water to form propyne, the ion C₃⁴⁻ has
 (a) One σ and two π bonds
 (b) Two σ and two π bonds
 (c) Two σ and one π bond
 (d) Two σ and three π bonds
- Triple super phosphate of lime is
 (a) 3Ca(H₂PO₄)₂ (b) Ca(HPO₄)₂
 (c) 2Ca(H₂PO₄)₂ (d) Ca₃(PO₄)₂
- The correct order of conductance of molten salts MCl (M = Be, Mg, Ca, Sr) is
 (a) SrCl₂ < CaCl₂ < MgCl₂ < BeCl₂
 (b) BeCl₂ < MgCl₂ < CaCl₂ < SrCl₂
 (c) CaCl₂ < SrCl₂ < BeCl₂ < MgCl₂
 (d) SrCl₂ < BeCl₂ < MgCl₂ < CaCl₂
- Sodium carbonate is added to a solution of MgCl₂. The product is

- (a) $\text{Mg}(\text{OH})_2$ (b) $\text{Mg}(\text{HCO}_3)_2$ 14. Which property of Gr 2 metals decreases with increasing atomic number?
(c) $\text{Mg}(\text{OH})_2 \cdot \text{MgCO}_3$ (d) MgCO_3 (a) Basicity of hydroxides
13. Which of the sulphates is used in the diagnostic investigation of stomach ulcers? (b) Atomic radii
(a) BaSO_4 (b) SrSO_4 (c) Solubility of Chlorides
(c) CaSO_4 (d) BeSO_4 (d) Thermal stability of sulphates

ANSWERS

1. (c) 2. (d) 3. (c) 4. (d) 5. (b) 6. (b) 7. (b) 8. (b) 9. (b) 10. (a)
11. (b) 12. (c) 13. (a) 14. (c)



12

GROUP – 11 (I_B) [Copper, Silver and Gold]

Copper, Ag and Au are known as coinage metals because they were used to make coins. All the metals are noble w.r.t. chemical activity.

ELECTRON CONFIGURATION AND POSITION IN THE PERIODIC TABLE

Table.12.1

| Element | Electron configuration | Outermost configuration | Valence electrons | Group | | Period |
|---------|------------------------|-------------------------|-------------------|-----------|-------|--------|
| | | | | Long form | IUPAC | |
| Cu(29) | [Ar] $3d^{10}4s^1$ | $3d^{10}4s^1$ | $3d^{10}4s^1$ | I_B | 11 | 4 |
| Ag(47) | [Kr] $4d^{10}5s^1$ | $4d^{10}5s^1$ | $4d^{10}5s^1$ | I_B | 11 | 5 |
| Au(79) | $4f^{14}5d^{10}6s^1$ | $5d^{10}6s^1$ | $5d^{10}6s^1$ | I_B | 11 | 6 |

As a general rule, they should have electronic configuration $(n-1)d^9ns^2$. But due to greater stability of fully and half filled orbitals, all have configuration $(n-1)d^{10}ns^1$.

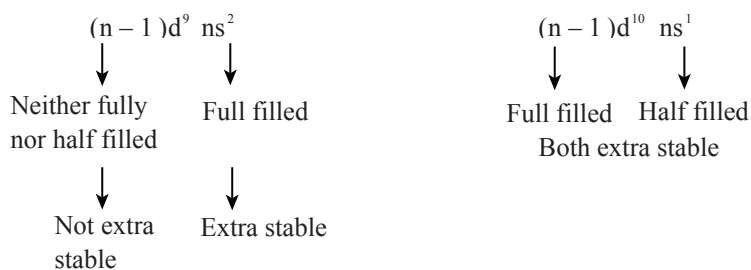


Figure 12.1

General Properties

Crystal structure

All coinage metals have similar lattice structure, faced-centred cubic (ccp)

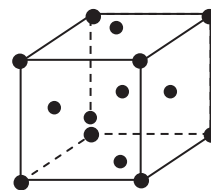


Figure 12.2

Metallic bond strength

In addition to ns^1 , $(n-1)d^{10}$ electrons are also involved in metallic bonding. So, metallic bonding is stronger than alkali metals, (ns^1 outer electron – configuration)

Sublimation energy, melting point and boiling point

Due to stronger metallic bonding, sublimation energy, mp and bp of coinage metals are relatively high (higher than alkali metals).

Atomic and ionic radii

Atomic radius of Ag ($4d^{10}5s^1$) is larger than Cu ($3d^{10}4s^1$) due to addition of higher orbits in Ag. But Ag and Au have almost equal atomic radii due to lanthanide contraction.

Table 12.2

| | Atomic radius (Å) | Ionic radii (Å) | | | (°C) | |
|----|-------------------|-----------------|------|------|------|------|
| | | +1 | +2 | +3 | mp | bp |
| Cu | 1.17 | 0.77 | 0.73 | - | 1083 | 2310 |
| Ag | 1.34 | 1.15 | 0.94 | - | 960 | 1950 |
| Au | 1.34 | 1.37 | - | 0.85 | 1062 | 2600 |

Ionization energy

Outer electron configuration of the metals is $(n-1)d^{10}ns^1$. The d electrons have much less screening effect on nucleus. So, nucleus has stronger attractive effect on ns^1 electron and IE, in general, is high for coinage metals (higher than GrI metals). The order found for first IE is

$$\text{Cu} > \text{Ag} < \text{Au}$$

$$\text{IE}_1(\text{ev}) \quad 7.72 \quad 7.57 \quad 9.22$$

The higher value for Au is due to convergence of energies of 5s, 5p and 5d. It results into increased nuclear attraction experienced by $6s^1$ electron in Au and so ionisation energy is high.

Noble metal nature

These metals are chemically noble.

Higher sublimation and ionization energies are responsible for noble nature of these elements.

Table 12.3

| | Cu | Ag | Au |
|--|-------|-------|-------|
| Sublimation energy KJmol^{-1} | 339.6 | 283.6 | 336.6 |
| IE (ev) | 7.72 | 7.57 | 9.22 |

Gold is most noble metal, but it dissolves in selenic acid, H₂SeO₄, forming selenate.



Malleability, Thermal and Electrical Conductivities

Gold is most malleable metal. Thermal and electrical conductivities of Ag is highest to any metal and Cu comes second.

Table 12.4

| Elements | Cu | Ag | Au |
|-------------------------|----|-----------|----|
| Electrical conductivity | 57 | 59 | 40 |
| Thermal conductivity | 46 | 49 | 35 |

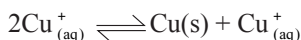
Oxidation states

These metals show variable oxidation states. It is due to participation of (n-1)d¹⁰ electron. Common oxidation states are

- The most stable oxidation states are +2 for Cu, +1 for Ag and +3 for Au.
- The +2 state for Ag is obtained by oxidizing Ag⁺ with strong oxidizing agents such as O₃, (NH₄)₂S₂O₈ etc.
- The +1 state of Cu is stable in aqueous medium only for those compounds, which are insoluble in water, like CuCl, CuI, CuCN, CuSCN etc. The compound CuSCN is used to estimate Cu(I) gravimetrically.



The Cu⁺_(aq) disproportionates in water as



$$K = \frac{[\text{Cu}^{2+}_{(\text{aq})}]}{[\text{Cu}^{+}_{(\text{aq})}]^2} = 1.6 \times 10^6$$

The equilibrium constant, K is high showing that equilibrium lies well towards the right. But it can be displaced in either side. It depends on the nature of ion present in the medium. In the presence of CN⁻, I⁻ etc. (reducing agents) the equilibrium lies towards left because insoluble CuCN or CuI are produced. In the presence of ions like SO₄⁻², ClO₄⁻ etc. Cu⁺² state is favoured.

The +1 state of gold is also not stable and it disproportionates as



$$K = \frac{[\text{Au}^{+3}_{(\text{aq})}]}{[\text{Au}^{+}_{(\text{aq})}]^3} = 1 \times 10^{10}$$

But in the presence of iodide ions, equilibrium lies toward left due to redox reaction $3\text{AuI} \longrightarrow \text{AuI} + \text{I}_2$.

- Nature of bonds in any of the oxidation states is appreciably covalent. It is due to larger number of core electrons. More the core electrons more the polarizing power and greater the covalency.

Table 12.5

| Metals | Oxidation states | |
|--------|------------------|----|
| Cu | +1 | +2 |
| Ag | +1 | +2 |
| Au | +1 | +3 |

Table 21.6

| Oxidation state | Core electrons |
|---|----------------|
| Cu ⁺ , Ag ⁺ , Au ⁺ | 18e |
| Cu ²⁺ , Ag ²⁺ | 17e |
| Au ³⁺ | 16e |

(v) The halogen compounds of Cu^+ and Ag^+ are different from other monovalent metals,

Stability

$F > Cl > Br > I$ for other $M^+(Gr I)$
 $I > Br > Cl > F$ for Cu^+ and Ag^+
 $F < Cl < Br < I$ for other $M^+(Gr I)$

Solubility

(AgCl, AgBr, AgI) \longrightarrow
F > sp. Soluble for Ag⁺

(CuBr, CuI) \longrightarrow
Cl > sp. Soluble for Cu⁺

(**Note:** 1. CuF is not known, 2. AgF is water soluble)

Magnetic properties

Magnetic properties of coinage metals depend on oxidation states.

(i) Compounds containing M^+ ions (i.e., Cu^+ , Ag^+ and Au^+) have no unpaired electrons and are diamagnetic.

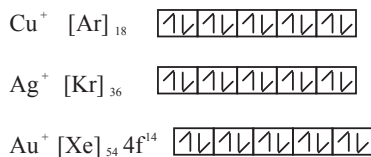


Figure 12.3

So, CuCl , AgCl , AuCl etc., are diamagnetic.

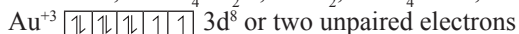
(ii) Compounds containing Cu^{2+} and Au^{+3} are paramagnetic. It is because +2 and +3 oxidation states have unpaired electrons in $(n-1)d$ orbitals Cu^{+2}

| | | | | |
|------------|------------|------------|------------|------------|
| \uparrow | \uparrow | \uparrow | \uparrow | \uparrow |
|------------|------------|------------|------------|------------|

 $3d^9$ or one unpaired electron.

$$\therefore \mu = \sqrt{n(n+2)}\text{BM} = \sqrt{1(1+2)} = \sqrt{3}\text{BM}$$

Therefore, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, CuCl_2 , CuCl_4^{2-} etc., are paramagnetic



$$\therefore \mu = \sqrt{n(n+2)}\text{BM} = \sqrt{2(2+2)} = \sqrt{8}\text{BM}$$

Although Au^{+3} contains unpaired electrons, compounds containing Au^{+3} are not paramagnetic rather they are diamagnetic. It is due to structural reasons. For example, AuCl_3 , AuCl_4^- and many others are diamagnetic. AuCl_3 is a dimer and has Cl – bridge square planar structure.

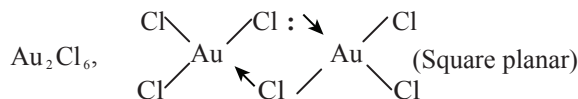


Figure 12.4

The ion AuCl_4^- is also square planar,

Gold in +3 oxidation state ($5d^8$) with square planar structure has all its electrons paired for dsp^2 hybridization and so the compounds are diamagnetic.

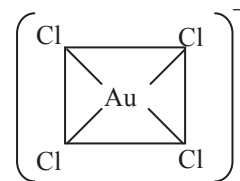
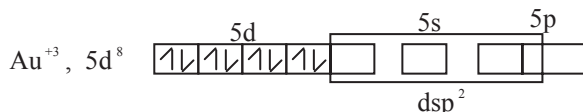


Figure 12.5

Colour of compounds

Many of the compounds of coinage metals are colored.

- Colour in compounds containing M^+ ions is due to charge–transfer. Many are colorless also.
- Compounds containing +2 or +3 ions may be coloured either due to $d - d$ transition or charge transfer.

Table 12.7

| Compounds | Colour | Reason for colour |
|--|------------|---|
| CuCl , AgCl | Colourless | No charge transfer as Cl^- is very weak reducing |
| AgBr , AgI | Yellow | Charge transfer |
| Cu_2O | Reddish | Charge transfer |
| CuS , Ag_2S , Au_2S_2 | Black | Charge transfer |
| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | Blue | $d - d$ transition |
| $\text{AuCl}_3 \cdot 4\text{H}_2\text{O}$ | Yellow | $d - d$ transition |
| AuCl_3 anhydrous | Yellow | Charge transfer |
| CuSO_4 anhydrous | Colourless | No $d - d$ transition is possible in the absence of ligands |
| Au_2O | | Charge transfer |
| Au_2S | | Charge transfer |

Occurrence and Isolation

Gold is found in native state or as tellurides. Cu and Ag are found as sulphide, chloride, CO_3^{-2} ores. It is because Cu^{2+} and Ag^+ are soft Lewis acid and S^{-2} is soft Lewis base.

Cu is recovered by thermal metallurgy and further purified by electrolysis.

Ag and Au are isolated by wet or hydrometallurgy using CN^- ion as leaching agent. These metals are also obtained by microbial methods. Further purification by electrolysis.

Reactions involved in the isolation of Ag and Au are

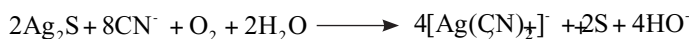
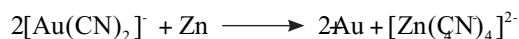
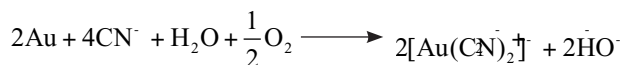


Table 12.8

| Metal | Ores |
|-------|---|
| Cu | CuFeS_2 [Copper pyrite] |
| Ag | Ag_2S [Argentite] AgCl [Hornsilver] |
| Au | Native AuTe_2 (alloy) [Calaverite] $(\text{Ag}, \text{Au})\text{Te}_2$ [Sylvanite] |



Solubility of Silver halides

Silver halides (AgCl , AgBr , AgI) are insoluble in water. The Ag^+ ion is small in size, has more core electrons (18e) so Ag^+ is highly polarizing. It results into formation of stable lattice; therefore, halides are insoluble in water.

However, the above halides are soluble in complexing agents like NH_3 , $\text{S}_2\text{O}_3^{2-}$ and CN^- .

- (a) AgCl is soluble in dil. NH_4OH , AgBr in conc. NH_4OH but AgI is insoluble even in conc. NH_4OH . Solubility in ammonia solution is due to complex formation.



- (b) All the above silver halides are soluble in $\text{Na}_2\text{S}_2\text{O}_3$ solution and NaCN solution. The solubility is due to complex formation.



- (c) Practically, all Ag^+ salts are insoluble in water, example, AgCl , AgBr , AgI , Ag_2SO_4 , CH_3COOAg etc.

- (d) Only AgF , AgNO_3 and AgClO_4 are soluble in water.

Chemistry of Photography

- (i) **Photographic Film** It is a celluloid strip coated with AgBr in gelatin. Some films contain AgI also which are specifically used in low light intensity or for photographing fast moving objects like racing cars.
- (ii) **Exposer of film to light** When a film is exposed to light, light sensitive AgBr is reduced to fine grains of Ag due to photochemical reactions, This is not a visible change but is called formation of a 'latent image'. Many AgBr grains are left activated.
- (iii) **Development** Exposed film is developed by washing with a mild reducing agent like quinol. It reduces activated AgBr grains to Ag ,

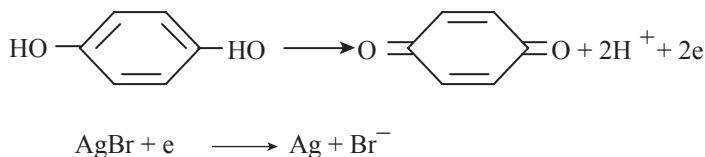


Figure 12.6

Ag produced in this way is deposited where Ag were present initially (2nd step). A visible image is developed which is called negative. The whole process is done in dark to avoid unnecessary exposure of the film.

- (iv) **Fixing** In this stage film is dipped in sodium thiosulphate (hypo) solution. It dissolves unreacted AgBr by forming a complex.



It is also performed in dark.

This process results into a fixed negative image.

- (v) **Printing** Print is obtained by shining light through negative on a photographic paper which contains AgBr. In this stage dark and light areas are reversed and a print is produced. The photographic paper is then washed with Na₂S₂O₃ solution and further with water and dried.

PRACTICE QUESTIONS

- Write balanced equations for isolation of
 - Cu from copper pyrite (or chalcopyrite) CuFeS₂
 - Silver from argentite, Ag₂S.
- A blue solution (M) containing Cu²⁺ is treated with aq. NH₃ until a light blue ppt (N) forms. Addition of excess NH₃ give deep blue solution (O). When dil. HNO₃ is added to the deep blue solution, a light blue ppt (N) appears and then dissolves in excess acid to restore the original blue solution (M). Tell what are M, N, O and write balance equation for the chemical changes.
- Excess aq. NH₃ is added dropwise to a solution of AgNO₃ until a brown ppt (A) that first appears dissolves to give a colourless solution (B). The colourless solution when treated with dil. HCl gives a white ppt (C). What are A, B, C? Write balanced equation for changes that occur
- How does gold react with aqua regia and NaCN? Write balanced equation.
- Explain the following:
 - Copper is a transition metal.
 - CuSO₄ forms I₂ with KI.
 - AgCl is insoluble in water but soluble in NH₄OH.
 - Ag is a noble metal but Na is highly reactive.
 - The mp of Au is higher than Ag.
 - The first IE of Au is greater than Ag.
 - Anhydrous CuSO₄ is colourless but turns blue on adding water.
 - Zn displaces Cu from a solution of CuSO₄.
 - CuCl unlike NaCl has covalent nature although Cu⁺ (r ~ 0.93 Å) and Na⁺ (r ~ 0.95 Å) have almost equal radii.
 - AgCl, AgBr and AgI all dissolve in sodium thiosulphate (hypo) and NaCN solution.
 - K₃[Cu(CN)₄] is colourless but [Cu(NH₃)₄]SO₄ is deep blue.
 - Chemistry of Photography.
 - Water solubility of CuCl increases in the presence of high Cl⁻ concentration.
 - In moist air copper corrodes to produce a green layer on its surface.
- A colourless crystalline solid (A) gives two gases B (brown) and C (colourless) on strong heating alone with a metallic residue (D). The gas B dissolves in water in the presence of O₂ to form a water soluble compound (E). The residue D is soluble in (E) regenerating (A). The solid (A) gives white ppt with KCN which is soluble in excess of KCN. Identify A to E giving chemical equations. (A = AgNO₃, B = NO₂, C = O₂, D = Ag, E = HNO₃).
- Complete and write balanced equation for the following:
 - $\text{CuSO}_4 + \text{CN}^- \longrightarrow$
 - $\text{CuSO}_4 + \text{I}^- \longrightarrow$
 - $\text{CuSO}_4 + \text{NH}_4\text{OH} \longrightarrow$
 - $\text{AgCl} + \text{NH}_4\text{OH} \longrightarrow$
 - $\text{AgCl} + \text{NaCN} \longrightarrow$
 - $\text{AgCl} + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow$
 - $\text{AgX} + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow$ [X = Br, I]
 - $\text{Au} + 3\text{HCl} + \text{HNO}_3 \longrightarrow$
 - $\text{AgNO}_3 + \text{PH}_3 \longrightarrow$
 - $\text{AgNO}_3 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \longrightarrow$
 - $\text{HAuCl}_4 + \text{FeSO}_4 \longrightarrow$
 - $\text{Cu}^{2+} + \text{NaOH} + \text{HOOC} \cdot (\text{CHOH})_2 \cdot \text{COOH} \longrightarrow$
- A silver compound (A) which leaves a black stain on skin gives white ppt. with hypo solution. The white ppt. changes to black after some time due to the formation of (B). This black ppt. dissolves in aq NaCN to form (C) which when treated with Zn metal gives a metal (D). Identify A, B, C and D and write balance equation for the reactions which occur. [A = AgNO₃, B = Ag₂S, C = [Ag(CN)₂], D = Ag]

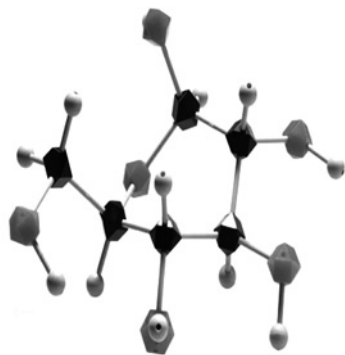
OBJECTIVE-TYPE QUESTIONS

- The correct order of ionization energy is
(a) $\text{Cu} > \text{Ag} > \text{Au}$ (b) $\text{Cu} > \text{Au} > \text{Ag}$
(c) $\text{Au} > \text{Cu} > \text{Ag}$ (d) $\text{Ag} > \text{Au} > \text{Cu}$
- Bonding in Cu is
(a) Covalent
(b) Electrovalent
(c) Ionic and covalent
(d) Coordinate covalent
- Which of the following is paramagnetic?
(a) $\text{K}_3[\text{Cu}(\text{CN})_4]$ (b) $\text{K}[\text{Cu}(\text{CN})_2]$
(c) CuCl (d) $\text{Cu}(\text{NO}_3)_2$
- When Cu_2S and FeS mixture is heated in air the product is
(a) Cu_2S (b) CuO , FeO
(c) Cu_2OFeS (d) Cu_2OFeO
- When a mixture of Cu_2S and Cu_2O are heated the product is
(a) Cu_2S (b) Cu
(c) CuSO_4 (d) CuSO_3
- When excess NH_4OH is added to CuSO_4 solution, the colour of the solution becomes
(a) Red (b) Deep blue
(c) Light blue (d) Green
- When excess KCN is added to CuSO_4 colour of the solution is
(a) Green (b) Blue
(c) Red (d) Colourless
- Which of the following is used in photography?
(a) CuBr_2 (b) CuBr
(c) AgBr (d) AuCl_3
- Which of the following does not disproportionate in water?
(a) Cu^{2+} (b) Au^{+1}
(c) Cu^{+} (d) Cl_2
- The solubility of AgBr in hypo solution is due to the formation of
(a) Ag_2SO_3 (b) $[\text{Ag}(\text{S}_2\text{O}_3)]^-$
(c) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ (d) Ag_2SO_3
- Verdigris is
(a) Basic silver acetate
(b) Basic copper acetate
(c) Basic lead acetate
(d) Basic ferric acetate
- Which of the following is expected to be coloured?
(a) CuCl (b) Ag_2SO_4
(c) CuF_2 (d) MgF_2
- The product 'A', in the following reaction is
$$2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{A} + \text{H}_2\text{SO}_4 + 2\text{HCl}$$

(a) CuSO_4 (b) Cu_2Cl_2
(c) CuCl_2 (d) Cu_2SO_3
- An alloy which does not contain Cu is
(a) Brass (b) Bronze
(c) Solder (d) Bell metal
- Silver sulphide dissolves in NaCN in the presence of O_2 to form the complex.
(a) $\text{Na}[\text{Ag}(\text{CN})_2]$ (b) $\text{Na}_2[\text{Ag}(\text{CN})_4]$
(c) $\text{Na}_3[\text{Ag}(\text{CN})_4]$ (d) All
- Which of the following is coloured due to d – d transition?
(a) CuO (b) Cu_2O
(c) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (d) CuS
- Which of the following is coloured and paramagnetic?
(a) CuCl
(b) $\text{Cu}(\text{NO}_3)_2$
(c) $\text{K}[\text{Cu}(\text{CN})_2]$
(d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
- Which of the following is not expected to exist?
(a) CuF (b) CuCl
(c) CuBr (d) CuI

ANSWERS

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|--------|---------|
| 1. (c) | 2. (c) | 3. (d) | 4. (a) | 5. (b) | 6. (b) | 7. (d) | 8. (c) | 9. (a) | 10. (c) |
| 11. (b) | 12. (c) | 13. (b) | 14. (c) | 15. (a) | 16. (c) | 17. (b) | 18. (a) | | |



13

Group 12 (II_B) – Zinc, Cadmium, Mercury

Zinc (Zn), cadmium (Cd) and mercury (Hg) are last d-elements in their periods. Their outer electron configuration is $(n-1)d^{10}ns^2$. They form +2 ions only (M^{+2} ions) which have configuration $(n-1)d^{10}$. As the elements or the ions they form have full filled $(n-1)d$ orbitals, they are not true transition elements. However, they form a group of their own and are placed with transition metals. There is some similarity to transition metals w.r.t. complex formation especially with NH_3 , CN^- , halide ions and amines.

Electronic configuration

Table 13.1

| Elements | Symbol | Atomic no. | Electronic configuration |
|----------|--------|------------|----------------------------------|
| Zinc | Zn | 30 | $[\text{Ar}] 3d^{10}4s^2$ |
| Cadmium | Cd | 48 | $[\text{Kr}] 4d^{10}5s^2$ |
| Mercury | Hg | 80 | $[\text{Xe}] 4f^{14}5d^{10}6s^2$ |

Mercury is unique. It is the only metal which is liquid at room temperature. It is due to very weak metallic bond in Hg. High promotion and ionization energies for Hg make difficult for electrons to form strong metallic bond. These effects may be due to inert pair ($6s^2$) valence shell of Hg.

Promotion and Ionization Energies

Table 13.2

| | Promotion energies $s^2 \rightarrow s^1p^1$ | Ionization energy (KJmol^{-1}) | |
|----|--|---|--------------|
| Zn | 433 | I (ev) | II (ev) |
| Cd | 408 | 906 (9.39) | 1733 (17.89) |
| Hg | 524 | 876 (8.99) | 1631 (16.84) |
| | | 1007 (10.43) | 1810 (18.65) |

Atomic and Ionic Radii

Atomic radii have the order, $\text{Zn} < \text{Cd} \sim \text{Hg}$.

The increase in radius from Zn to Cd is due to addition of higher orbit in Cd.



Radii of Cd and Hg are very similar due to lanthanide contraction. Mercury is after lanthanides [Ce(58) to Lu(71)]. Therefore, increase in orbit number in Hg ($5d^{10}6s^2$) is counter balanced by lanthanide contraction. Hence, Cd and Hg have similar radii.

Ionic radii increase from Zn^{2+} to Hg^{2+} .

Melting and Boiling Points

All the metals have low cohesive energies and so are soft compared to other transition metals. It indicates weak metallic bonds in Zn, Cd and Hg. It may be due to non-participation of $(n-1)d$ electrons in metallic bonding. The overall effect results into low mp and bp of these elements.

Table 13.4

| Elements | mp(°C) | bp(°C) |
|----------|--------|--------|
| Zn | 420 | 907 |
| Cd | 321 | 765 |
| Hg | -39 | 357 |

Metallic bond in Hg is so weak that it is highly vaporizable. It is the main reason of Hg poisoning. The vapour contains monoatomic Hg. Mercury should, thus, be kept covered.

Ionization Energy

Variation of ionization energy is not regular for Zn, Cd and Hg. The order found is, $Zn > Cd < Hg$.

The ionization energy of Zn is greater than Cd because atomic radius of Cd is greater than Zn. Although the radii of Cd and Hg are very similar, the ionization energy of Hg is greater than Cd. It is due to the fact that 4f electrons in Hg ($4f^{14}5d^{10}6s^2$) shields nucleus poorly. Therefore, 6s electrons experience greater effective nuclear charge. Hence ionization energy of Hg is greater than that of Cd. (The $6s^2$ electrons are popularly called “Inert Pair”).

The first ionization energy of Hg is highest among the metals. It is due to the fact that valence electrons of Hg are inert pair ($6s^2$) electrons.

Oxidation states

These elements have valence shell electron configuration $(n-1)d^{10}ns^2$. First two elements Zn and Cd show fixed oxidation state of +2 corresponding to ns^2 electrons. But Hg shows variable oxidation states, +1 and +2.

| | |
|----|--------|
| Zn | +2 |
| Cd | +2 |
| Hg | +1, +2 |

However, in +1 oxidation state Hg is not Hg^+ , but is a dimer, Hg_2^{+2} .

Table 13.3

| Element | Atomic radius (Å) | Ionic radius M^{+2} , (Å) |
|---------|-------------------|-----------------------------|
| Zn | 1.25 | 0.74 |
| Cd | 1.41 | 0.95 |
| Hg | 1.44 | 1.02 _{vw} |

Table 13.5

| Elements | $r_M(\text{Å})$ | IE(ev) | |
|----------|-----------------|--------|-------|
| | | I | II |
| Zn | 1.25 | 9.39 | 17.89 |
| Cd | 1.41 | 8.99 | 16.84 |
| Hg | 1.44 | 10.43 | 18.65 |

The Hg₂²⁺ ion has metal–metal bond i.e., [Hg – Hg]²⁺. It becomes possible due to 6s¹ electronic structure of Hg⁺. There is enough proof for Hg – Hg bond in Hg₂²⁺. It includes X ray analysis of dry salts and Raman spectral analysis of salt solutions etc.

Nature of Bonds

The +2 oxidation state is stable for all the metals. Ionic compounds in this oxidation state possess considerable covalent nature. It arises due to relatively small size and larger number of core electrons (18e) in M⁺² ions. It is not found in +2 ions of group 2 metal ions, Ca⁺², Sr⁺² and Ba²⁺ (larger radii and less core electrons, 8e).

Table 13.6

| Nature | Radius (Å) | Core electrons | Ion | Radius (Å) | Core electrons |
|------------------|------------|----------------|------------------|------------|----------------|
| Ca ⁺² | 1.00 | 8e | Zn ⁺² | 0.74 | 18e |
| Sr ⁺² | 1.18 | 8e | Cd ⁺² | 0.95 | 18e |
| Ba ⁺² | 1.35 | 8e | Hg ⁺² | 1.02 | 18e |

Thus ZnCl₂, CdCl₂ and HgCl₂ in anhydrous state are covalent. HgCl₂ is so much so covalent that it does not give chromyl chloride test which is common and most authentic for ionic chlorine i.e., Cl[–]. Therefore ZnCl₂ in anhydrous state is a Lewis acid but not the CaCl₂ because CaCl₂ is not covalent. It is ionic and has lattice structure.

However, in hydrated state, ZnCl₂ is ionic and is formulated as [Zn(H₂O)₄]²⁺ . 2Cl[–].

Electrode Potential

Standard electrode potentials for these elements are very different. The order is Zn < Cd << Hg. It shows that Zn is most reactive and Hg least reactive.

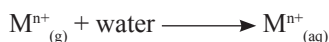
High positive E° of Hg shows its noble nature. The large difference between Cd and Hg may be due to high ionization energy of Hg and higher hydration energy of Cd⁺². Zinc and Cd are above H in electro chemical series but Hg is below H. Therefore, Zn and Cd are reducing agents but not Hg.

Table 13.7

| Elements | M ⁺² _(aq) + 2e | E°(volt) | M _(s) |
|----------|--------------------------------------|----------|------------------|
| Zn | | –0.76 | |
| Cd | | –0.40 | |
| Hg | | +0.85 | |

Hydration Energy

Energy released for the process,



is called hydration energy. It is given by

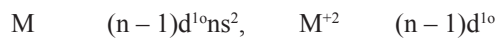
$$\Delta H_{\text{Hvd}} = \frac{Z^*e^2}{r} [1 - (1/D)]$$

It shows that $\Delta H_{\text{Hvd}} \propto Z^*$ and $\propto 1/r$, i.e., higher the Z* and lower the radius of the ion, higher the ΔH_{Hvd} .

Zinc, Cd and Hg in +2 have high Z^* so their hydration energy is high, greater than hydration energies of group 2 metals +2 ions (i.e., Ca^{+2} , Sr^{+2} etc.) another factor responsible for higher hydration energies of Zn^{+2} , Cd^{+2} and Hg^{+2} is greater number of core electron (18e) over Gr 2, M^{+2} ions (8e). Although Ca^{+2} and Cd^{+2} have almost equal ionic radii (00.94Å) hydration energy of Cd^{2+} is larger than Ca^{2+} .

Magnetic Properties

The metals and their +2 ions have all their electrons paired and so are diamagnetic



The Hg^+ ion has electron configuration, $6s^1$ i.e., unpaired electron but it exists as Hg_2^{2+} which has no unpaired electron. Therefore, mercurous compounds are also diamagnetic.

Colour of Compounds

Some of the compound of Zn, Cd and Hg are coloured but not due to d – d transitions as d orbitals are full filled ($\text{Zn}^{+2} - 3d^{10}$, $\text{Cd}^{+2} - 4d^{10}$, $\text{Hg}^{2+} - 5d^{10}$).

The compounds are coloured due to crystal defect and charge transfer.

Zinc oxide is yellow when hot but colourless in cold. It is due to defect structure, electron excess. When ZnO is heated, some O^{2-} is converted to O_2 ($\text{O}^{2-} \longrightarrow \frac{1}{2}\text{O}_2 + 2e$) and escapes the lattice leaving behind electrons. These electrons move in the lattice from one point to another, making ZnO yellow. But when ZnO is cooled, it takes up O_2 from the atmosphere converting it to O^{2-} by the electron present in the lattice, ($\frac{1}{2}\text{O}_2 + 2e \longrightarrow \text{O}^{2-}$). A normal lattice is regenerated and ZnO becomes colourless.

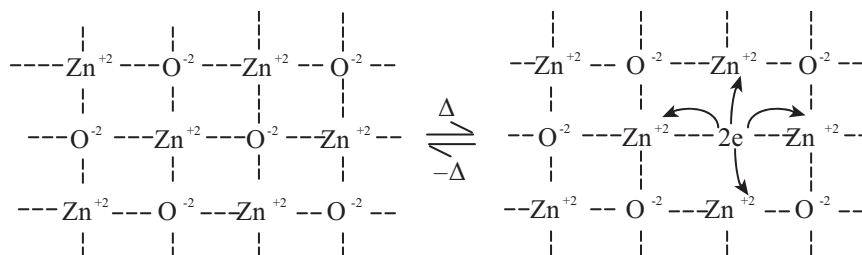


Figure 13.1

Cd and Hg compounds are coloured due to charge transfer and defect structure.

Table 13.9

| Compound | Colour | Reason |
|-------------------------|----------|---|
| CdO | Brown | Charge transfer |
| CdS | Yellow | Charge transfer |
| HgS | Black | Charge transfer |
| HgS | Red | Defect structure |
| HgO | Yellow | Charge transfer |
| | Red | Charge transfer |
| Hg_2I_2 | Greenish | (but difference in colour due to particle size) |
| HgI_2 | Red | Charge transfer |
| | | Charge transfer |

Some useful compounds

1. ZnO: (Philosopher's Wool)

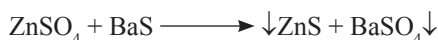
Applications

- As white pigment
- Ointment base
- Cosmetic industry
- As filler and vulcanization activator in rubber tyres
- As a photoconductor in the Xerox method of electrostatic printing.

2. ZnS: It is white and insoluble in water.

Applications

- In making fluorescent screen
- Impure ZnS is a phosphor (i.e., can convert energy, electron beam, into visible light). Such ZnS is used in making phosphorescent screens useful for X – rays, radioactivity work, radar and television.
- Used in making white pigment, lithopone (ZnS + BaSO₄)



3. Hg₂Cl₂: (Mercurous chloride):

Applications

- Preparation of calomel electrode.

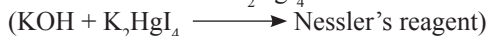
4. Hg₂SO₄: (Mercurous sulphate):

Applications

- A depolarizer in Weston standard cell.

5. K₂HgI₄ [Pot. tetraiodomercurate (II)]

Alkaline solution of K₂HgI₄ is known as Nessler's reagent.



Nessler's reagent is very sensitive reagent for NH₃ or ammonium salts. It forms brown colouration or ppt with NH₃ or ammonium salts.



The brown pp is a basic Hg(II) amido iodide and is formulated as

This reaction is used to detect traces of NH₃ in drinking water. Drinking water is contaminated by NH₃ through sewage water.

6. Cadmium is used in rechargeable dry cells with Ni, Ni/Cd batteries.

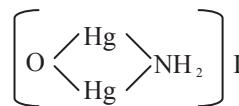


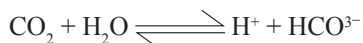
Figure 13.2

Biochemistry of Zn, Cd and Hg

1. Zinc

It has many important biological roles. A normal human contain about 2g of Zn which is next to Fe, 4g. Many enzymes contain Zn, some important ones include—

- Carbonic anhydrases: Fast acting, speeds up absorption of CO₂ by red blood cells in muscles and tissues. Also helpful in release of CO₂ in the lungs. It also regulates pH of blood by creating a buffer medium containing HCO₃⁻ ion.



- Dehydrogenases – sugar metabolism
- Alcohol dehydrogenase – metabolism of alcohol.

- (d) Carboxy peptidase (MW 34300, IZ): Found in pancreas of mammals, catalyses the hydrolysis of peptide bond at the carboxyl end.

2. Cadmium

It is a major environmental pollutant.

Effects

- (a) Itai–Itai diseases (Japan) and oost–oost diseases (English): It is joint pain and bone deformation. Ultimately leads to multiple bone fractures even by coughing. Weakness of bones may be due to replacement of Ca by Cd as both have very similar radii in +2 oxidation state.
- (b) Tobacco smoke contains Cd. It affects liver and kidney. Replaces Zn in some enzymes and thus preventing their normal function.
- (c) Metallothionein: It is the only biological material known to contain Cd. Its function is unknown.

3. Mercury

Mercury is unique in its biochemistry. Mercury vapours and many of its soluble compounds are toxic. But some mercury compound, such as the red crystalline variety of HgS, known as “Makardhwaj” is regarded as life saving drug in “Ayurveda” the classical Indian method of treatment.

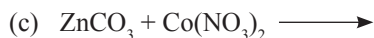
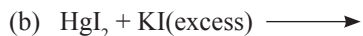
Toxic effect of Hg (Hg^{+2}) is mainly due to two reasons-

- (i) There is no body chemistry for excreting Hg.
- (ii) Hg^{2+} inhibits enzymes, especially those containing the thiol groups (Hg^{2+} is a soft Lewis acid and S^{-2} or S soft Lewis base. So greater affinity for each other). The most famous case of Hg poisoning is “Miamata disease” of Japan. Organo Hg compounds are more toxic than inorganic ones. Example, $(\text{CH}_3)_2\text{Hg}$ is highly toxic.

PRACTICE QUESTIONS

A. Explain the following:

- (a) Position of Zn, Cd and Hg in the periodic table.
- (b) Mercury does not resemble Zn and Cd in its chemistry.
- (c) Unipositive mercury is a dimmer, Hg_2^{2+} .
- (d) Unlike Zn cadmium compounds are extremely poisonous.
- (e) Zn salts dissolve in water as well as in alcohol.
- (f) Hot ZnO is yellow.
- (g) ZnCl_2 solution is slightly acidic.
- (h) ZnCO_3 is not prepared by adding Na_2CO_3 in ZnCl_2 solution.
- (i) Hg and not Zn and Cd shows variable oxidation states.
- (j) Hg_2Cl_2 and HgCl_2 form black and white precipitates with NH_4OH respectively.
- (k) An amalgam, and give a few uses.
- (l) HgO is found in different colours (red and yellow).
- (m) ZnCl_2 and MgCl_2 differ in mp.
- (n) ZnS is insoluble in water but CaS is soluble.
- (o) $\text{Zn}(\text{OH})_2$ dissolves in NaOH and NH_4OH both.
- (p) Hg is liquid.

B. Complete the following reactions:**OBJECTIVE-TYPE QUESTIONS**

- Which of the following is phosphorescent?
 - ZnO
 - ZnS
 - ZnCl₂
 - Zn₃P₂
- Spelter is
 - Zn – Hg
 - Pure Zn
 - impure Zn
 - Zn – Cu
- Which of the following contains Ni?
 - Brass
 - Bronze
 - German silver
 - Gun metal
- Which of the following reactions produces yellow HgO?
 - $\text{HgCl}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\Delta} \text{HgO} + 2\text{KCl} + \text{CO}_2$
 - $\text{Hg}_2\text{O} + \frac{1}{2} \text{O}_2 \xrightarrow{\Delta} \text{HgO}$
 - $\text{Hg}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{HgO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$
 - $\text{Hg} + \frac{1}{2} \text{O}_2 \xrightarrow{\Delta} \text{HgO}$
- Which of the following gives black ppt. with NH₄OH?
 - HgCl₂
 - Hg₂Cl₂
 - K₂[HgI₄]
 - Hg(NO₃)₂
- Nessler's reagent is
 - K₂HgI₄
 - K₂HgI₄ + NH₄OH
 - K₂HgI₄ + KOH
 - HgI₂ + KOH
- Lucas reagent is
 - HgCl₂ + HCl
 - ZnCl₂ + conc. HCl
 - CdCl₂ + HCl
 - HgCl₂ + conc. HCl
- Corrosive sublimate is
 - HgCl₂
 - Hg₂Cl₂ + Hg
 - Hg₂Cl₂
 - HgCl₂ + Hg
- Mercury does not form amalgam with
 - Al
 - Ag
 - Fe
 - Zn
- Which of the following forms H₂ when heated with caustic soda?
 - Zn
 - Hg
 - Mg
 - Cu
- Zinc blende ore is concentrated by
 - Gravity separation
 - Magnetic separation
 - Froth floatation
 - Leaching
- Calamine is an ore of
 - Ca
 - Cd
 - Cu
 - Zn
- Which of the following is a carbonate?
 - Cuprite
 - Villemitite
 - Siderite
 - Limonite
- One mole zinc phosphide on reaction with excess water will give
 - One mole phosphine
 - Two mole phosphine
 - Two moles phosphoric acid
 - Three moles phosphine
- A metal forms two chlorides A and B. The chloride A gives white ppt. with NH₄OH but B gives black ppt. Also A forms a red ppt. with KI, which dissolves in excess KI to form a colourless solution. A and B respectively are
 - HgCl₂ and Hg₂Cl₂
 - Hg₂Cl₂ and HgCl₂
 - ZnCl₂ and Hg₂Cl₂
 - HgCl₂ and ZnCl₂

ANSWERS

1. (b) 2. (c) 3. (c) 4. (c) 5. (b) 6. (c) 7. (b) 8. (a) 9. (c) 10. (a)
 11. (c) 12. (d) 13. (c) 14. (b) 15. (a).

14

Group – 13 (III_A) B, Al, Ga, In, Tl



Boron, Al, Ga, In and Tl are p – block elements and have three valence electrons (ns^2np^1).

Group in p – block = valence electrons + 10.

So, these elements belong to group – 13.

Electron configuration and core electrons

Table 14.1

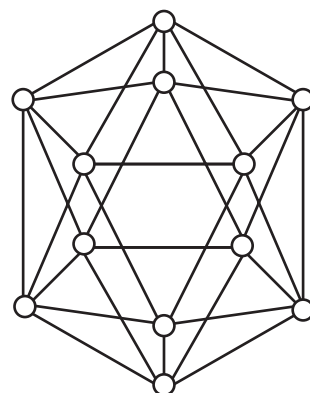
| Electron | At. No. | Electron configuration | Core electrons |
|----------|---------|-------------------------------|----------------|
| B | 5 | [He] $2s^22p^1$ | 2 |
| Al | 13 | [Ne] $3s^23p^1$ | 8 |
| Ga | 31 | [Ar] $3d^{10}4s^24p^1$ | 18 |
| In | 49 | [Kr] $4d^{10}5s^25p^1$ | 18 |
| Tl | 81 | [Xe] $4f^{14}5d^{10}6s^26p^1$ | 18 |

The difference in the number of core electrons and presence of 4f electrons in Tl has profound effect on the chemistry of these elements. Valence orbitals include p-orbitals. With the filling of p – orbitals, non-metallic property develops. Boron is thus a non-metal (slightly metallic). However, non-metallic nature decreases with increase in atomic number and Al, Ga, In and Tl are metals. Boron is a semiconductor but others display metallic conduction. All the elements are solid.

B has rhombohedrae structure, B₁₂.

Gallium and In have unusual structures. Gallium has exceptionally low melting point (~30°C) but its boiling point is high (~2070°C). It is the longest liquid range (30–2070°C) of any known substance. Therefore, Ga is used for high temperature thermometry in a quartz envelope.

Aluminium and Ga are amphoteric and dissolves in NaOH solution on boiling.



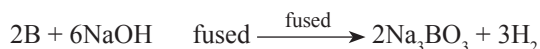
Al → ccp

Tl → hcp

Figure 14.1



Boron reacts when fused with NaOH.



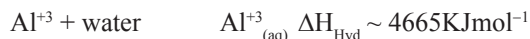
General Properties

Table 14.2

| Property | B | Al | Ga | In | Tl |
|-----------------------------------|-------|-------|-------|-------|-------|
| Atomic radius (Å) | 0.82 | 1.18 | 1.26 | 1.44 | 1.48 |
| Ionic radius, M ³⁺ (Å) | 0.2 | 0.5 | 0.62 | 0.81 | 0.95 |
| Metallic radius (Å) | — | 1.43 | 1.41 | 1.66 | 1.71 |
| Ionisation I | 8.3 | 5.95 | 6.0 | 5.8 | 6.1 |
| Enthalpy (ev) II | 25.2 | 18.82 | 20.0 | 18.8 | 20.3 |
| III | 38.0 | 28.44 | 30.6 | 28.0 | 29.7 |
| Electronegativity | 2.0 | 1.5 | 1.6 | 1.7 | 1.8 |
| mp (°C) | 2180 | 660 | 29.8 | 157 | 303 |
| bp (°C) | — | 2327 | ~2250 | 2070 | 1553 |
| E°, M ³⁺ /M (V) | −0.73 | −1.66 | −0.56 | −0.34 | +0.72 |

Note:

- Radius of Tl⁺ is 1.44Å and E° Tl⁺/Tl is −0.34V.
- Variation of atomic radius is not regular, (i.e., do not increase down the group), and $r_{\text{Al}} \sim r_{\text{Ga}}$ and $r_{\text{In}} \sim r_{\text{Tl}^+}$. The equivalence is due to d – orbital contraction for Al – Ga and lanthanide contraction for In – Tl.
- The first IE of Al and Ga are almost equal due to similarity in radii.
- The IE of In < Tl. It is due to higher effective nuclear charge (Z*) for Tl. It results as 4f electrons are least shielding.
- E° for Al (Al³⁺ – Al) is high inspite of its very high III ionisation energy. The very high hydration energy of Al³⁺ causes this reaction to proceed,



The main reason for high hydration energy is very high charge to radius ratio for Al³⁺ (~6)

Oxidation states and nature of bond

The group –13 elements show variable oxidation states of +3 and +1. For lighter members +3 state is more stable than +1. Thus for Tl, +1 state is more stable than +3. It is due to inert pair effect. The 6s² pair does not prefer to form bonds and is called inert pair. The basic reason for such an effect is bond energy. The M–Cl bond energy in MCl₃ compounds are as follows:

Table 14.3

| MCl ₃ | M – Cl, energy (KJmol ^{−1}) |
|------------------|---------------------------------------|
| Ga | 242 |
| In | 206 |
| Tl | 153 |

The ionization energies of B is very high. It is, therefore, covalent in its compounds, always tricovalent ($2s^2 2p^1$ electrons).

In +3 oxidation state, Al has very high charge to radius ratio (~ 6.0). So, it is also covalent in its anhydrous compounds. However, in aq. solution tricovalent Al (e.g., AlCl_3) becomes ionic due to high hydration energy of Al^{+3} (4665 kJ mol^{-1}) $[\text{Al}(\text{OH}_2)_6]^{3+} \cdot 3\text{Cl}^-$. The soluble compounds are quite acidic due to hydrolysis (high charge to radius ratio of Al^{+3}).



Tl is ionic in +1 oxidation state, TlCl ionic. The Tl^+ ion resembles K^+ and Rb^+ . It is because radii of the ions are comparable ($\text{K}^+ \sim 1.38 \text{ \AA}$, $\text{Tl} \sim 1.5 \text{ \AA}$, $\text{Rb} \sim 1.52 \text{ \AA}$). Therefore, TlOH is a strong base like group – 1 hydroxides. Tricovalent compounds, MX_3 , are electron deficient as octet around the central atom is not complete.

Such compounds remove their electron deficiency by:

(i) Back – bonding

In BX_3 , B is sp^2 and has a vacant p – orbital perpendicular at the triangular plane. X – atom has filled p – orbital. They overlap resulting into π –bonding.

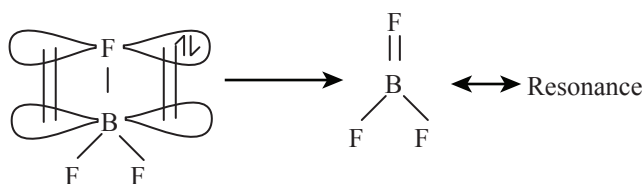


Figure 14.3

(ii) Coordination with Lewis bases

B has vacant orbital which accepts electron pair from F^- .

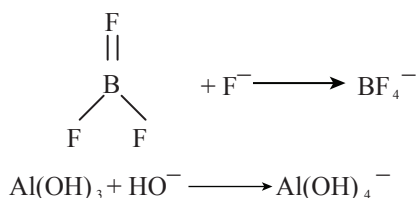
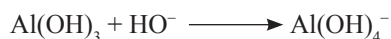


Figure 14.4



(iii) Polymerization

AlCl_3 removes electron deficiency by dimerization.



Dimer is made easily because Cl has lp and Al has vacant orbital.

AlCl_3 is not stabilized by back bonding. It is due to the following facts:

- p – orbital of Al is large, so p – p overlap is not effective.
- 8 electron core in Al causes larger repulsion ($8e - 8e$) destabilizing back bonding effective.

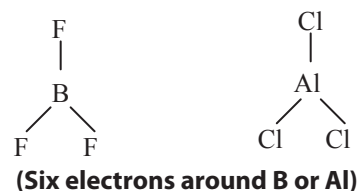


Figure 14.2

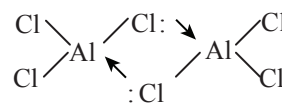


Figure 14.5

BX_3 can not stabilize by dimerization.
B is small in size. The dimer has a small ringn
have so, it is not stable.

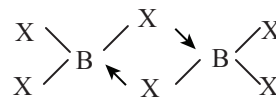
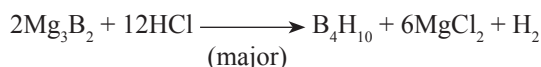
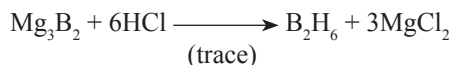


Figure 14.6

Hydrides

Boron forms a series of volatile molecular hydrides called Boranes, B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{10} etc. Boranes were first prepared by Alfred Stock in the year 1912 to 1936.



Diborane, B_2H_6 , is simplest. Two series of boranes are found:

- (i) B_nH_{n+4} B_2H_6 , B_5H_9 ect (nideo – boranes)
- (ii) B_nH_{n+6} B_4H_{10} , B_5H_{11} ect. (arachno – boranes)

The B_nH_{n+4} series compounds are more stable. Boranes are named as

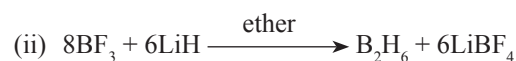
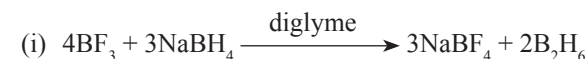
The last number in the name indicates number of hydrogen atoms.

Table 14.4

| Formula | Name |
|---------------------------|------------------|
| B_2H_6 | Diborane – 6 |
| B_4H_{10} | Tetraborane – 10 |
| B_5H_9 | Pentaborane – 9 |

Diborane (B_2H_6)

It is a gas (bp – 92.6°C) spontaneously flammable in air. It can be prepared in many ways:



This reaction is quantitative

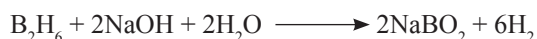
(diglyme – diethylene glycol dimethyl ether $\text{H}_3\text{C OCH}_2 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_2\text{OCH}_3$)

Properties

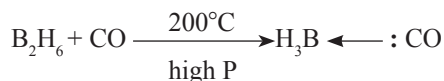
- (i) It spontaneously burns in air.



- (ii) It is instantly hydrolyzed by water or alkali.



(iii) It is electron deficient and forms addition compound with Lewis bases.



(iv) Some more reactions are summarized.

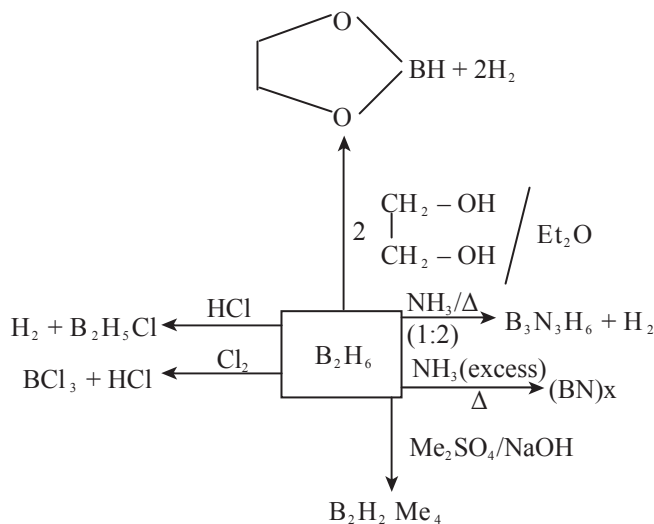


Figure 14.7

(v) Hydroboration: The reaction of B_2H_6 in ether with unsaturated hydrocarbons, called hydroboration. It gives mainly anti-Markownik off, cis-hydrogenation or hydration.

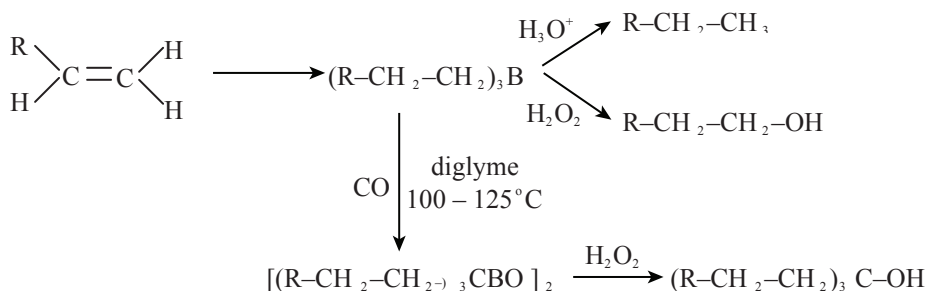
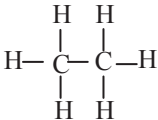


Figure 14.8

Structure of B_2H_6

Diborane (B_2H_6) is stoichiometrically identical to C_2H_6 . But they have different structures.

Table 14.5

| Molecule | Valence electrons | Structures |
|-------------------------------|-------------------|---|
| C ₂ H ₆ | 4x2 + 1x6 = 14 |  |
| B ₂ H ₆ | 3x2 + 1x6 = 12 | Electron deficient structure as above not possible |

Ethane has 14 valence electrons and there are seven bonds in C₂H₆. Therefore a 2c – 2e bonding scheme is possible. But B₂H₆ has only 12 valence electron. Therefore 2c – 2e bonding scheme is not possible in B₂H₆ as it is basically electron deficient.

Methods of structure determination reveal that B₂H₆ has a H – bridge structure like

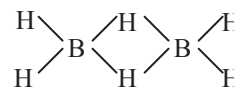


Figure 14.9

This structure has two types of B – H bonds

(i) **Terminal B – H bonds.** These are 2c – 2e bonds.

(ii) **Bridge B – H – B bonds (a 3c – 2e bond).** This bridge bond is explained by the concept of multicentre bonding.

In a 3c – 2e multicentre bonding, 2 electrons are used to join three centres (3 atoms).

In B₂H₆ structure, B is sp³.

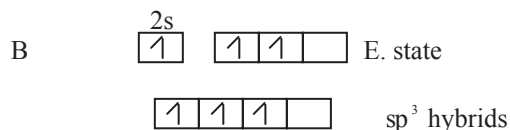


Figure 14.10

Two out of these four hybrids at each B overlap with the 1s orbital of the H-atom to give four terminal B – H bonds.



Figure 14.11

All these B – H bonds are in the same plane.

The bridge B – H – B bonds are formed when sp³ hybrid at B having electron, sp³ hybrid vacant at other B – atom and 1s orbital of H – atom overlap.

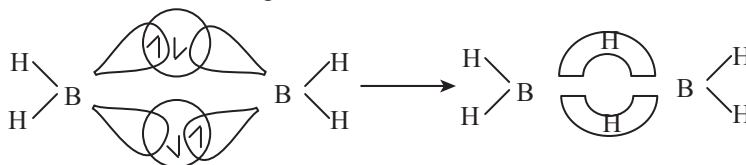


Figure 14.12

These are perpendicular to the terminal bonds. This is three centre – 2 electron multicentre bonding ($3c - 2e$ bonding). This bond is called τ -bond or banana bond or bent bond.

Terminal and bridge H atoms are not equivalent. It is proved by IR, Raman spectra and chemical reaction also.

Diborane forms tetramethyl derivative, $B_2H_2Me_4$, only showing chemical equivalence of four H – atoms.

Aluminium hydride is polymeric, $(AlH_3)_x$. It has also H – bridge structure,

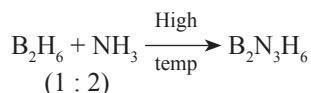


Figure 14.13

The H – bridge, $Al - H - Al$ has $3c - 2e$ bonding.

Borazole ($B_2N_3H_6$)

When B_2H_6 and NH_3 in the ratio 1 : 2 heated at high temperature borazole is formed.



Borazine resembles benzene in structure. The π bond in borazine is, however, formed by back bonding, involving filled p – orbital at N and vacant orbital at B.

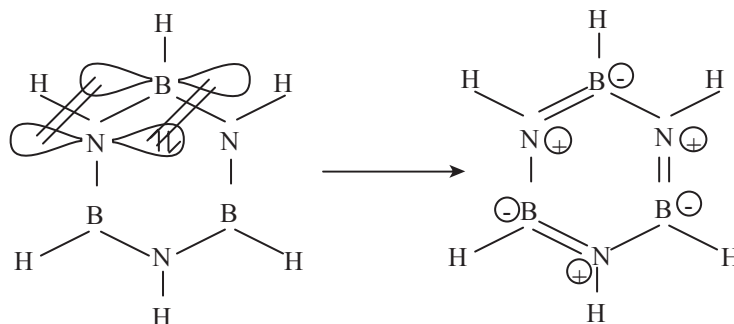


Figure 14.14

Thus borazine has aromatic character $(4n + 2)\pi$ electrons. It is called inorganic benzene.

Borazine unlike benzene is more reactive towards addition reactions.

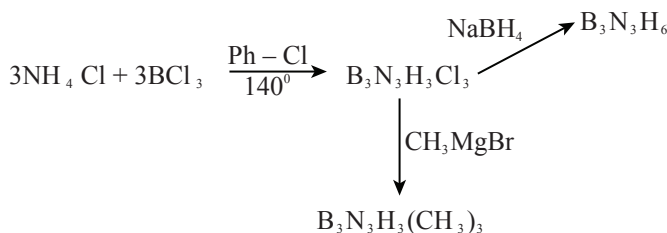
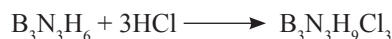


Figure 14.15

Substituted borazine can be prepared as

Disubstituted borazine $\text{B}_3\text{N}_3\text{H}_4\text{X}_2$ can have four isomers (there are only three for $\text{C}_6\text{H}_4\text{X}_2$).

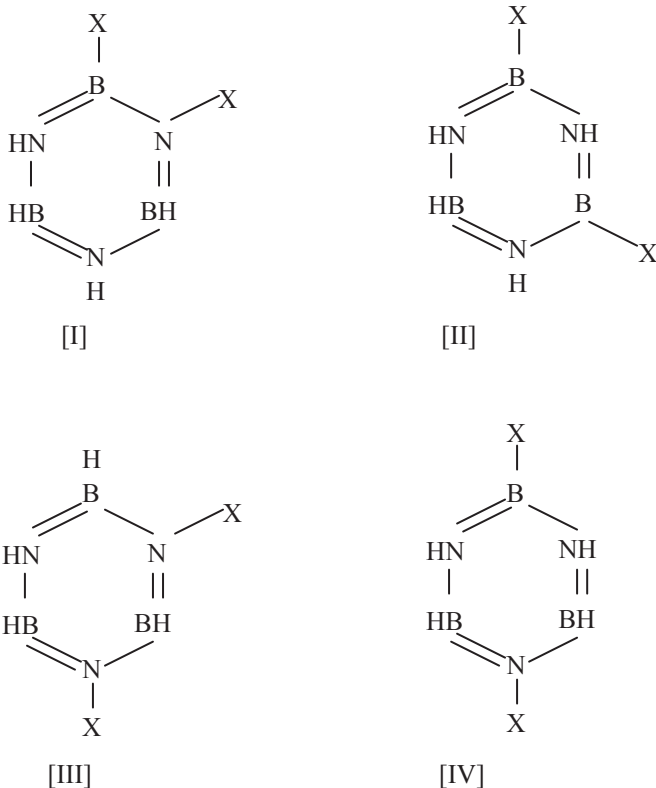


Figure 14.16

Boron nitride (BN)_x

When B_2H_6 is heated at high temperature with excess NH_3 , boron nitride is formed.

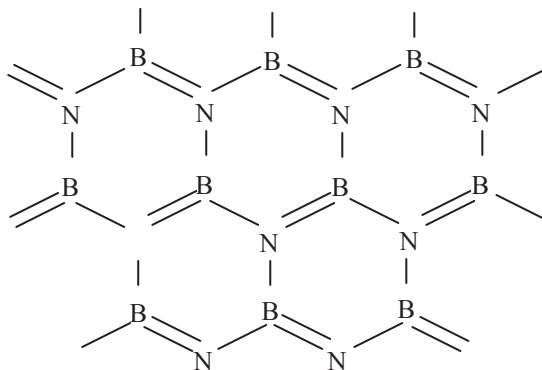
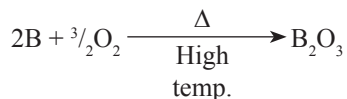


Figure 14.17

The B – N, π bond is formed by overlap of filled p-orbital at N and vacant p-orbital at B.

Oxygen compounds (oxide and hydroxides)

Boron is inert towards O_2 at ordinary temperature. But it burns with green flame when heated strongly in O_2 .



But B_2O_3 is usually made by dehydrating boric acid.



Boric oxide (B_2O_3) is acidic in nature. On being heated with transition metal oxides B_2O_3 forms metaborates which have colours.



This is the basis of borax bead test in salt analysis.

Boric oxides (B_2O_3) also react with very highly acidic oxides like P_4O_{10} forming boron phosphate.



In this reaction B_2O_3 is basic.

Aluminium reacts rapidly with O_2 but only at the surface to form Al_2O_3 . The thin film of Al_2O_3 on the surface prevents further reaction.

At high temperature Al burns in O_2 with brilliant white light forming Al_2O_3 . The reaction is highly exothermic.

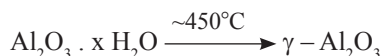
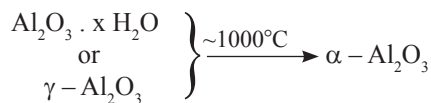


The ΔH_f of this reaction is very high, -1670 KJmol^{-1} , higher for any other metal oxide.

There are two forms of anhydrous Al_2O_3 (alumina):

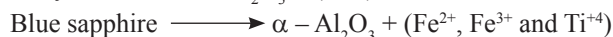
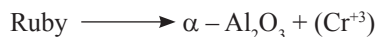
- (i) $\alpha - Al_2O_3$ (corundum) and
- (ii) $\gamma - Al_2O_3$

Hydrous oxide



The $\alpha - Al_2O_3$ is very hard (9 on Moh's scale), and resistant to hydration and attack by acids.

Gem stones ruby, blue sapphire are mixed metal oxides:



Fibrous Al_2O_3 and ZrO_2 form a fiber known as "Saffil".

Alumina (Al_2O_3) is extremely stable ($\Delta H_f = -1670 \text{ KJmol}^{-1}$). Therefore, Al-powder is used to reduce metal oxides to metal, especially transition metal oxides,



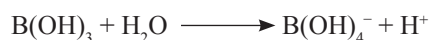
The reactions are highly exothermic. So much so heat is evolved that the reduced metal is obtained in the molten state. This process is known as Alumino Thermic Reduction or Thermite Reduction or Goldsmidt Alumino Thermic Reduction.

Boric Acid

B₂O₃ is acidic and dissolves in water to form Boric Acid.



It is a weak acid ($\text{p}K_a = 9.0$), moderately soluble in water. In water it acts as a Lewis acid, accepting HO⁻ from water and thereby releasing a proton, (H⁺).



Thus, B(OH)₃ behaves a monoprotic acid. The acid strength of boric acid is increased in the presence of a polyol like glycerol, mannitol etc., (but not ethylene glycol). The acidity is increased due to formation of a complex (chelate), and so boric acid can be titrated with NaOH.

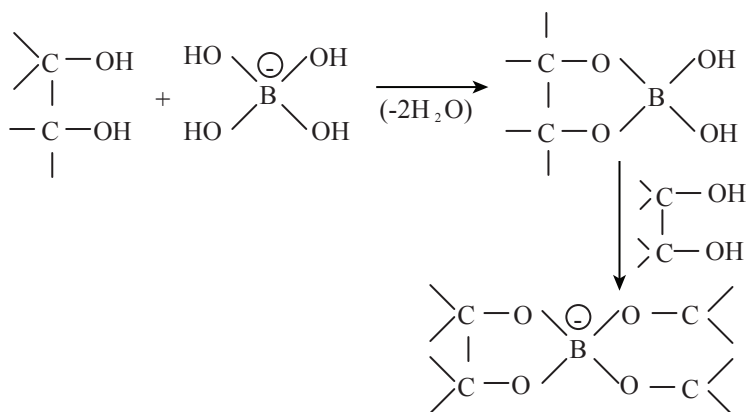
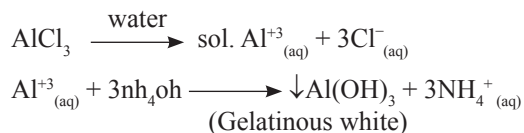


Figure 14.18

The complex has spiran like structure. Hence, often called Borospiranic acid.

Structure of Boric Acid

The aluminium hydroxide is amphoteric. It can be precipitated when an aluminum salt solution is treated with NH₄OH.



The ppt. is actually [Al(H₂O)₃(OH)₃]

Al(OH)₃ is amphoteric because Al – OH and O – H bonds can react with equal ease.

Therefore, Al(OH)₃ dissolves in conc. NaOH or dil. HCl both.

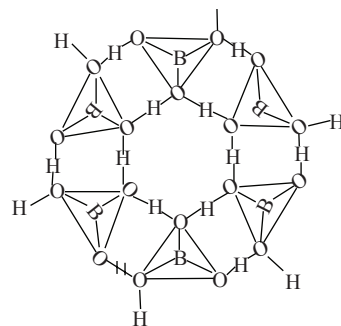


Figure 14.19

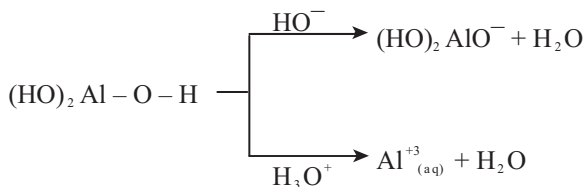
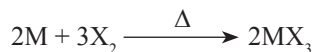


Figure 14.20

Halides

All elements form halides of the type MX_3 .



The compound TlI_3 is not Tl(III) iodide but is Tl(I) triiodide, Tl^+I_3^- . Many other metals in their higher oxidation state also do not form stable iodides. Example,

The iodides actually formed are CuI , FeI_2 and PbI_2 .

Boron trihalides, BX_3 , are known for all the halogens. Their general properties are as follows:

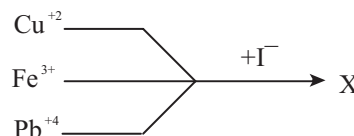


Figure 14.21

Table 14. 6

| Property | BF_3 | BCl_3 | BBr_3 | BI_3 |
|---|---------------|----------------|----------------|----------------------|
| Physical state | Gas | Volatile liq. | Volatile liq. | Unstable white solid |
| ΔH_f (250°C) gas, KJmol^{-1} | -1123 | -408 | -208 | — |
| mp (°C) | -127 | -107 | -46 | 50 |
| bp (°C) | -99.9 | 12.5 | 91.3 | 210 |
| Bond distance (Å) (B – X) | 1.30 | 1.75 | 1.87 | 2.10 |
| Bond energy (KJmol^{-1}) (B – X) | 646 | 444 | 368 | 267 |

The boron trihalides, BX_3 , are hydrolyzed by water, but BF_3 is hydrolyzed partially.



Other halides are hydrolyzed completely to boric acid.



The fluoride of Al (and Ga, In, Tl also) is ionic (X_F large) having high mp.

The other halides of Al i.e., AlX_3 ($X = Cl, Br, I$) are covalent when anhydrous.

They exist as dimer.

The dimeric formula is retained when it dissolves in benzene (non-polar solvent). But when it is dissolved in water, the covalent dimer is broken to ionic species.

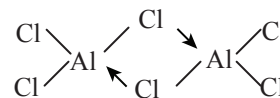


Figure 14.22



It is due to very high hydration enthalpy of Al^{+3} ($\sim 4665 \text{ KJmol}^{-1}$)

Lewis Acid Strength of BX_3

Boron trihalides are electron deficient (only six electrons around B) and function as Lewis acids. If electronegativity and steric factor are considered, the Lewis acid strength should be, $BF_3 > BCl_3 > BBr_3 > BI_3$.

However, the actual strength found is, $BF_3 < BCl_3 < BBr_3 < BI_3$

It is explained, in terms of B-halogen π -bonding. In BX_3 , boron is sp^2 hybridized and BX_3 is triangular planar. The pz orbital at B is vacant.

But Pz orbitals at each halogen is filled (i.e., has 2 electrons). These orbitals overlap side-wise forming π bond.

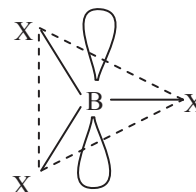


Figure 14.23

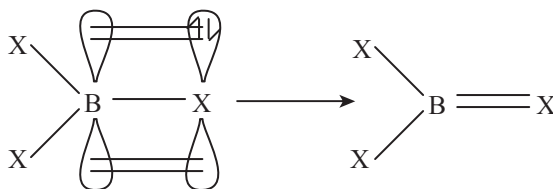
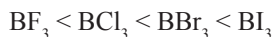


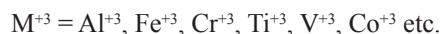
Figure 14.24

Such a π -bond is delocalized as all the halogens are capable of forming π -bonds. The π -bond effectiveness is maximum in BF_3 as B and F are comparable in size. With increase in size of the halogen π -bond effectiveness decreases. Thus electron deficiency at B is maximum in BI_3 and minimum in BF_3 . Hence the Lewis acid strength is



Alums

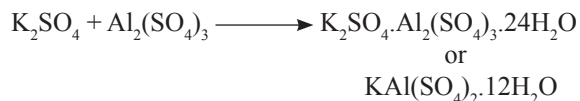
Alums are hydrated double salts which contain large M^+ , small M^{+3} and SO_4^{-2} ions. Their general formula is, $M^+ M^{+3} (SO_4)_2 \cdot 12H_2O$, where,



The Li^+ ion does not form alum as it is too small to produce a stable crystal structure. The alum crystals are large octahedra which contain $[M(H_2O)_6]^+$, $[M(H_2O)_6]^{+3}$ and two SO_4^{-2} ions. They are found very pure.



Alums are prepared by crystallization of equimolar solutions of the two sulphates.



Potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (fitkiri) is used as a mordant in dyeing. It is also used as antiseptic.

Isolation of B

Ores

- | | | |
|----|------------|--|
| 1. | Borax | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ |
| 2. | Kernite | $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ |
| 3. | Coleminite | $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ |

Most important ore is borax and B is isolated from borax.

Steps

1. Borax to Boric acid crystal
2. Boric acid to B_2O_3
3. Red. Of B_2O_3 to B.

Reactions

(a) Powdered borax + conc. HCl is heated to produce boric acid.



Hot solution on cooling gives crystals of H_3BO_3 .

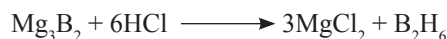
(b) $2\text{H}_3\text{BO}_3 \xrightarrow{\Delta} \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \uparrow$ Crystal

(c) $\text{B}_2\text{O}_3 \longrightarrow \text{B}$ (amorphous)



Boron produced contains impurities of Mg_3B_2 , B_2O_3 and MgO .

The impurities are removed by washing with aqueous NaOH, HCl and finally with HF; which produces B of ~95% purity.

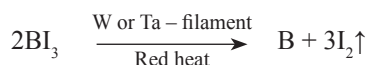


Crystalline B

It may be obtained by the following methods.

(i) $2\text{BF}_3 \xrightarrow[\Delta]{\text{Ta-filament}} 2\text{B} + 3\text{F}_2 \uparrow$

(ii) Van Arkel method



PRACTICE QUESTIONS

A. Explain the following:

- Atomic radii of Al and Ga are almost equal.
- B₂ is paramagnetic.
- First IE of Al is lower than Mg.
- The B – F bond is more polar than B – Br bond but BF₃ is a weaker Lewis acid than BBr₃.
- Boric acid is strong in the presence of glycerol (or other polyols).
- Cupric oxide forms blue mass when heated with borax.
- Al is a good reducing agent for transition metal oxides.
- Boron does not exist as B⁺³ in its compounds.
- Al is stable in air and water although it is very electropositive.
- Tl is more stable in +1 oxidation state.
- How does H₃BO₃ ionize in water?
- The substance TlI₃ contains what ions and why?
- AlF₃ does not resemble BF₃ and is a weak Lewis acid.
- Boric acid in methanol when heated gives vapours, which will colour a flame green.
- Draw the structure of B₂H₆ and explain bonding.
- Anhydrous AlCl₃ is covalent but hydrated salt is ionic.

- Al₂O₃ when heated with Co(NO₃)₂ forms blue mass.
- Al(OH)₃ is an amphoteric hydroxide.
- Anhydrous AlCl₃ is not obtained when AlCl₃·6H₂O is heated.
- Progressive addition of NaOH solution to a solution of AlCl₃ till higher pH (pH ~ 10)
- LiBH₄ is soluble in water whereas LiAlH₄ explode in water.

B. (i) How will you convert B₂H₆ into

- (BN)X
- B₃N₃H₆
- B₂H₂Me₄
- B₂H₅Cl
- B(OCH₃)₂
- B(OH)₃

(ii) How will you convert...

- B₂O₃ into crystalline Boron
- BCl₃ into B₂H₆
- Al₂O₃ into potash alum
- AlCl₃ into LiAlH₄

(iii) Draw the structure of the following:

- B₂H₆
- B₃N₃H₆
- Na₂B₄O₇·10H₂O
- Al(O.t-Bu)₃
- (BN)X
- Isomers of B₃N₃H₄Cl₂

OBJECTIVE-TYPE QUESTIONS

- Which of the following is expected not to exist?
 - B₅H₁₁
 - B₅H₉
 - B₅H₁₀
 - B₆H₁₀
- The correct Lewis acid strength order is
 - BBr₃ > BCl₃ > BF₃
 - BF₃ > BCl₃ > BBr₃
 - BCl₃ > BBr₃ > BF₃
 - BBr₃ > BF₃ > BCl₃
- Which of the following processes does not involve a catalyst?
 - Ostwald process
 - Contact process
 - Thermite process
 - Lane's process
- The correct order of atomic radii of Gr 13 elements is
 - B < Al < Ga < In
 - B < Al ~ Ga < In
 - B < Al < Ga ~ In
 - B < Ga < Al ~ In
- Which of the following represents an alum where M₁ and M₂ are mono and tripositive metal ions?
 - (M₁)(M₂)(SO₄)₂·12H₂O
 - (M₁)₃(M₂)(SO₄)₃·12H₂O
 - (M₁)₂(M₂)₂(SO₄)₄·12H₂O
 - (M₁)₄(M₂)₂(SO₄)₅·12H₂O

1. (c) 2. (a) 3. (c) 4. (b) 5. (a) 6. (c) 7. (a) 8. (b) 9. (a) 10. (a)
11. (c) 12. (b) 13. (a) 14. (c) 15. (b) 16. (d) 17. (a) 18. (c) 19. (a) 20. (b)
21. (c) 22. (b)



15

Group – 14 (IVA) C, Si, Ge, Sn, Pb

Element of this group are p-block element. Carbon and Si are non-metals (Si slightly metallic), Ge is metalloid, Sn and Pb are metals.

CARBON

Carbon has three isotopes, they are:

Table 15.1

| Isotope | No. of neutron | Abundance | Nature |
|-----------------|----------------|-----------|---|
| ^{12}C | 6 | 98.9% | Stable isotopes |
| ^{13}C | 7 | 1.1% | |
| ^{14}C | 8 | Trace | Radioactive $t_{1/2} = 5770\text{yrs}$ |

The radioisotope ^{14}C ($t_{1/2} = 5770$ years) can be produced by thermal neutron irradiation of Al – nitride.



In the atmosphere, ^{14}C is produced by the action of the neutrons in cosmic rays on nitrogen (like above reaction). Its formation and absorption of $^{14}\text{CO}_2$ by living systems (plants and organisms) is used in radiocarbon dating to determine age of archaeological species. Libby developed this method for which he got Nobel Prize for Chemistry (1960).

Catenation

The property of self-linking is known as catenation. It depends mainly on bond energy. The C – C bond energy is very high. Therefore, C has maximum catenation property. The bond energy decreases down the group and so also the catenation property, i.e.,



Sulphur also shows catenation because S – S bond energy is relatively high. Boron, Si, P shows heterocatenation as B – O, Si – O and P – O bond energies are high. (Table 15.3)

Table 15.2

| Bond | Bond Energy (KJmol^{-1}) |
|---------|--|
| C – C | 356 |
| Si – Si | 210 – 250 |
| Ge – Ge | 190 – 210 |
| Sn – Sn | 105 – 145 |

Allotropy and Structure

All the elements are solid. Only Carbon and Sn show allotropy.

Carbon has three crystalline allotropes:

- (a) Graphite
- (b) Diamond
- (c) Fullerenes

Tin is found as α -Sn, and β -Sn.

Table 15.3

| Bond | Bond Energy (KJmol ⁻¹) |
|--------|------------------------------------|
| S – S | 226 |
| B – O | 560 – 790 |
| Si – O | 368 |
| P – O | ~ 340 |

Table 15.4

| Element | Allotrope | Structure |
|---------|---------------|------------------------|
| C | Graphite | Layer structure |
| | Diamond | Cubic structure |
| | Fullerenes | Carbon cluster |
| Si | – | Diamond structure |
| Ge | – | Diamond structure |
| Sn | α – Sn | Diamond structure |
| | β – Sn | Cubic structure |
| | γ – Sn | Simple cubic structure |
| Pb | – | ccp |

Graphite

It is soft dull looking greasy substance and is good conductor of electricity. Graphite has two-dimensional layered structure.

The layers are made up of sp^2 hybridized C atoms. Each C is joined with three other C atoms through σ -bonds forming hexagonal rings. Each C is left with its fourth valence electron in a p -orbital. They overlap and form π bonds. These π bonds are delocalized. Therefore, all C – C bond distances in graphite are equal (1.415 Å). Sheet to sheet distance in graphite is 3.35 Å. It is known as C – dimension. Layers are joined by weak van der Waals force.

The weak force between layers allows one layer to slide over the other. It imparts softness to graphite. It is, therefore, used in pencils for writing. Due to delocalized π electrons graphite is a conductor (though along the sheet not perpendicular to it). Hence, it is used as electrode.

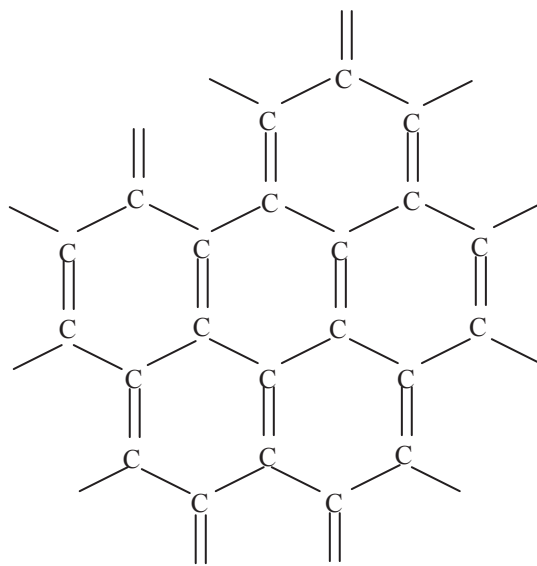


Figure 15.1

Intercalation compounds of graphite

The layered structure of graphite allows molecules and ions to penetrate between the layers. Such aggregates are known as intercalation or lamellar compounds. These are of two types:

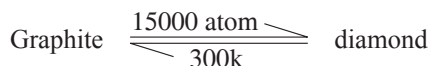
- (i) Those in which graphite becomes non-conducting. Example, graphite oxide and graphite fluoride, and
- (ii) Those in which conductivity of graphite is retained or even enhanced. For example, C_8M ($M = K, Rb, Cs$). They have high electrical conductivity because metal is present between the layers as M^+ .

Diamond

It is a colourless, transparent, an hardest substance known and is an insulator. Cut diamond is sparkling solid (due to refraction). Diamond has cubic unit cell. Each C is sp^3 hybridized and is joined with four other C atoms through σ – bonds.

As C – C bond energy (356KJmol^{-1}) is very high and diamond has a giant structure, it is very hard. This structure is responsible for its insulator property.

Density of diamond (3.51g/cc) is greater than graphite (2.22g/cc). This shows that to change graphite into diamond, pressure must be applied. There is an equilibrium.



Graphite can be transformed into diamond at a reasonable rate at high pressure and $\sim 3000\text{ K}$ in the presence of a transition metal (Fe, Cr, Pt) catalyst.

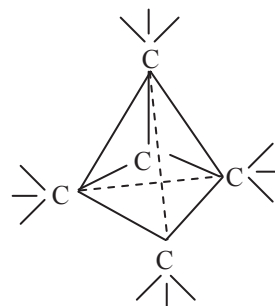
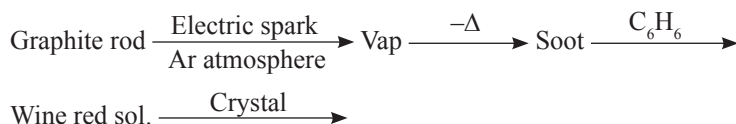


Figure 15.2

Fullerenes

Fullerenes are carbon clusters having cage like structures. They were discovered by R. F. Curl, H. W. Croto and R.E. Smalley. They were awarded the 1996 Nobel Prize for the discovery of fullerenes.



Mustard colour crystal C_{60} , C_{70} (trace)

Fullerenes C_{60} and C_{70} can be separated by chromatographic method over alumina. Many other fullerenes also exist such as C_{32} , C_{50} , C_{76} , C_{84} etc. Carbon clusters upto 600 atoms have been observed.

The C_{60} cluster is called Buckminster fullerene in the honour of American architect Robert Buckminster Fuller.

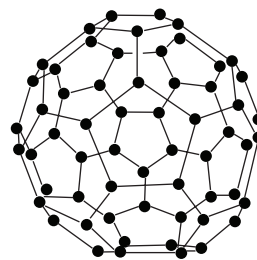
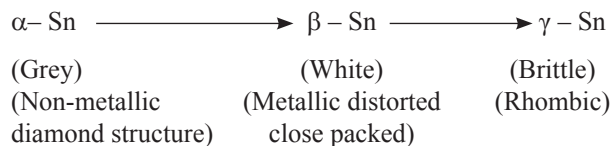
Its (C_{60}) structural features are as follows:

- Spherical structure (like a soccer ball)
- It has twelve (12) five-membered rings and twenty (20) six-membered rings.
- Five-membered rings are fused with six-membered rings only.
- Six-membered rings are fused with five-membered and six-membered rings both.
- Carbon atoms in C_{60} are sp^2 hybridized making three σ bonds.
- Rest one electron with each C-atom in a $2p$ orbital forms π -bonds.
- The π -bonds are delocalized to impart aromatic nature to C_{60} .
- Average C — C distance is around 1.44\AA .

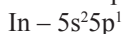
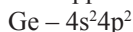
Structure of C_{60}

Silicon exists only in diamond structure. A graphite like structure for Si is not possible because it has no propensity to form $(p-p)\pi$ bond.

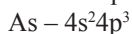
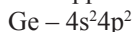
Tin exists in three forms, α -Sn, β -Sn and γ -Sn.

**Figure 15.3****Semiconductor property of Si and Ge**

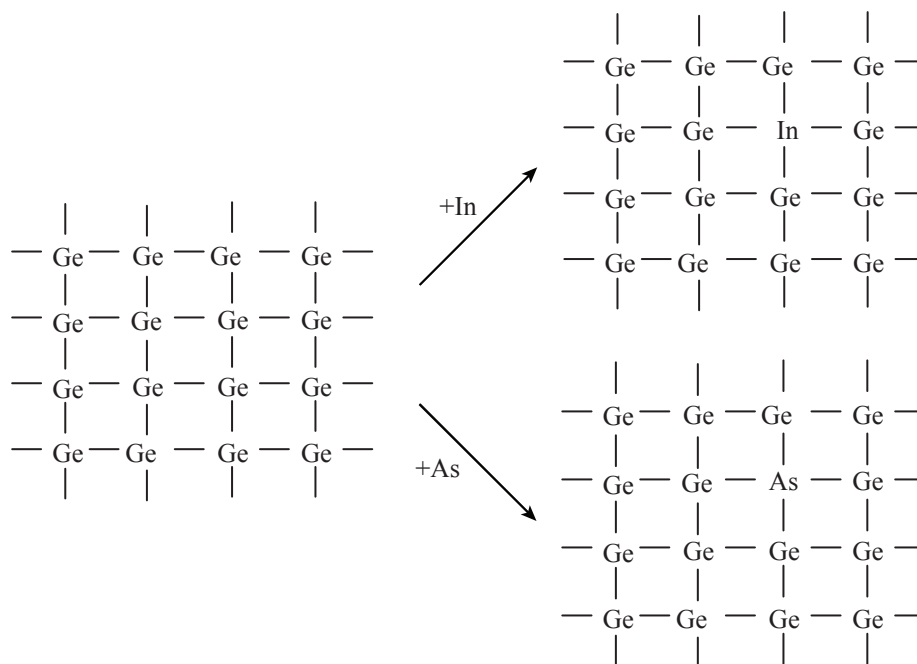
Silicon and Ge are important semiconductor materials. Pure Si and Ge are non-conductor of electricity. However, when they are dopped with group-13 or group-15 elements, they become semiconductor.

(i) Ge dopped with In

When Ge is dopped with In, there is one electron less at In site. There develops a positive hole in the lattice which makes Ge conducting. Such a semiconductor is called p - type (positive - type) semiconductor.

(ii) Ge dopped with As

When As is dopped in Ge, there is one electron excess at As site. Due to this excess electron Ge conducts electricity. Such a semiconductor is called n - type (negative type).

**Figure 15.4**

Physical properties of group – 14 elements**Table 15.5**

| Property | C | Si | Ge | Sn | Pb |
|--|---------|---------|------------|------------|----------------|
| Atomic no. | 6 | 14 | 32 | 50 | 82 |
| Electronic structure | –2s22p2 | –3s23p2 | 3d104s24p2 | 4d105s25p2 | 4f145d106s26p2 |
| Atomic radius (Å) [covalent radius] | 0.77 | 1.17 | 1.22 | 1.40 | 1.44 |
| Ionic radius (Å) | 0.15 | 0.41 | 0.53 | 0.71 | 0.84 |
| Metallic radius (Å) | – | – | 1.37 | 1.62 | 1.75 |
| Ionization energy (ev) [I] | 11.3 | 8.2 | 7.8 | 7.3 | 7.4 |
| [II] | 24.4 | 16.3 | 15.9 | 14.6 | 15.0 |
| Electronegativity | 2.5 | 1.9 | 1.8 | 1.7 | 1.7 |
| mp (°C) | >3550 | 1410 | 937 | 232 | 327 |
| bp (°C) | 4827 | 2355 | 2830 | 2260 | 1744 |

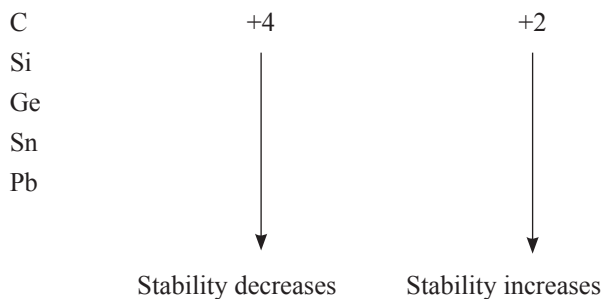
Note:

- The radii of Si and Ge are very similar due to d – block contraction. Also Sn and Pb have almost similar radii due to lanthanide contraction.
- Ionization energy vary as $C > Si \sim Ge > Sn < Pb$. Silicon and Ge have comparable IE due to similarity in their radii.

The radius of Sn is smaller than Pb but Pb has higher IE than Sn. It is due to higher Z^* for Pb as f – orbital is least shielding.

Oxidation states and Bonding

Group – 14 elements show variable oxidation states of +2 and +4. The stability of +2 state is very stable for Pb. It is due to inert pair effect.



Carbon and Si have high ionization energy. Therefore, they are covalent in their compounds.

Tin and Pb form ionic compounds having appreciable covalent nature. It is because Sn and Pb are not very large and have 18e core.

Carbon and Si differ widely in their bonding pattern. It is because of the following reasons:

Table 15.6

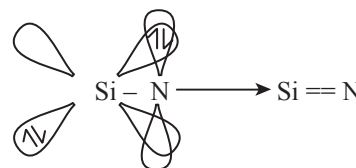
| Property | C | Si |
|--|--------------------------------------|---|
| Valence orbitals and electrons | 2s22p2 | 3s23p2 (3d0) |
| Number of bonds or coordination number | 4 only | More than 4 (5 or 6) |
| π – bonding | Very effective (p – p) π bonding | No (p – p) π bonding but (p – d) π bonding. Using vacant 3d orbitals |
| C – C bond energy | 356KJmol ⁻¹ | 226KJmol ⁻¹ |
| Catenation property | Very high | Low, however, heterocatenation is pronounced due to strong Si – O bond (368KJmol ⁻¹). |

The features of certain Si compounds having Si – O and Si – N bonds are explained by (d – p) π bonding. For example,



Trisilylamine, $(\text{SiH}_3)_3\text{N}$, is trigonal planar due to (d – p) π bonding involving filled N $2p_z$ orbital and vacant Si $3d_{xy}$ orbitals,

The large angles at O of disilyl ethers $(\text{R}_3\text{Si})_2\text{O}$, is due both to electronic and steric factors.

**Figure 15.5**

Carbides

Binary compounds of carbon are called carbides, SiC , CaC_2 , Al_4C_3 etc. These are of three types.

Ionic carbides

There are Three types of ionic carbides

- Methanides
- Acetylides
- Propynide

Ionic carbides are decomposed by water (or dil. Acid) at room temperature. The liberated anions are also immediately hydrolysed. It affords a method of classification.

(a) Methanides : (C^{-4} unit)

Those carbides which are hydrolysed to give CH_4 are called methanide. They are supposed to contain C^{-4} unit.



(b) Acetylides : (C_2^{-2} unit)

Those which are hydrolysed to C_2H_2 are called acetylides. They are common and formed by Group – 1, Group – 2, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Ag, Al and La metals.

| | |
|--------|----------------------------|
| Gr – 1 | |
| Cu, Ag | M_2C_2 |
| <hr/> | |
| Gr – 2 | |
| Zn, Cd | MC_2 |
| <hr/> | |
| Al, La | $\text{M}_2(\text{C}_2)_3$ |

**(c) Propynide : (C_3^{4-} unit)**

Such carbides hydrolyse to propyne

**Covalent carbides**

Elements which compares with C in size and electronegativity form such carbides, Be, B, Si etc. Boron and Si carbides are more important.



Silicon carbide (SiC) is called carborundum. It is very inert and extremely hard.



B_4C is also very hard, infusible and inert. It is used to make bulletproof clothing.

These covalent carbides (or $\alpha - \text{Al}_2\text{O}_3$) are comparable in hardness to diamond (Moh's scale)

**Interstitial carbides**

Transition metals form such carbides, in which C atoms occupy octahedral voids. Such materials are very hard, electrically conducting and have very high mp. For example, TiC , ZrC , MoC , WC etc.

Oxides

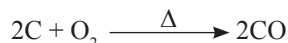
Elements of this group form oxides of the type MO and MO_2 . Carbon forms suboxides also, e.g., C_3O_2 .

Table 15.7

| Oxides | C | Si | Ge | Sn | Pb |
|-----------------|-----------------|------------------|------------------|-------------------|------------------|
| MO | CO (neutral) | X | GeO | SnO amphoteric | PbO |
| MO ₂ | CO ₂ | SiO ₂ | GeO ₂ | SnO ₂ | PbO ₂ |
| | ← acidic → | | | amphoteric | |

Carbon monoxide (CO)

CO is formed when carbon burns in limited O₂ (or air).



In laboratory, CO is prepared by heating formic acid, HCOOH (or oxalic acid) with conc. H₂SO₄.

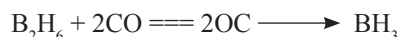


It is dehydration of HCOOH.

It forms many important gaseous mixtures for the industrial use.

- (i) Water gas or synthesis gas CO + H₂
- (ii) Producer gas CO + N₂
- (iii) Coal gas CO + H₂ + CH₄ + CO₂

- CO is a neutral oxide
- Carbon monoxide has a triple bonded C atom, one σ and two π bonds (best explained by MO model).
- It has highest bond energy (1070 KJmol⁻¹) among diatomic molecules.
- CO is a weak Lewis base but forms stable aggregate with B₂H₆.



However, with BF₃, it interacts only weakly.



In this adduct, BF₃ is found to be planar and B – C distance is very large 2.89 Å. Such an adduct is often called van der Waals molecule.

- CO, however, is a strong ligand towards transition metals and form variety of complexes known as carbonyls, Ni(CO)₄, Fe(CO)₅ etc. They are stable due to synergic bonding (of organometallic compounds).
- CO is very toxic and rapidly forms a bright red complex with haemoglobin of blood. Thus preventing haemoglobin to carry oxygen to cells, causing oxygen deficiency to unconsciousness and then death.

Carbon dioxide (CO₂)

It is produced when C burns in excess of O₂ (or air).



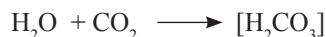
Thermal decomposition of di- and trivalent (M⁺² and M⁺³) metal carbonates gives CO₂



All metal carbonates give CO_2 with dil. acid.

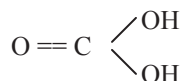


- CO_2 is an acidic oxide.
- It dissolves in water to form a weakly acidic solution (carbonic acid).

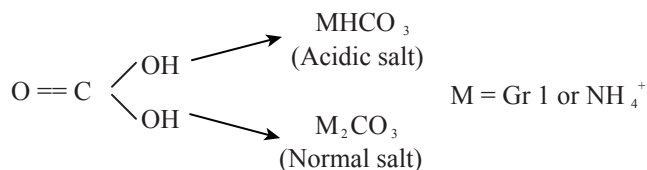


Free acid is not stable enough to be isolated.

- Carbonic acid is a gem diol and is, therefore, unstable.



However, salts are known

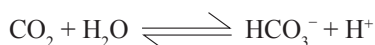


Solid acidic salts, MHCO_3 , are known only of Gr-metals (not Li) and NH_4^+ ion.

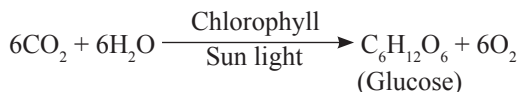
- The CO_3^{2-} ion is conjugate base of a weak acid. Therefore, hydrolyze in water to give basic solution.



- CO_2 is biologically important.
 - (i) It maintains pH of blood, due to the equilibrium.



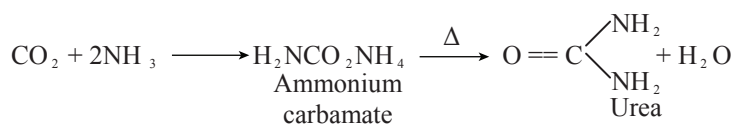
- (ii) It is the main component of photosynthesis.



- (iii) The reverse process of the above takes place in the process of respiration.



- CO_2 is used in the synthesis of urea.

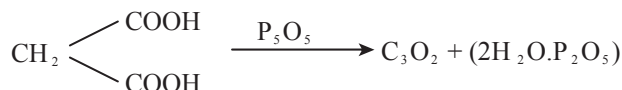


- CO_2 is also used in soft drinks.
- CO_2 is gas at NTP and has the structure $\text{O}=\text{C}=\text{O}$. The (p-p) π bonding is very effective. Therefore, even in solid state discrete CO_2 molecules exist. The intermolecular forces are weak van der Waals' force.
- Solid CO_2 is called 'dry ice' or 'cardice'.

Silicon dioxide, SiO_2 , unlike CO_2 is a solid. The $(p-p)\pi$ bonding is not effective in SiO_2 like CO_2 . It is due to larger size of Si and more core electrons (8e) in Si. Therefore, to stabilize, SiO_2 contains a continuous lattice of Si and oxygen atoms joined by covalent bonds. Each Si is sp^3 and is joined with 4 O – atoms and each O – atoms with two Si – atoms. A macromolecule is formed; hence, SiO_2 is a solid.

Suboxide (C_3O_2)

It is a foul smelling gas. It can be produced by dehydrating malonic acid with P_2O_5 in vacuum at $\sim 150^\circ\text{C}$.



The molecule is linear, $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$, carbon atoms are sp – hybridized.

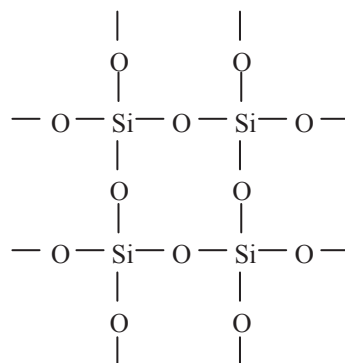


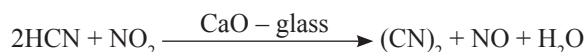
Figure 15.6

Compounds with C – N bonds

Cyanogens (CN)₂

It is flammable gas, vary toxic and is water soluble. It can be prepared by the reactions

(i) Catalytic oxidation of HCN by NO_2 .



(ii) aq. phase oxidation of CN^- by Cu^{2+}



[Acidified $\text{S}_2\text{O}_8^{2-}$ also oxidize CN^- to $(\text{CN})_2$

(iii) Dry $(\text{CN})_2$ can be made by the reaction



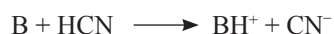
- Cyanogen is similar in many ways to halogens, and is known as pseudohalogen. Like halogens it disproportionate in basic solution.



- A mixture of O_2 and $(\text{CN})_2$ (1 : 1) burns, producing one of the hottest flames (5050K) known from a chemical reaction.
- The $(\text{CN})_2$ molecule is linear $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$ (C atoms are sp – hybridized).

Hydrogen cyanide (HCN)

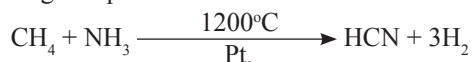
It is a covalent poisonous colourless gas. Liquid HCN (b.p. 25.6°C) is highly associated molecule through H – bonding (like H_2O). Its dielectric constant is very high (107 at 25°C). It is a very weak acid in aq. solution ($\text{p}^{\text{ka}} = 9.1$) but pure liquid is a strong acid.



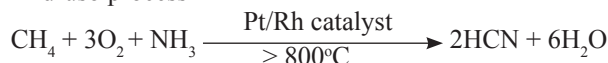
It can be prepared as:

(i) Small scale**(ii) Manufacture**

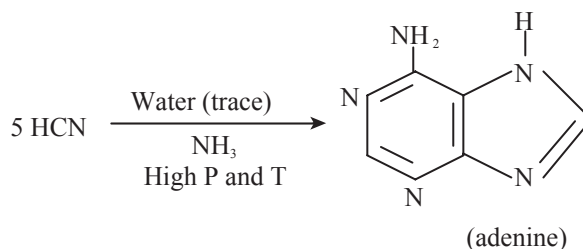
(a) Degussa process



(b) Andruso process



Hydrogen cyanide is thought to be a small molecule in the earth's primeval atmosphere to produce biologically important chemicals. It is because under pressure with traces of water and NH_3 , HCN pentamerizes to adenine, one of the constituents of DNA.

**Uses**

- (a) As a laboratory reagent.
- (b) To produce adiponitrile $\text{NC} - \text{CH}_2 - \text{CN}$ for Nylon
- (c) To make NaCN and many cyanocomplexes.

Figure 15.7**Cyanides (CN^-)**

NaCN is very important, among the cyanides. It can be prepared as:

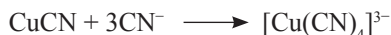
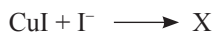
- (a) $\text{NaOH} + \text{HCN} \longrightarrow \text{NaCN} + \text{H}_2\text{O}$
- (b) $\text{CaCN}_2 + \text{C} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{fuse}} \text{CaCO}_3 + 2\text{NaCN}$
- (c) $\text{NaNH}_2 + \text{C} \xrightarrow{\sim 600^\circ\text{C}} \text{NaCN} + \text{H}_2$

General observation for the cyanides

- Cyanides of electropositive metals are water soluble. Example NaCN, KCN etc.
- Cyanides of Ag^+ , Hg^+ and Pb^{+2} are very insoluble.
- Cyanide forms many stable complexes with transition metals, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CN})_4]^{2-}$ etc.
- With respect to bonding it is similar to CO (synergic bonding).
- Cyanide is a π – acid ligand.
- The cyanide complex $\text{K}_4[\text{Fe}(\text{CN})_6]$ is analytically important, to detect Fe^{3+} and Cu^{2+} .
- Cyano complexes of Ag and Au are important in their extraction.
- Cyanide is similar to I^- in reducing action



But CN^- is different from I^- with respect to complexation.



- Cyanides are called pseudo halide.
- KCN is extremely toxic. Its toxicity is due to complexation with metals in enzymes and haemoglobin in the body. Thus preventing normal body chemistry and quickly causing death.
- Cyanide is isoelectronic to N_2 and has the structure $[\text{:N} \equiv \text{C:}]^-$
- Cyanides are ambidentate i.e., it can bond through C (cyanide) or N (isocyanide).

Halides

Compounds containing C – F bond

The chlorofluorocarbons (Freons) are prepared by replacement of chlorine in a chloroalkane.



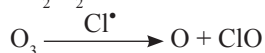
The CFC are

- Odourless
- Inert
- Non-toxic
- Non-corrosive

They are used as:

- Refrigerant
- Propellant gas in aerosol spray

The CFCs are harmful as green house gas and can deplete O_3 concentration.



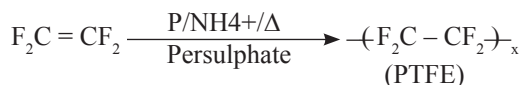
The use of CFCs is banned in many countries (UK, USA)

Tetrafluoroethene ($\text{F}_2\text{C} = \text{CF}_2$)

It is made as follows:



The C_2F_4 polymerizes to polytetrafluoroethene (PTFE).



It is

- Hard solid plastic
- Chemically inert
- Heat resistant (softening above 300°C)
- Electrical insulator
- Lowest coefficient of friction of any known substance which decreases with temperature.
- Polymer is used for coating frying pans (non-stick) and in non-lubricated bearings.
- It is also used as patch material in heart surgery.

Halides MX_2 and MX_4

Group – 14 elements form tetrahalides of the type MX_4 ($X = F, Cl, Br, I$) except PbI_4 .

PbI_4 does not exist due to strong oxidizing power of Pb^{+4} and reducing nature of I^- ion. The Pb^{+4} is strong oxidizing agent due to greater stability of Pb^{+2} (inert pair effect).

Thus, MX_4 , [$M = C, Si, Ge, Sn, X = F, Cl, Br, I$]

Germanium, Sn and Pb also for MX_2 . The stability of MX_2 is maximum for Pb^{+2} .

SnF_2 is sparingly soluble in water and is used in fluoride containing tooth pastes.

The MX_4 halides are all colourless except GeI_4 and SnI_4 which are bright orange solids. Colour in these halides is due to charge transfer.

Silicon tetrahalides differ in physical state.

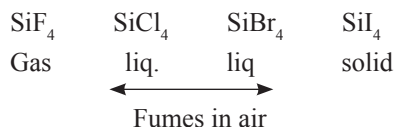


Figure 15.8

All tetrachlorides except CCl_4 are hydrolyzed by water.

Carbon tetrachloride is not hydrolyzed because:

- carbon in CCl_4 is coordinatively saturated.
- $C - Cl$ bond is less polar.

$$X_C = 2.5, X_{Cl} = 3.0, \Delta\chi = 0.5$$

Silicon tetra chloride ($SiCl_4$) is extensively hydrolyzed. It is because:

- $Si - Cl$ bond is more polar

$$X_{Si} = 1.8, X_{Cl} = 3.0, \Delta\chi = 1.2$$

- Si in $SiCl_4$ can increase its coordination number by using 3d orbitals

The hydrolysis of $SiCl_4$ can be represented as

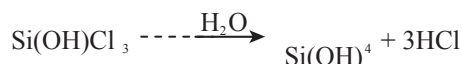
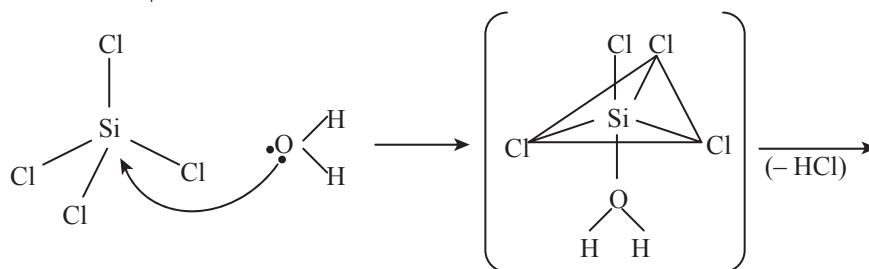
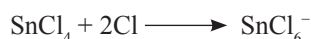
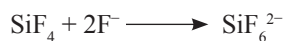


Figure 15.9

The tetra halides of Si, Ge, Sn and Pb can increase their coordination numbers by using d orbitals and can form haloanions.

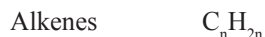


The hexacoordinated halo anions are octahedral having sp^3d^2 hybridized central atom (Si)

Hydrides

All elements of this group form covalent hydride.

Carbon forms a large number of chain and ring compounds due to high catenation property. They are:



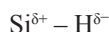
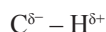
Cyclo alkanes and cycloalkynes

Aromatic hydrocarbons (C_6H_6)

Silicon (others also) form saturated hydrides only which are called silanes, $Si_n H_{2n+2}$ ($Si \sim 8$).



Silanes are much more reactive than alkanes due to partial positive charge at Si,



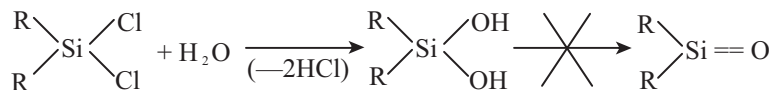
Silicones

They are organosilicon polymers having empirical formula approximately R_2SiO . Polymers are very stable due to strong Si – O and Si – C bonds. Silicones can be prepared as oils, resins, plastics etc. They are:

- Inert
- Water repellent
- Heat resistant
- Electrical insulator

All these properties make silicones very useful.

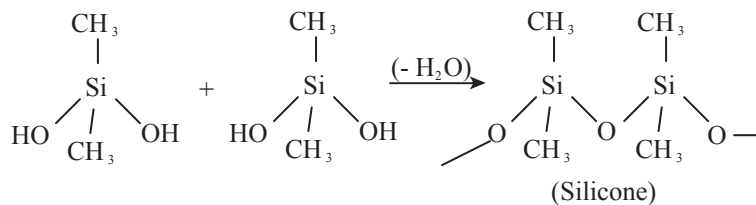
Hydrolysis of alkyl chlorosilanes produces products having Si – OH bonds. They do not dehydrate like gem diols (of C).



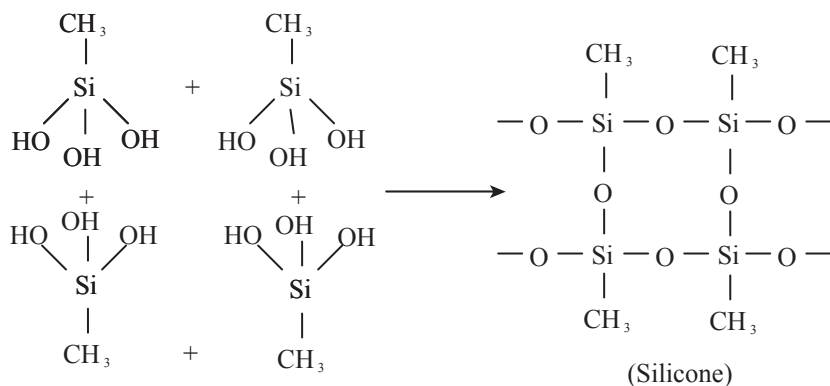
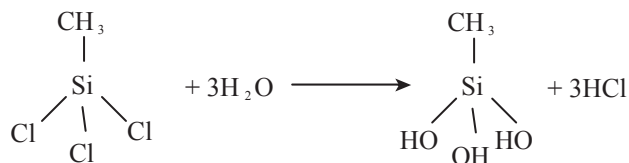
On the other hand, as soon as Si – OH bonds are formed, condensation sets in, and polymers (silicones) are formed. By regulating the condition of the reactions silicones of desired

- Chain lengths,
- Ring sizes, and
- Cross links can be produced.

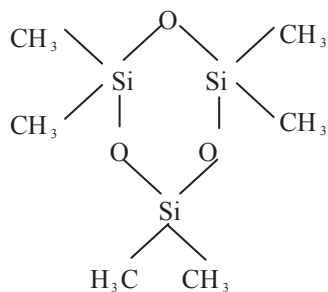




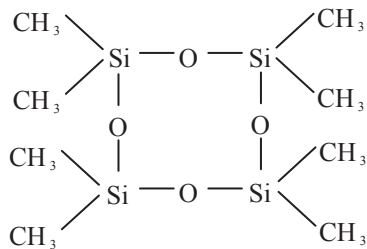
Ring Polymer



Carefully controlled hydrolysis produces rings of desired size,—three, four etc—Si atoms



Tris cyclo demethylsiloxane



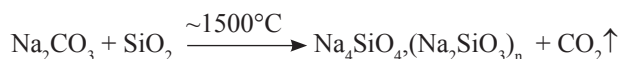
Tetrakis – cyclodimethylsiloxane

Uses

- As a protective coating.
- As lubricants.
- Oils as insulators in high voltage transformers.
- In silicone rubbers.

Silicates

Silicates are solids having Si – O bonds. Most of the rocks and even soil contain silicates. Alkali metal silicates are water soluble. They are made on a large scale as



They are used in detergents. The concentrated aq. solution of Na_4SiO_4 is solid like and as known as water glass. Variety of silicates are found but in all the basic unit is the SiO_4 tetrahedron.

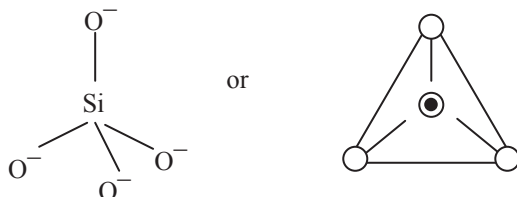


Figure 15.10

Each O – atom carries one unit negative charge. In polymeric silicates SiO_4 units share O – atom(s). It provides a way of classification.

Orthosilicates (Mononuclear silicates)

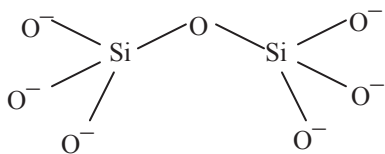
These are silicates having discrete SiO_4^{4-} ions. Metal ions are surrounded by O-atoms.

Table 15.8

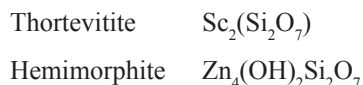
| Silicate | M^{n+} coordination no. |
|--|----------------------------------|
| Phenacite Be_2SiO_4 | 4 |
| Willemite Zn_2SiO_4 | 4 |
| M_2SiO_4 (M+2, Mg+2, Mn+2, Fe2+) | 6 |
| Zircon ZrSiO_4 | 8 |

Pyrosilicates ($\text{Si}_2\text{O}_7^{-6}$)

When two SiO_4 units share only one O – atom pyrosilicates, $\text{Si}_2\text{O}_7^{-6}$, are formed. These are also discrete units.



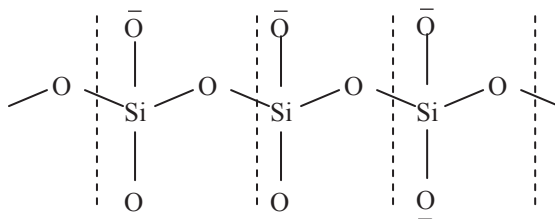
The Si – O – Si angle varies from $131 - 180^\circ$.



Chain silicates

- (a) Pyroxenes
- (b) Amphiboles

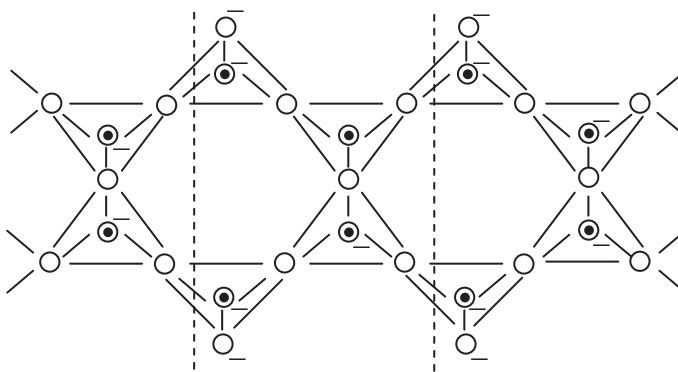
Pyroxenes are single strand infinite chains of composition $(\text{SiO}_3^{2-})_n$. They are produced by sharing two O – atoms of SiO_4 units.

**Figure 15.11**

| | |
|--------------|-------------------------------|
| Spodumene | $\text{LiAl}(\text{SiO}_3)_2$ |
| Diopside | $\text{CaMg}(\text{SiO}_3)_2$ |
| Wollastonite | $\text{Ca}_3(\text{SiO}_3)_2$ |

Amphiboles

They are double-strand cross-linked chains of composition $(\text{Si}_4\text{O}_{11}^{6-})_n$. In amphiboles some SiO_4 share two and others three O – atoms. Amphiboles always contain (HO) groups joined to the metal ions. Asbestos are amphiboles.

**Figure 15.12**

Tremolite, $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$ is an amphibole.

Cyclic silicates

When two O – atoms of SiO_4 tetrahedron are shared, a cyclic silicate is formed. They have general formula $\text{Si}_n\text{O}_{3n}^{2n-}$.

Rings with three and six tetrahedra are common: $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$. For example,

| | |
|--------------|--|
| Wollastonite | $\text{Ca}_3(\text{Si}_3\text{O}_9)$ |
| Beryl | $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$ |

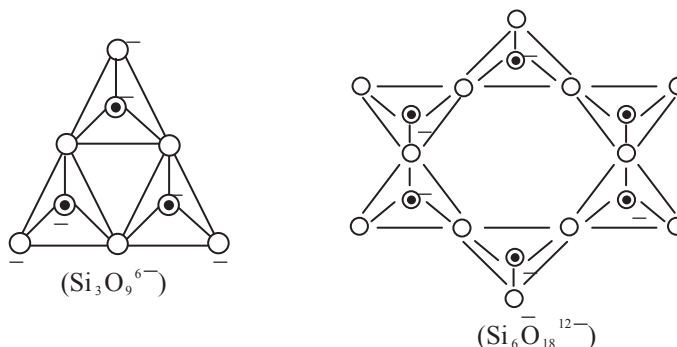


Figure 15.13

Sheet silicate

When three O – atoms of SiO_4 tetrahedra are shared infinite two-dimensional sheet is formed. Their general formula is $\text{Si}_2\text{O}_5^{2-}$. Sheets are held together by weak forces. Sheets are bound together by metal ions in between them.

Clays and Mica are sheet silicates.

| | |
|-----------|---|
| Kaolinite | $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$ |
| Talk | $\text{Mg}_3(\text{OH})_2(\text{Si}_2\text{O}_5)_2$ |

Three dimensional silicates

When all the four O – atoms of SiO_4 units are shared, a three dimensional lattice is formed. Quartz (SiO_2) is an example of this class. The structure is a tetrahedral net work.

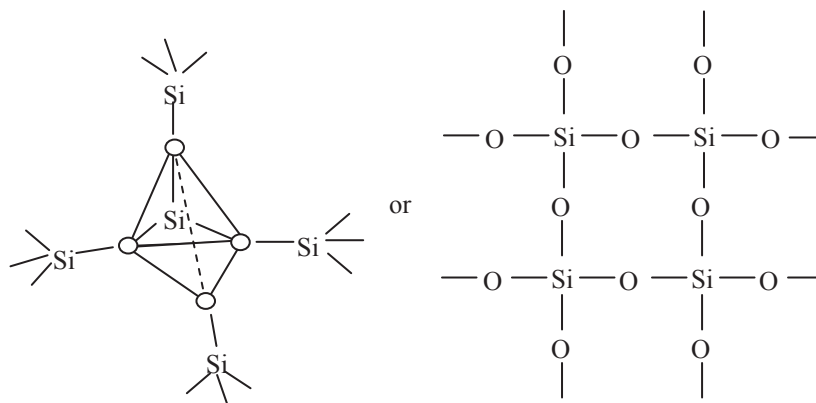


Figure 15.14

Isolation of Si

Occurrence: Silicon is found as,

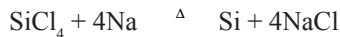
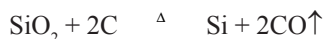
- Silica – SiO_2
- Silicates – These are of various types.

Silicon is mainly obtained from silica, SiO_2 .

(i) Si is isolated by heating SiO_2 with high purity coke (or CaC_2).



(ii) Pure Si is made by reducing SiCl_4 with Na or Mg.



(iii) Ultra pure Si for transistors or computer chips is prepared by zone-refining.

PRACTICE QUESTIONS

A. Explain the following:

- Graphite is electrical conductor but diamond in an insulator.
- Si has diamond structure only but not an allotrope like graphite.
- CCl_4 is not hydrolysed but SiCl_4 is rapidly hydrolyzed in water.
- Silicon does not form $\text{R}_2\text{Si}=\text{O}$ like ketones ($\text{R}_2\text{C}=\text{O}$).
- Catenation property. (Why does Si has much less tendency to catenation than C).
- HCN is a weak acid in water but in the pure state is a strong acid.
- CO_2 is gas but SiO_2 is a solid.
- SiF_4 is incompletely hydrolyzed in water.
- $\text{R}_3\text{Si}-\text{OH}$ (silanol) is stronger acid than $\text{R}_3\text{C}-\text{OH}$.
- The single bond energies are as $\text{C} > \text{Si}$ but $\text{N} < \text{P}$, $\text{O} < \text{S}$ and $\text{F} < \text{Cl}$.
- CF_4 is not a Lewis acid but SiF_4 is a Lewis acid.
- The first ionization energy of C is greater than that of B but reverse is true for second ionization energy.
- Trisilylamine $[(\text{SiH}_3)_3\text{N}]$ is a weaker base than $(\text{CH}_3)_3\text{N}$.
- Diamond is hard but graphite is soft.
- Carbon monoxide is not a good Lewis base for Fe^{3+} .

B. Fill in the blanks

- The hydrolysis of R_3SiCl yields _____.
- The allotrope of carbon C_{60} is called _____.
- Photosynthesis is a reaction which is followed with _____ ΔG .
- Tin(II) oxide [i.e., SnO] on dissolution in NaOH produces _____.
- With an excess of SnCl_2 , HgCl_2 gives _____ precipitate due to the formation of _____.
- Chrome yellow is _____.
- Pb_3O_4 is called _____.
- The structure of SiC is like _____.
- SiF_4 is _____ hydrolyzed in water.
- SnI_4 is _____ stable and coloured due to _____.

C. What happen when

- Pb_3O_4 is treated with conc. HCl .
- Aluminium carbide is treated with water.
- Dil HNO_3 is slowly reacted with Sn.
- NaOH solution is added to SnCl_2 solution.
- Carbon dioxide is passed in a suspension of lime stone (CaCO_3) in water.

- (f) CO_2 is passed through a concentrated aq. solution of NaCl (brine) saturated with NH_3 .
- (g) Pb_3O_4 is treated with HNO_3 .
- (h) CO_2 is passed over heated potassium superoxide (KO_2).
- (i) AlCl_3 solution is treated with NaHCO_3 .
- (j) Calcium carbide is strongly heated with N_2 .

OBJECTIVE-TYPE QUESTIONS

- Synthesis gas is a mixture of
 - $\text{CO} + \text{N}_2$
 - $\text{CO} + \text{H}_2$
 - $\text{CH}_4 + \text{CO}$
 - $\text{CO}_2 + \text{N}_2$
- Which of the following is true for CO ?
 - Acid
 - Base
 - Doner
 - Door and acceptor both.
- The number and type of bonds between two carbon atoms in CaC_2 are
 - One σ bond
 - One σ and one π bond
 - One σ and two π bonds
 - One σ and one and a half π bond.
- Which of the following is least stable and has doubtful existence?
 - PbI_4
 - SnI_4
 - GeI_4
 - Cl_4
- The material used in solar cells contain
 - Ti
 - Sn
 - Si
 - Cs
- Which of the following is correct for glass?
 - Crystalline solid
 - Covalent solid
 - Amorphous solid
 - Super cooled liquid
- The correct order of decreasing C – O bond length of CO , CO_2 and CO_3^{-2}
 - $\text{CO}_2 > \text{CO} > \text{CO}_3^{-2}$
 - $\text{CO}_3^{-2} > \text{CO}_2 > \text{CO}$
 - $\text{CO}_2 > \text{CO}_3^{-2} > \text{CO}$
 - $\text{CO} > \text{CO}_2 > \text{CO}_3^{-2}$
- CO is absorbed by
 - Pyrogallol
 - CHCl_3
 - $\text{NH}_4\text{OH} + \text{CuCl}$
 - CCl_4
- Which of the following halide of C is used as refrigerant?
 - CF_4
 - CCl_4
 - CH_2F_2
 - CCl_2F_2
- Malonic acid is dehydrated over conc. H_2SO_4 , the product is
 - CO
 - CO_2
 - C_3O_2
 - CO_3^{-2}
- Butter of Sn is
 - $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
 - $\text{SnCl}_2 \cdot 4\text{H}_2\text{O}$
 - $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
 - $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$
- The basic unit in chain and cyclic silicates is
 - $\text{Si}_2\text{O}_7^{6-}$
 - $(\text{SiO}_3)_n^{2n-}$
 - $(\text{Si}_2\text{O}_5)_n^{2n-}$
 - SiO_4^{4-}
- Which of the following statements is correct for Gr – 14 elements?
 - Atomic radius decreases
 - The hydroxides are getting less basic
 - The stability of +2 oxidation state increases.
 - The first ionization energy increases.
- Lead pencil contains
 - PbS
 - CuS
 - Pb
 - Graphite
- CO_2 in water is an equilibrium system, $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$. Mark the correct statements.
 - It maintains pH of blood.
 - CO_2 lowers pH causing haemoglobin to release more O_2 .

- (iii) Carbonic acid is strong.
(iv) Carbonic acid HCO_3^- system is not a buffer.
- (a) I, II (b) II, III
(c) III, IV (d) I, IV
16. The common basic structural unit of asbestos, mica and quartz is
(a) SiO_2
(b) $(\text{SiO}_3)_n^{2n-}$
(c) SiO_4^{4-}
(d) $(\text{Si}_2\text{O}_5)_n^{n-}$
17. Which of the following elements forms only one hydride?
(a) Si (b) Ge
(c) Sn (d) Pb
18. Carbon is not used as a reducing agent in the extraction of transition metals because
(a) C is a weaker reducing agent
(b) C is converted into CO_2 at high temperature
(c) C forms stable carbide.
(d) None of these

ANSWERS

1. (b) 2. (d) 3. (c) 4. (a) 5. (d) 6. (d) 7. (b) 8. (c) 9. (d) 10. (c)
11. (c) 12. (b) 13. (c) 14. (d) 15. (a) 16. (c) 17. (d) 18. (c)

16

Group – 15 (V_A) N, P, As, Sb, Bi



Elements of this group are called Pnicogens. (Greek, pnigmos-suffocation, many compounds of the group elements have suffocating odour, so this name). There is a transition from non-metal to metal.

Nitrogen and Bi do not show allotropy whereas P, As and Sb have allotropes.

Table 16.1

| Property | N | P | As | Sb | Bi |
|----------------|---------------------|--|-------|-------|-------|
| Physical state | Diatomic gas, N_2 | Solid | Solid | Solid | Solid |
| Structure | $N \equiv N$ | Allotropic forms \longleftrightarrow | | | BCC |
| Allotropes | – | White (P_4) As ₄ Sb ₄ Red (P_4) _x Black P Black As and Sb | | | |

Note:

- (i) Nitrogen is diatomic gas, N_2 at NTP. It is due to very effective (p – p) π bonding in N_2 . N $2s^2 2p^3$ i.e., three unpaired electrons in p – orbitals. There are one σ and two π bonds in N_2 . Nitrogen is sp –hybridized.

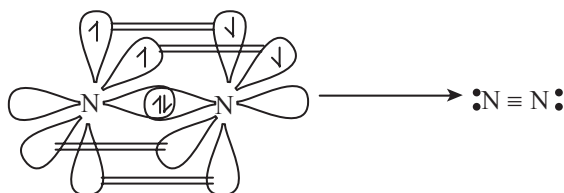


Figure 16.1

The σ bond is formed by linear overlap of sp – hybrids, and π bonds by side wise overlap of px – px and py – py p – atomic orbitals. The lps are in sp type hybrids. The molecule is non–polar.

- (ii) P is large in size. The (p – p) π bonding is not effective in P. Therefore, P is not stabilized as P_2 . In normal conditions, phosphorous is P_4 (white P). The P_4 unit is tetrahedral. Each P is sp^3 hybridized and is joined with three other P atoms. The fourth sp^3 orbital is occupied by a l.p. The structure is

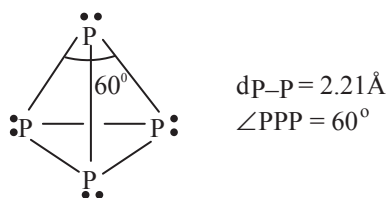


Figure 16.2

The PPP angle in P_4 is 60° . Therefore, there is large angle strain in P_4 , which makes it highly reactive (white P inflames in air, so it is kept in water).

Allotropes of P

Phosphorous has three main allotropes:

- White phosphorous (P_4)
- Red phosphorous ($(P_4)_x$)
- Black phosphorous (layer structure)

- The white phosphorous, P_4 is Td (explained above). It is highly reactive, inflames in air. So it is kept under water.
- Red phosphorous is polymeric solid which has P_4 units joined together.

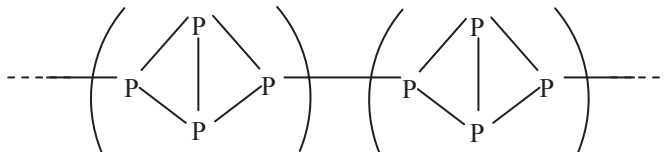


Figure 16.3

- It is stable, less reactive (than P_4) due to polymeric structure.
- It is insoluble in organic solvents (CS_2 , CCl_4 etc.).
- $P_4 \xrightarrow[(CO_2 + I_2)]{250^\circ C} \text{Red P i.e., } (P_4)_x$

Black P

It has layer structure having hexagonal rings. The P – P – P angle $\sim 100^\circ$ i.e., it is almost a strainless structure. The P – P distance is 2.20 Å. It is most stable form and is inert.

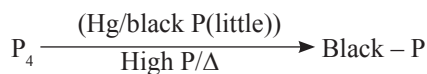


Table 16.2

General properties of group elements

| Property | N | P | As | Sb | Bi |
|----------------------|----------------------|----------------------|-----------------------------|-----------------------------|-------------------------------------|
| Atomic no. | 7 | 15 | 33 | 51 | 83 |
| Electronic structure | [He] $2s^2 2p^3$ | [Ne] $3s^2 3p^3$ | [Ar] $3d^{10} 4s^2 4p^3$ | [Kr] $4d^{10} 5s^2 5p^3$ | [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$ |
| Atomic radius (Å) | 0.70 | 1.10 | 1.21 | 1.41 | 1.52 |
| Ionic radius (Å) | 1.71 (N^{3-}) | 2.12 (P^{3-}) | 2.22 (As^{3-}) | 0.92 (Sb^{+3}) | 1.08 (Bi^{+3}) |

(Continued)

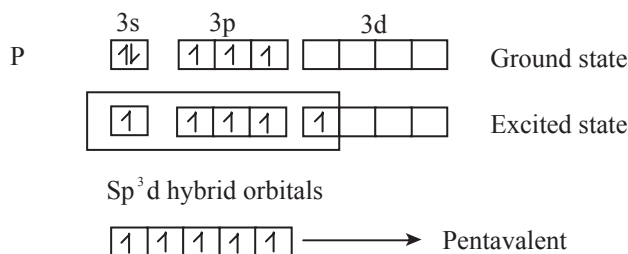
| Property | | N | P | As | Sb | Bi |
|-------------------------|----|-------|------------------------|-------------------|------|------|
| Electronegativity | | 3.07 | 2.06 | 2.0 | 1.82 | 1.67 |
| m.p. (°C) | | 210 | 44.1 (P ₄) | 841 (36 atm) | 630 | 271 |
| b.p. (°C) | | 195.8 | 280 | 615 (sublimes) | 1375 | 1560 |
| Ionization energy (eV)) | I | 14.5 | 10.5 | 9.8 | 8.6 | 7.3 |
| | II | 29.6 | 19.7 | — | — | — |

Note:

- (i) Nitrogen is generally trivalent and can expand its valence (or coordination number) only to a maximum of four i.e., tetravalent.



- (ii) Phosphorous is tri and tetra valent as well as penta and hexavalent. The penta and hexavalency is achieved by P using its vacant 3d orbitals.

**Figure 16.4**

P is hexavalent when a pentavalent P (PCl₅) accepts a Lewis base



- (iii) N cannot form NCl₅ as N – has no d orbitals in its valence shell.

Oxidation state and nature of bond

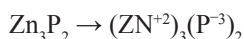
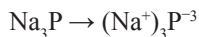
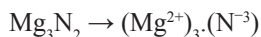
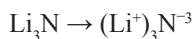
Nitrogen shows oxidation states from –3 to +5 and forms stable compounds in all the oxidation states.

Table 16.3

| Oxidation states | Example |
|------------------|--|
| –3 | NH ₃ , NH ₄ ⁺ |
| –2 | NH ₂ – NH ₂ (hydrazine) |
| –1 | H ₂ N – OH (hydroxylamine) |
| 0 | N ₂ |
| +1 | N ₂ O |
| +2 | NO |
| +3 | N ₂ O ₃ , HNO ₂ |
| +4 | NO ₂ |
| +5 | N ₂ O ₅ , HNO ₃ |

Phosphorous shows following oxidation states only:

- (i) Nitrogen and P in their -3 oxidation states have noble gas configuration. However, this change requires large amount of energies (P^{-3} , 1450KJmol^{-1}). Therefore, ionic nitrides and phosphides are formed by a few metals,



- (ii) Nitrogen and P have high ionisation energies. Therefore, nature of bonds in N and P compounds are mostly covalent. Nitrogen achieve stable configuration in the following way:

- (a) By forming three single covalent bonds.



- (b) Double and triple bonds.



- (c) Tricovalent N (using lp) is a Lewis base,



- (iii) There are some stable compounds of N in which its valence shell is not complete. Example, NO, NO_2 . These species have unpaired electrons and are paramagnetic.

- (iv) P does not form many of the compounds like N. It is because P can not enter into $(p-p)\pi$ bonding which is very effective in the case of N.

Table 16.5

| N | P (species do not exist) |
|------------------------|--------------------------|
| N_2O | P_2O |
| N_2O_3 | P_2O_3 |
| N_2O_5 | P_2O_5 |
| NO_2^- | PO_2^- |
| NO_3^- | PO_3^- |
| N_3^- | P_3^- |
| CN^- | PN^- |

- (v) The tri and penta oxides of P are actually dimeric P_4O_6 and P_4O_{10} .

Hydrides

All elements of this group form MH_3 type hydrides. They are colourless, foul smelling, poisonous gases. General characteristics of the hydrides vary as:

Table 16.4

| Oxidation states | Example |
|------------------|--|
| -3 | PH_3 |
| -2 | P_2H_4 |
| 0 | P_4 |
| $+1$ | H_3PO_2 |
| $+3$ | $\text{P}_4\text{O}_6, \text{H}_3\text{PO}_3$ |
| $+5$ | $\text{P}_4\text{O}_{10}, \text{H}_3\text{PO}_4$ |

(i) Properties which decrease down the group

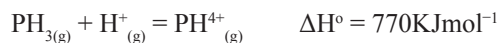
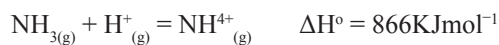
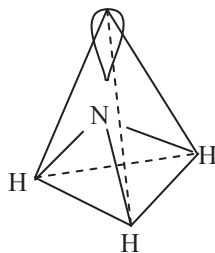
Table 16.6

| Property | NH ₃ | PH ₃ | AsH ₃ | SbH ₃ | BiH ₃ |
|---|--|-----------------|------------------|------------------|------------------|
| Heat of formation (ΔH_f) | Decreases \longrightarrow | | | | |
| M – H bond energy (KJmol^{-1}) | 391 | 322 | 247 | 255 | |
| Thermal stability | Decreases \longrightarrow | | | | |
| Donor property | Decreases \longrightarrow | | | | |
| HMH bond angle | Decreases \longrightarrow | | | | |
| Water solubility | NH ₃ water soluble (due to H – bonding) others are insoluble | | | | |

(ii) Properties which increase down the group

Table 16.7

| Property | NH ₃ | PH ₃ | AsH ₃ | SbH ₃ | BiH ₃ |
|---------------------------|-----------------------------|-----------------|------------------|------------------|------------------|
| Reducing power | Increases \longrightarrow | | | | |
| Mp ($^{\circ}\text{C}$) | Increases \longrightarrow | | | | |
| Toxicity | Increases \longrightarrow | | | | |

Note:(i) Phosphine is a poor donor than NH₃. It can be seen from their proton affinities,That is, NH₃ is a stronger base than PH₃(ii) **Structure of hydrides:** NH₃ is tetrahedral in structure and N in NH₃ is sp³ hybridized. It is because N is small in size and to reduce bp – bp resulsion it uses hybrid orbitals. Three sp³ orbitals form N – H bonds and fourth sp³ orbital accommodates lp.

$$\pi \text{ HNH} \approx 107^{\circ}$$

Figure 16.5

Shape of NH_3 is Δ^r pyramidal.

H – atoms are at the corners of an equilateral triangle and N – atom is above that triangle.

The hydrides PH_3 , AsH_3 and SbH_3 have bond angles very near to 90° .

| | | | |
|---------|-------------------|-----------------|-----------------|
| Hydride | PH_3 | AsH_3 | SbH_3 |
| LHMH | $\sim 93.5^\circ$ | $\sim 92^\circ$ | $\sim 91^\circ$ |

These angle suggest that pure p-orbitals (np^3) are used for M – H bonds by P, As and Sb. It is due to large size of P, As and Sb. The central atoms are not sp^3 hybridized. Therefore, lp in these MH_3 molecules are present in s-type atomic orbital. This explains their poor donor ability. Therefore, PH_3 is a much weaker base than NH_3 . The molecules are Δ^r pyramidal.

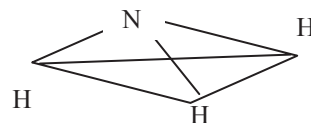


Figure 16.6

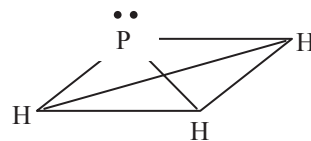


Figure 16.7

Important hydrides of N and P

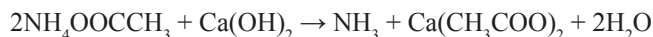
Table 16.8

| N | P |
|--|------------------------------------|
| Ammonia – NH_3 | Phosphine – PH_3 |
| Hydrazine $\text{NH}_2 - \text{NH}_2$ | Diphosphine P_2H_4 |
| Hydroxylamine $\text{H}_2\text{N} - \text{OH}$ | (not stable) |

Ammonia NH_3

It can be prepared in many ways:

- (i) Any ammonium salt on heating with alkali forms NH_3 .



- (ii) Ionic nitrides are hydrolyzed by water to produce NH_3 .



- (iii) NH_4^+ – salts, which contain non-oxidizing anions, on heating gives NH_3 .

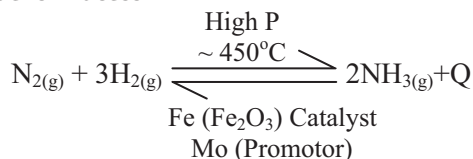
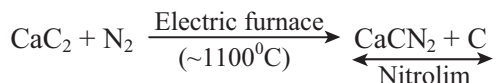


Non-oxidizing anions are Cl^- , SO_4^{2-} , CO_3^{2-} , CH_3COO^- , PO_4^{3-} etc.

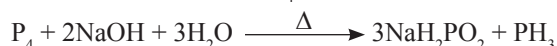
However, NH_4^+ salts which contain oxidizing anions forms N_2 or N_2O on heating.



- (iv) NH_3 is manufactured by

(a) Haber's Process**(b) Cyanamid Process****Phosphine PH₃**

- (i) When a mixture of white P (P₄) and NaOH solution are heated, PH₃ is formed.



In this reaction some P₂H₄ is also formed as side product. It is inflammable in air.

- (ii) Ionic phosphides react with water to form PH₃



NH₃ is highly soluble in water but PH₃ is insoluble in water. Ammonia dissolves in water due to H – bonding

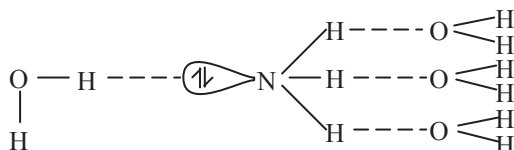


Figure 16.8

PH₃ cannot form H – bond, so it is insoluble in water.

Oxides of N and P

Nitrogen forms stable oxides from +1 to +5 oxidation states whereas common P oxides are found in +3 and +5 oxidation states only.

Nitrogen and P oxides

Table 16.9

| Oxide | Oxidation state of N/P | Physical state | Colour | Magnetic property |
|--------------------------------|------------------------|----------------|------------|-------------------|
| N ₂ O | +1 | Gas | Colourless | Diamagnetic |
| NO | +2 | Gas | Colourless | Paramagnetic |
| N ₂ O ₃ | +3 | Solid | Blue | Diamagnetic |
| NO ₂ | +4 | Gas | Brown | Paramagnetic |
| N ₂ O ₄ | +4 | Gas | Colourless | Diamagnetic |
| N ₂ O ₅ | +5 | Gas | Colourless | Diamagnetic |
| P ₄ O ₆ | +3 | Solid | Colourless | Diamagnetic |
| P ₄ O ₁₀ | +5 | Solid | Colourless | Diamagnetic |

The oxides of N can be prepared as:

Dinitrogen oxide (or nitrous oxide) N₂O

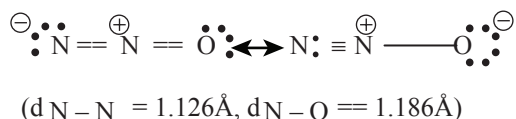
It is obtained when a melt of NH₄NO₃ is heated (250 – 260°C)



Nitric oxide (NO) is impurity in this preparation. It is removed by passing the gaseous mixture through FeSO₄ solution; which absorbs NO.

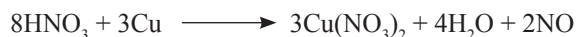
Structure

It is iso electronic to CO₂ and has linear structure. But unlike CO₂ it has dipolemoment (0.16D). It shows resonance

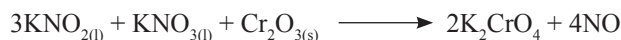


Nitric oxide (NO)

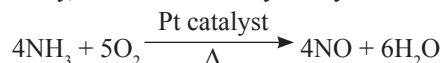
- Copper reacts with dil. HNO₃ (8M) to form NO. It is reduction of NO₃⁻.



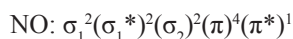
- Dry NO can be prepared by the reaction,



- Commercially, NO is obtained by catalytic oxidation of NH₃ (Ostwald process for HNO₃)



It is odd electron molecule (11 electrons) and is paramagnetic. Bonding in NO is best understood by molecular orbital model. The MO configuration is



$$\text{Bond order} = (8 - 3)/2 = 2.5$$

The N – O distance is 1.14Å which is intermediate between double and triple bond distances. The π* electron is lost easily to give nitrosonium ion, NO⁺, which forms many salts.

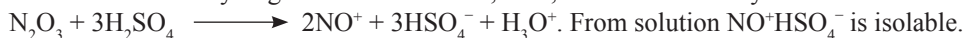


Table 16.10

| | NO | NO ⁺ |
|------------------------|--|---|
| Electron configuration | $\sigma_1^2(\sigma_1^*)^2(\sigma_2)^2(\pi)^4(\pi^*)^1$ | $\sigma_1^2(\sigma_1^*)^2(\sigma_2)^2(\pi)^4$ |
| Bond order | 2.5 | 3.0 |
| N – O distance (Å) | 1.14 | 1.05 |
| Magnetic property | Paramagnetic $\mu = \sqrt{3}\text{BM}$ | Diamagnetic |
| Stability | NO ⁺ > NO | |

Nitric oxide is a good ligand and form variety of complexes with transition metal which are known as nitrosyls, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$.

Dinitrogen trioxide N_2O_3

It can be obtained by mixing NO and NO_2 in equimolar quantities at low temperature.



In gaseous state it has the structure

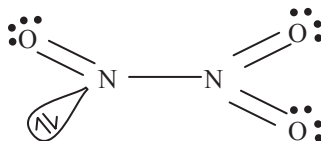
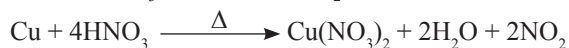


Figure.16.9

The N – N distance is very large, 1.864\AA .

Nitrogen dioxide NO_2 (N_2O_4)



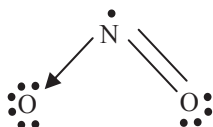
(ii) Nitric oxide is oxidized easily to produce NO_2



(iii) Di or trivalent metal nitrate decomposes on heating to NO_2 .



NO_2 is an odd electron (17 electrons) molecule and is paramagnetic. It has the structure



$$\pi\text{ONO} \sim 132^\circ$$

$$d_{\text{N-O}} = 1.2\text{\AA}$$

Figure 16.10

The unpaired electron ensures ready dimerization to a diamagnetic colourless species N_2O_4 (dinitrogen tetraoxide).



N_2O_4 is planar.

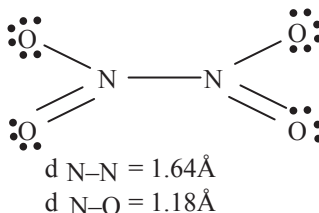


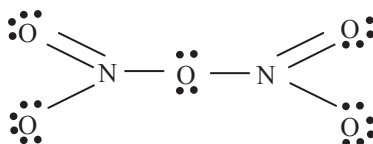
Figure 16.11

Nitrogen pentaoxide N_2O_5

It is obtained by dehydration of HNO_3 by P_2O_5 .



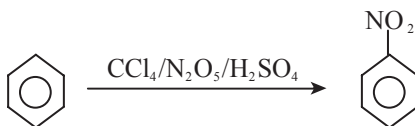
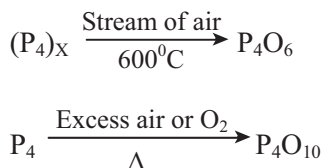
N_2O_5 is solid and in this state it is $NO_2^+ \cdot NO_3^-$ i.e., nitronium nitrate. In gaseous state it has the structure,

**Figure 16. 12**

In anhydrous H_2SO_4 (or HNO_3 or H_3PO_4) it produces NO_2^+ .



Therefore, this mixture is often used for anhydrous nitration of benzene

**Figure 16. 13****P – oxides P_4O_6 and P_4O_{10}** 

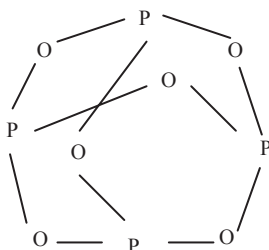
These oxides are solids.

They differ from N oxides in stoichiometry and structure. It is due to inability of P to form $(p-p)\pi$ bonds.

P_4O_6 and P_4O_{10} both have cage structure. The structures are based upon P_4 tetrahedra.

 P_4O_6

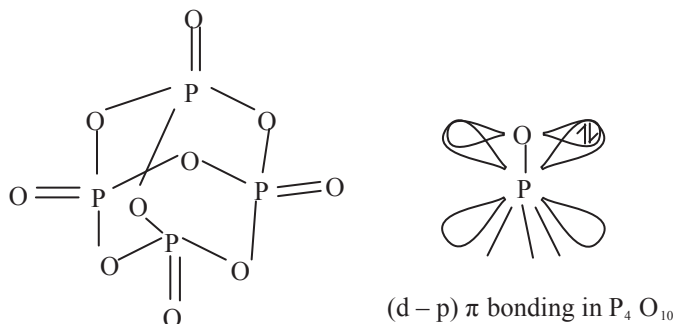
In this oxide P – atoms form a regular tetrahedron and O – atoms are present at six edges of the tetrahedron and bridge P – atoms.

**Figure 16. 14**

All O – atoms are equivalent and P – O distance is 1.64\AA .

P₄O₁₀

In this oxide P₄ tetrahedron has six edge-bridging O – atoms and four terminal O – atoms. The terminal P – O bonds have (d – p)π bonding. Therefore, there are two types of P – O distances in P₄O₁₀ large bridging P – O and small terminal P – O distances.

**Figure 16.15**

$$d_{\text{P-O}} (\text{bridging}) = 1.604 \text{ \AA}$$

$$d_{\text{P-O}} (\text{terminal}) = 1.429 \text{ \AA}$$

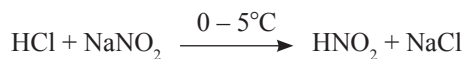
Oxy acids of N

| | | |
|----|--------------|------------------|
| +3 | nitrous acid | HNO ₂ |
| +5 | nitric acid | HNO ₃ |

Nitrous acid (HNO₂)

It is a weak acid ($p_{\text{Ka}} = 3.3$, $K_a = 4.5 \times 10^{-4}$) and the pure liquid acid is unknown.

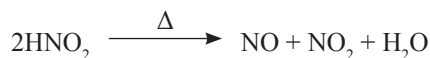
Cold metal nitrite solution when treated with dil. acid (HCl) HNO₂ is formed.



Salt free acid can be prepared by the reaction.



In gaseous state it decomposes as



In aq. solution it decomposes on heating as

**HNO₂ as oxidizing and reducing agent**

Nitrogen in HNO₂ is in +3 oxidation state which is intermediate for nitrogen. This oxidation state can decrease as well as increase. Therefore, HNO₂ is oxidizing and reducing agents both.

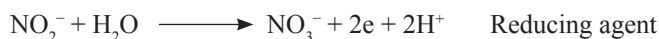


It oxidizes

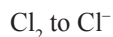
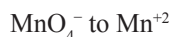




HNO₂ as reducing agent



It reduces



Nitrites are very toxic. But is used for preservation of ham and other meat products. It is because NO_2^- decomposes into NO, forms red colour with haemoglobin and so improves the colour of meat.

But during cooking NO_2^- (or NO) react with protein to form carcinogenic nitrosoamines ($R_2N \rightarrow NO$). Also, nitrite inhibit the growth of clostridium botulinum which may cause food poisoning. Thus, nitrite is a toxic substance.

Structure of NO_2^- ion

It is trigonal planar in structure but angular in shape. Nitrogen atom in NO_2^- is sp^2 hybridized.

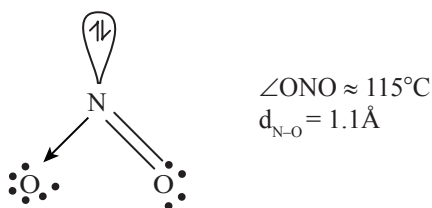
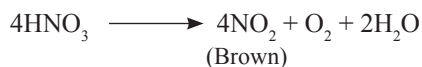


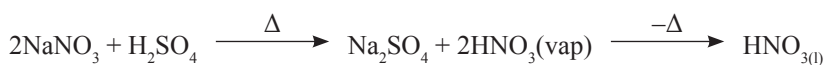
Figure 16. 16

Nitric acid (HNO_3)

Pure HNO_3 is a colourless covalent compound. It has no action on metal and carbonates. But in aq. solution it is a strong monoprotic acid (ionizes 100%). It is oxidizing agent and oxidizing power increases with concentration. Solution or conc. acid looks yellowish. It is because of its decomposition to produce NO_2 .

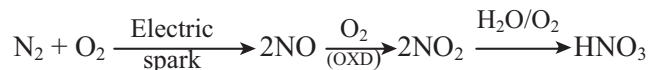


The acid can be prepared by heating a metal nitrate with conc. H_2SO_4 .



Methods of Manufacture

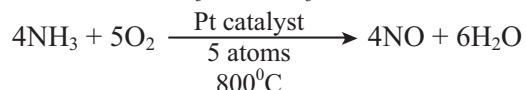
(i) Birkeland – Eyde process



This method is obsolete.

(ii) Ostwald process

This method uses NH_3 for HNO_3 .



NO is oxidized by O_2 to NO_2 and NO_2 is dissolved in water counter current to give HNO_3 .



NO is recycled in oxidation chamber. This process produces $\sim 60\%$ HNO_3 by wt. Further distillation gives only upto $\sim 68\%$ acid (a constant boiling mixture is formed).

Very concentrated acid is produced as

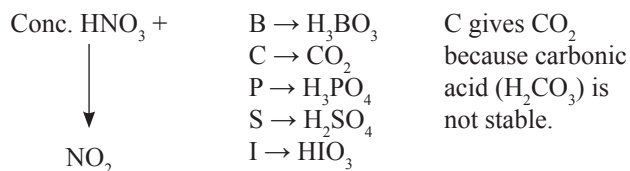
- (i) Dehydrating HNO_3 with conc. H_2SO_4 .
- (ii) Mixing the acid with a 72% $\text{Mg}(\text{NO}_3)_2$ solution followed with distillation.

Reactions

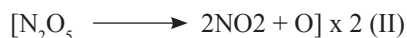
This is an oxidizing agent and reacts with metals, non-metals, and other chemical substances.

(i) HNO_3 + Non-metals

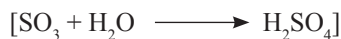
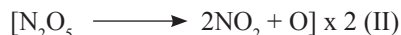
- dil. HNO_3 has no action on any non-metal.
- Even conc. HNO_3 has no action on N_2 , O_2 , F_2 , Cl_2 and Br_2 .
- Conc. HNO_3 reacts with B, C, P, S and iodine. The reaction is



The reactions can be written as:



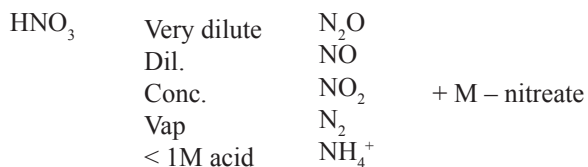
First two steps (I and II) are common to all reactions.



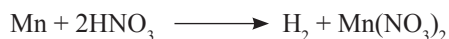
(ii) HNO_3 + Metal

Reaction product depends on conc. of HNO_3 , temperature and nature of the metal.

- Gold does not react even with conc. HNO_3 .
- Relatively noble metals Cu, Ag etc form NO with dil. and NO_2 with conc. HNO_3 (metal forms nitrate)
- Reactive metals Fe, Zn, Sn, Mn, Mg etc., react as:



- Very dil HNO_3 forms H_2 with Mg and Mn



(iii) Devarda's alloy (Cu/Al/Zn) with NaOH reduces NO_3^- to NH_3 . This reaction is quantitative and may be used for the estimation of nitrate.

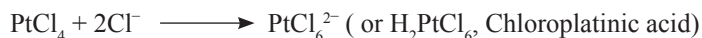
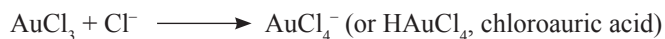


Aquaregia

A mixture of conc. HCl and HNO_3 in the ratio 3 : 1 is called aquaregia. This is a powerful oxidizing agent and dissolves metals like Au and Pt. The two acids on mixing react as



The presence of NOCl and Cl makes aquaregia a powerful oxidizing agent.



It is the high conc. of Cl^- which further stabilizes the product (AuCl_3 or PtCl_4).

Oxy acids of P

The common oxy acids of P are:

Table 16.11

| Oxidation state of P | Name | Formula | Proticity | Structure |
|----------------------|--|----------------------------------|-----------|---|
| +1 | Hypophosphorous acid (phosphinic acid) | H_3PO_2 | 1 | Td. |
| +3 | Phosphorous acid | H_3PO_3 | 2 | Td. |
| +5 | Metaphosphoric acid | $(\text{HPO}_3)_n$ | 1 | Td. Polymeric and contain PO_4 Td. units |
| +5 | Orthophosphoric acid | H_3PO_4 | 3 | Td. Highly hydrogen bonded |
| +5 | Pyrophosphoric acid | $\text{H}_4\text{P}_2\text{O}_7$ | 4 | Td. (two tetrahedra joined through O – atom) |

Note:

- (i) In H_3PO_2 two H – atoms are directly linked with P i.e., $\text{PH}_2(\text{O})\text{OH}$. So it is monoprotic (OH ionizes)
- (ii) In H_3PO_3 there is only one P – H linking $\text{PH}(\text{O})(\text{OH})_2$ i.e., diprotic.
- (iii) Metaphosphates have polymeric structure chain like as well as cyclic, $(\text{PO}_3)_n^{n-}$.

Hypophosphorous acid H_3PO_2 [$\text{H}_2\text{PO}(\text{OH})$]

It can be prepared by heating white P with $\text{Ba}(\text{OH})_2$ and then treating the reaction mixture with dil. H_2SO_4 to ppt. out BaSO_4 .

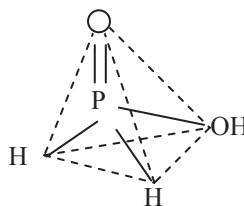


The solution crystallizes to H_3PO_2 .

It is a reducing agent due to P – H bonds.

**Structure**

H_3PO_2 is Td,
P is sp^3 hybridized.

**Figure 16.17****Phosphorous acid H_3PO_3 [$\text{HPO}(\text{OH})_2$]**

It is a diprotic acid i.e., has two OH groups and third hydrogen is directly linked to P i.e. a P – H bond.

It can be prepared as:

- (i) By dissolving P_4O_6 in water (P_4O_6 is anhydride of H_3PO_3).



(ii) By the hydrolysis of PCl_3 with water

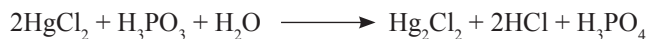


The sols on crystallization give white crystals of H_3PO_3 .

- H_3PO_3 disproportionate on heating.



- It is reducing agent due to P – H bond.



Structure

H_3PO_3 is Td, P is sp^3 hybridized.

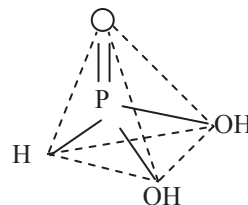


Figure 16.18

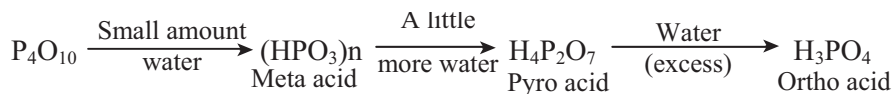
Phosphoric acids

Orthophosphoric acid H_3PO_4

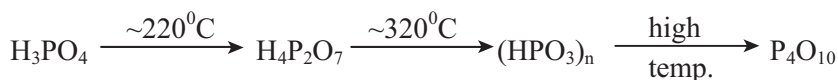
Metaphosphoric acid $(\text{HPO}_3)_n$

Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$

These all can be obtained by controlled hydration of P_4O_{10} (P – pentaoxide).

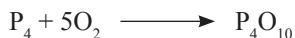


The reverse process takes place when H_3PO_4 is heated

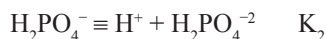


The pure H_3PO_4 is manufactured by furnance process.

The molten P is burnt in a furnance with air and steam which produces H_3PO_4



- It is solid but is highly hygroscopic and changes into solution by absorbing water.
- It is a tribasic acid.



$$K_3 < K_2 < K_1 \quad (K = \text{ionization constants})$$

- H_3PO_4 forms three types of salts.

NaH_2PO_4 (acid salt) Primary (or 1°) phosphate

NaH_2PO_4 (acid salt) secondary (or 2°) phosphate

Na_3PO_4 (normal salt) Tertiary (or 3°) phosphate

These salts behave differently on heating.

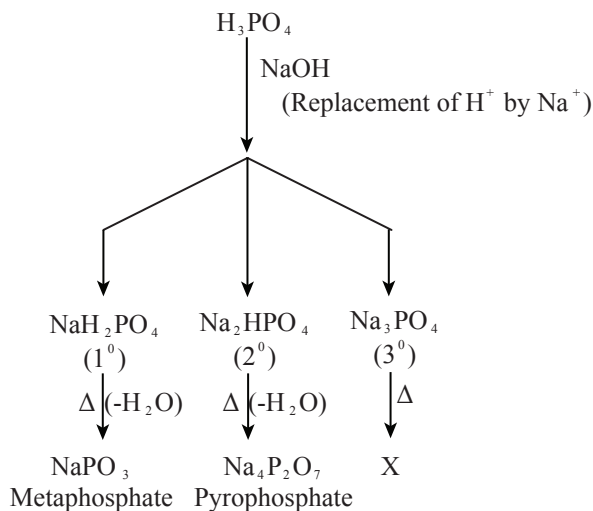


Figure 16.19

Dehydration of 1° and 2° phosphates takes place because of the presence of H atoms in the salts. The 3° salts do not dehydrate, as it has no H.

- In aq. solution H_3PO_4 is extensively H – bonded.

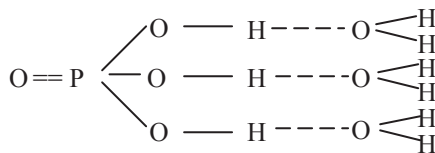


Figure 16.20

The H – bonding makes concentrated H_3PO_4 syrupy and viscous.

Metaphosphoric acid is polymeric. Linear and cyclic polymeric structures are found.

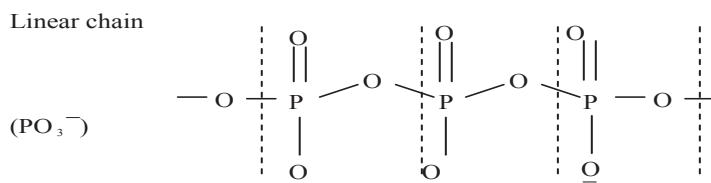
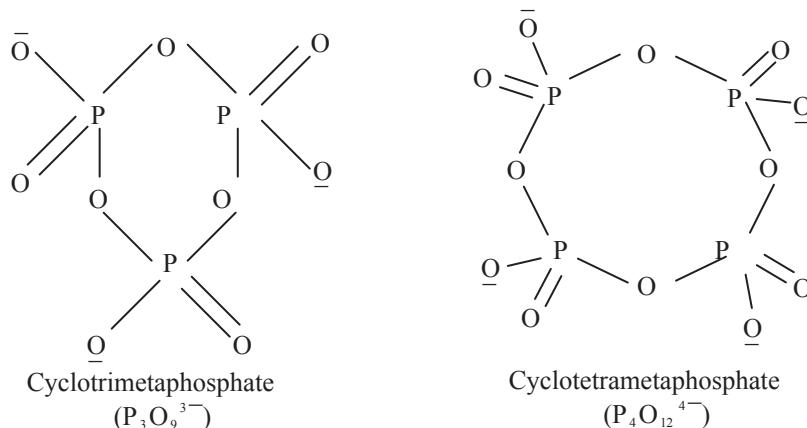


Figure 16.21

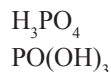
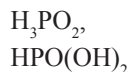
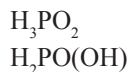
The most common cyclic ones are cyclotrimetaphosphates ($\text{P}_3\text{O}_9^{3-}$) and cyclotetrametaphosphates ($\text{P}_4\text{O}_{12}^{4-}$)

**Figure 16. 22**

There are two types of P – O bonds,

- (i) The ring and terminal bonds.
- (ii) The terminal O – atoms are equivalent due to resonance.

Acid strength of H_3PO_2 , H_3PO_3 and H_3PO_4



All have only one free O – atom, so seems similar in acid strength

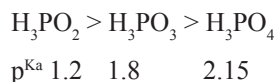


But there is difference in acid strength.

Table 16. 12

| | H_3PO_2 | H_3PO_3 | H_3PO_4 |
|------------------------------|--------------|---------------|---------------|
| Conjugate base | $H_2PO_2^-$ | HPO_3^{2-} | PO_4^{3-} |
| Negative charge per O – atom | $-1/2 = 0.5$ | $-2/3 = 0.66$ | $-3/4 = 0.75$ |

When negative charge per O – atom is high, the anion has larger attraction for H^+ . The acid ionizes less and is weak and vice versa. Thus, decreasing order of acid strength is,



Halides

Two series of halides are formed by the elements of this group. The MX_3 and MX_5 halides. Nitrogen forms only NX_3 type halides. It is due to the fact that N does not have suitable d – orbital in its valence shell. The other elements P, As and Sb form MX_3 and MX_5 halides both. MX_5 halides are formed due to the presence of d – orbitals in the valence shell. Bismuth forms only BiX_3 halides. (The +3 state is stable for Bi due to inert pair effect).

Tihalides MX_3 Properties of MX_3 **Table 16. 13**

| Property | N | P | As | Sb | Bi |
|----------------------|---------------------|---|----|----|----|
| Stability | Increases —————→ | | | | |
| Ionic nature of bond | Increases —————→ | | | | |
| mp | Increases —————→ | | | | |
| bp | Increases —————→ | | | | |
| Hydrolysis tendency | Decreases —————→ | | | | |

N Trihalides**Table 16. 14**

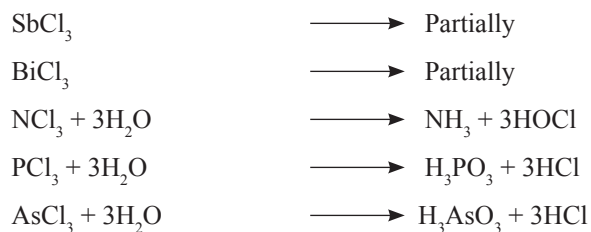
| Property | NF_3 | NCl_3 | NBr_3 | NI_3 |
|----------------|---------------------|--------------------|----------------|---------------|
| Physical state | Gas | Liquid | Unstable | |
| Structure | Td | Td | -- | -- |
| Stability | Very stable | Explosive | -- | -- |
| Reactivity | Unaffected by water | Readily hydrolyzed | -- | -- |

P Trihalides**Table 16. 15**

| Property | PF_3 | PCl_3 | PBr_3 | PI_3 |
|--------------------------|---------------------------------|----------------|----------------|---------------|
| Physical state | Gas | Liquid | Liquid | Solid |
| Structure | Pyramidal ←—————→ | | | |
| Stability | Decreases —————→ | | | |
| Bond angle | Increases —————→ | | | |
| Reactivity towards water | All hydrolyzed by water rapidly | | | |

The trichlorides hydrolyze by water.

 $\text{NCl}_3, \text{PCl}_3$ —————→ Completely AsCl_3 —————→ Like NCl_3 and PCl_3



The SbCl_3 and BiCl_3 are hydrolyzed to oxy salts.



The NCl_3 is hydrolyzed to a base (NH_3) whereas PCl_3 is hydrolysed to an acid (H_3PO_3). It is due to the fact that NCl_3 is an electron pair donor but PCl_3 is an acceptor as P has vacant 3d orbitals.

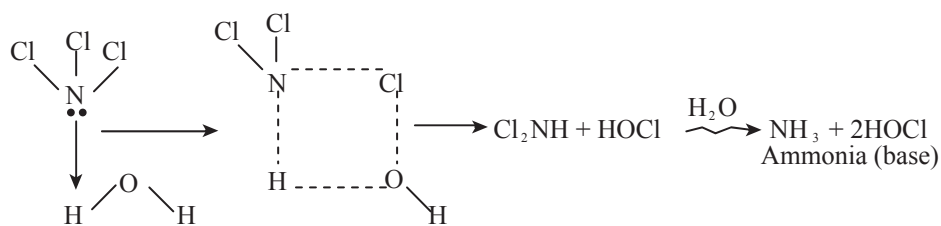


Figure 16. 23

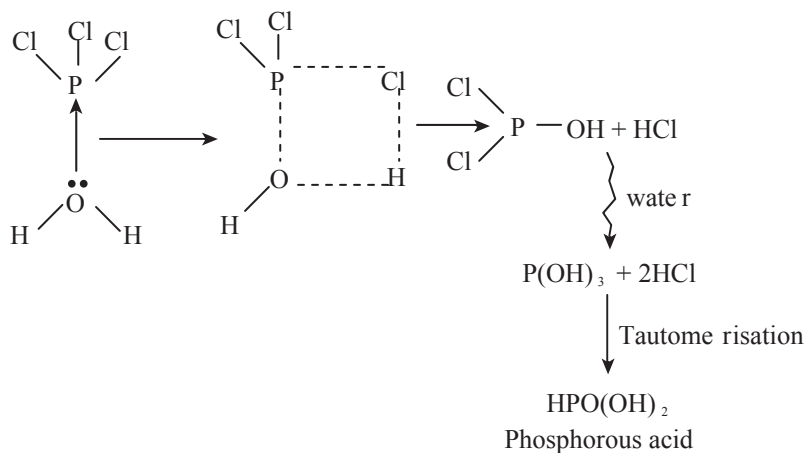


Figure 16. 24

Pentahalides of P

The pentahalides of P are PX_5 . In this group of compounds P has more than eight electrons around it. It is valence expansion of P by the use of vacant d orbitals present in phosphorus.

Table 16. 16

| | PF₅ | PCl₅ | PBr₅ | PI₅ |
|---------------------------------------|-----------------------|------------------------|--|--|
| Physical state | Gas | Liquid | Solid | Solid |
| Structure (gas) | tbp | Tbp | Present as PBr ₄ ⁺ Br ⁻ | Not well known and appears to be PI ₄ ⁺ I ⁻ |
| Stability | | | Decreases | |
| Reactivity (towards H ₂ O) | | | Increases | |

The PF₅ is tbp in gas, liquid and solid states. However, PCl₅ gas or liquid is tbp but it crystallizes to form [PCl₄]⁺ [PCl₆]⁻. In this change, PCl₅ is a Cl⁻ ion donar as well as Cl⁻ acceptor.

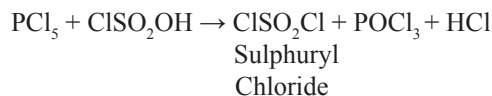
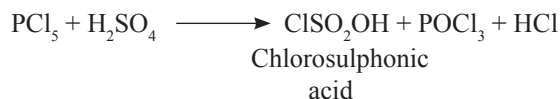


The ions PCl₄⁺ and PCl₆⁻ are Td and octahedral respectively.

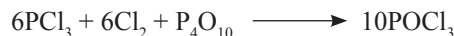
PCl₅ is widely used to prepare chloroderivatives of RCOOH and R – OH.



It also replaces –OH from H₂SO₄.



PCl₃ and PCl₅ both react with P₄O₁₀ to produce phosphoryl chloride.



PCl₅ is hydrolyzed by water to H₃PO₄.

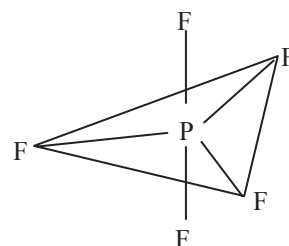


Isolation of N and P

Nitrogen occurs in nature mainly as N₂, (~78% by volume of the earth's atmosphere). It is also found as nitrates. NH₄⁺ compounds and organic compounds.

N₂ in laboratory

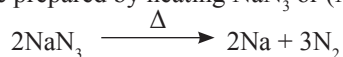
A mixture of NH₄Cl and NaNO₂ is heated to prepare N₂ in laboratory.

**Figure 16. 25**

Ammonium nitrite is an explosive so it is not heated alone.

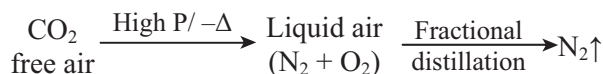
Pure N₂

It can be prepared by heating NaN₃ or (NH₄)₂Cr₂O₇



Manufacture of N₂

It is prepared in large scale by liquefaction and fractional distillation of liquid air. It is because N₂ and O₂ differ in their bps (N₂ bp – 196°C, O₂ – 183°C)

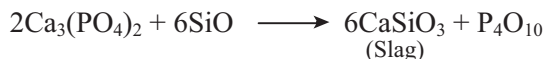


Isolation of P

Phosphorus occurs mainly as Ca₃(PO₄)₂ in

- | | |
|------------------|---|
| (a) Phosphorite | Ca ₃ (PO ₄) ₂ |
| (b) Fluorapatite | 3Ca ₃ (PO ₄) ₂ CaF ₂ |
| (c) Chlorapatite | 3Ca ₃ (PO ₄) ₂ ·CaCl ₂ |

P is obtained by the reduction of phosphate rock [Ca₃(PO₄)₂] with SiO₂ and coke in an electric furnace.



P₄ (white)

White phosphorus is inflammable in air. So, it is kept under water.

Fertilizers

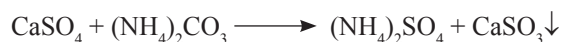
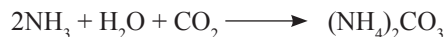
The substance, which increases the fertility of soil, is known as fertilizer. Chemical fertilizers are substances which provide essential nutrients to plants. Among various essential elements N, P and K are most vital. Therefore, nitrogenous, phosphatic and potash fertilizers are most common. Those fertilizers which provide all the three are called NPK or mixed or complete fertilizers.

Essential qualities of a good fertilizer

- The fertilizer should be water soluble so that assimilated by the plants easily.
- It should provide essential nutrients over a long period.
- It should not be heat producing with soil; otherwise the plants will be damaged.
- It must be basic, as slightly alkaline soil is essential for the proper growth of plants (any soil above pH – 10 and below pH – 3 becomes sterile).
- It should keep the soil loose.
- It should be dry and finely powdered for uniform distribution.

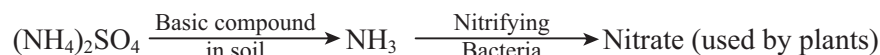
Nitrogenous fertilizers**1. Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$**

Aqueous suspension of gypsum is saturated with NH_3 gas and then CO_2 gas is passed. It produces $(\text{NH}_4)_2\text{SO}_4$.

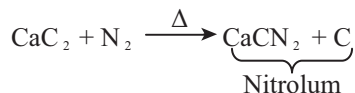


Solid CaCO_3 is filtered out. The solution on evaporation under vacuum and cooling gives crystals of $(\text{NH}_4)_2\text{SO}_4$.

Fertilizer action

**2. Calcium cyanamide (CaCN_2)**

It is prepared by heating a mixture of CaC_2 and N_2 gas at high temperature ($\sim 1100^\circ\text{C}$).



When added to soil it decomposes to CaCO_3 and NH_3 . Ammonia is then converted into nitrate, which is used by plants. It is a slow acting substance.

3. Calcium ammonium nitrate (CAN, $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3)

Manufacture of this fertilizer uses N_2 from air and H_2 from water. NH_3 is produced by Haber's process and HNO_3 from NH_3 by Ostwald process.

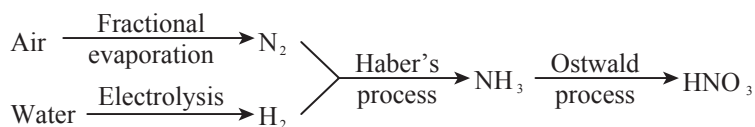
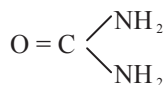


Figure 16. 26

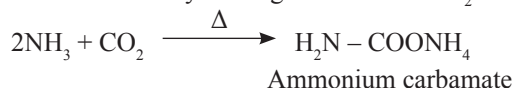
Nitric acid is finally neutralized by powdered lime stone (CaCO_3) and NH_3 to get the fertilizer CAN.

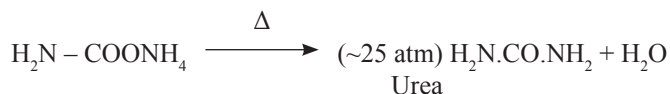


The pellets of CAN are coated with calcium silicate (soapstone) to protect them from moisture.

4. Urea

It is manufactured by heating a mixture of CO_2 and NH_3 at high pressure (~ 200 atm).

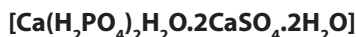




It is most commonly used fertilizer and is preferred over $(\text{NH}_4)_2\text{SO}_4$ and CAN. The latter ones make soil acidic ($\text{NH}_4^+ + \text{H}_2\text{O} \longrightarrow \text{NH}_3 + \text{H}_3\text{O}^+$) which is bad.

Phosphatic fertilizers

1. Calcium superphosphate or Super phosphate of lime



(a) *From phosphonite*

It is prepared by treating phosphonite or bone ash with calculated quantity of H_2SO_4 (~70%).



It has undesirable CaSO_4 (insoluble).

(b) *From fluorapatite* $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$

Fluorapatite on reaction with calculated amount of H_2SO_4 gives calcium superphosphate



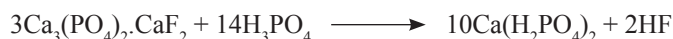
2. Triple superphosphate $3\text{Ca}(\text{H}_2\text{PO}_4)_2$

(a) *From phosphorite*

It is manufactured by the action of orthophosphoric acid on phosphorite rock.



(b) *From fluorapatite* $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$



3. Calcium superphosphate nitrate or nitrophosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{Ca}(\text{NO}_3)_2$

It is manufactured by the action of HNO_3 on phosphorite rock



It is better as N and P both are present.

4. Phosphatic slag or Thomas slag

It is the byproduct of steel industry. When iron ore is blasted with limestone, calcium phosphate and Ca silicate are produced as slag. This is cooled and finally powdered and used as fertilizer.



Potash fertilizers

Potassium is essential for growth of plants. It also helps uptake of other nutrients. Potassium chloride, KNO_3 and K_2SO_4 are used as fertilizers.

PRACTICE QUESTIONS

A. Account for the following:

- Nitrogen is gaseous N_2 whereas phosphorus is P_4 solid.
- Phosphorus exists in allotropic forms but not nitrogen.
- Nitrogen forms only NCl_3 but P forms PCl_3 and PCl_5 both.
- NH_3 is stronger base than PH_3 .
- Bond angle in NH_3 ($\sim 107^\circ$) is much larger than in PH_3 ($\sim 93^\circ$).
- NH_3 is soluble in water but PH_3 is insoluble.
- The hydrolysis of NCl_3 gives a base (NH_3) whereas PCl_3 gives an acid (H_3PO_3).
- The b.pt. of NH_3 is greater than PH_3 although molecular wt. of PH_3 is high.
- Red P is less reactive than white P.
- Iron reacts very slowly with conc. HNO_3 .
- Coloured paramagnetic NO_2 dimerizes readily to colourless diamagnetic N_2O_4 .
- H_3PO_2 is monoprotic acid.
- The P – O bond length in $POCl_3$ is short (1.45\AA) compared to the sum of the single bond covalent radii of P and O (1.83\AA).
- There are two types of P – O bond distances in P_4O_{10} .
- NF_3 is not a Lewis base for BF_3 but $F_3N - O$ is stable compound.
- The oxyacids of N and P in their +5 oxidation state differ in formula ($N \rightarrow HNO_3$, $P \rightarrow H_3PO_4$).
- On gentle heating HNO_3 give NO_2 but H_3PO_4 gives a condensation product pyrophosphoric acid, $H_4P_2O_7$.
- NaH_2PO_4 on heating gives sodium metaphosphate but Na_3PO_4 resist temperature.
- Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state.
- The experimentally determined N – F bond length in NF_3 is greater than the sum of the single bond covalent radii of N and F.
- Mg_3N_2 hydrolyzed to NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature.

- Why is pure phosphoric acid syrupy?
- The N – N bond energy ($\sim 160 \text{ KJmol}^{-1}$) in $NH_2 - NH_2$ is much less than C – C bond energy (350 KJmol^{-1}) in $CH_3 - CH_3$.

B. Write equations for effect of heat on:

- | | |
|------------------------------|--------------------|
| (a) NH_4NO_3 | (b) $NaNO_3$ |
| (c) $Cu(NO_3)_2 \cdot xH_2O$ | (d) NH_4NO_2 |
| (e) NaN_3 | (f) NaH_2PO_4 |
| (g) $(NH_4)_2Cr_2O_7$ | (h) $(NH_4)_2CO_3$ |
| (i) $(NH_4)_2C_2O_4$ | |

C. Write balanced equations when water reacts with the following:

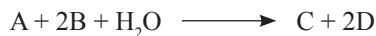
- | | |
|-----------------------------------|-------------|
| (a) NCl_3 | (b) PCl_3 |
| (c) $CaCN_2$ | (d) AlN |
| (e) Li_3N | (f) NO_2 |
| (g) P_4O_{10} with little water | |

D. Complete the following writing balanced equations.

- $KNO_{2(l)} + KNO_{3(l)} + Cr_2O_{3(s)} \longrightarrow$
_____ + _____.
- $NH_4NO_{3(s)} \longrightarrow$ _____ + _____.
- $NH_4NO_{3(l)} \longrightarrow$ _____ + _____.
- I. $NH_3 + NaOCl \longrightarrow$ _____ + _____.
II. $NH_3 + H_2N - Cl + NaOH \longrightarrow$ _____ + _____.
- $HNO_3 + P_4O_{10} \longrightarrow$ _____ + _____.
- $N_2O_5 + HClO_4 \longrightarrow$ _____ + _____.
- I. $[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow$
 $[Fe(H_2O)_6]^{+3} +$ _____ + H_2O .
II. $[Fe(H_2O)_6]^{2+} +$ _____ \longrightarrow
_____ + H_2O .
- $NO + SO_2 + H_2O \longrightarrow$ _____ + _____.
- $P_4 + \text{conc. } HNO_3 \longrightarrow$ _____ + _____ + _____.
- $CaC_2 + N_2 \longrightarrow$ _____ + _____.

- (k) $\text{Sn} + \text{conc. HNO}_3 \longrightarrow \underline{\hspace{2cm}}$
 $+ \underline{\hspace{2cm}} + \underline{\hspace{2cm}}.$
- (l) $\text{NH}_3 + \text{Cl}_2 \longrightarrow \underline{\hspace{2cm}} + \underline{\hspace{2cm}}.$
- (m) $\text{P}_4\text{O}_{10} + \text{PCl}_5 \longrightarrow \underline{\hspace{2cm}}.$

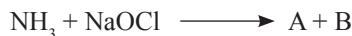
E. (a) In the following equation, identify D and sketch structures of A, B, C and D.



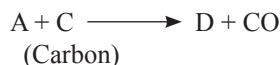
(b) Identify A, B, C and D in the reactions



(c) In the following reactions identify A, B, C and D and write structure of D.



(d) Identify A, B and D in the following reactions and write structure of A.



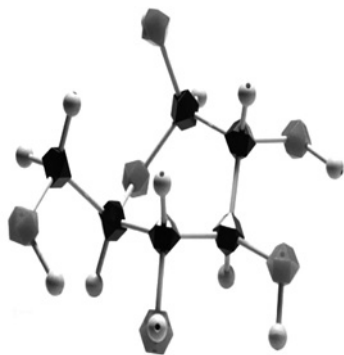
OBJECTIVE-TYPE QUESTIONS

- Which of the following is formed when conc. HNO_3 is mixed with P_4O_{10} ?
 (a) N_2O (b) NO_2
 (c) N_2O_3 (d) N_2O_5
- Very dilute HNO_3 forms NH_4NO_3 with
 (a) Cu (b) Ag
 (c) Zn (d) Hg
- Brown ring compound is
 (a) $[\text{Fe}(\text{H}_2\text{O})_4\text{NO}]\text{SO}_4$
 (b) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$
 (c) $[\text{Fe}(\text{H}_2\text{O})_6\text{NO}]\text{SO}_4$
 (d) $[\text{Fe}(\text{H}_2\text{O})_5]\text{NO}_2$
- Which of the following gives metaphosphate on heating?
 (a) NaH_2PO_2 (b) Na_3PO_4
 (c) Na_2HPO_4 (d) NaH_2PO_4
- Mark the correct answer using codes. White phosphorus has
 (I) Six P – P σ bonds
 (II) Four lone pairs
 (III) Four P – P σ bonds
 (IV) P P P angle of 60°
 (a) I, II, III (b) I, II, IV
 (c) II, III, IV (d) I, III, IV
- Which of the following is correct for white and red phosphorus both?
 (a) PPP angles are equal. (b) Each P forms three bonds in both.
 (c) Each P forms four bonds in both.
 (d) Both have similar solubility.
- For the reaction, $\text{MH}_3 + \text{H}^+ \longrightarrow \text{MH}_4^+$ (M = N, P, As, Sb), which of the following has highest proton affinity?
 (a) NH_3 (b) PH_3
 (c) AsH_3 (d) SbH_3
- Ammonia on reaction with hypochlorite anion form
 (a) NO (b) N_2H_4
 (c) HNO_2 (d) N_2O
- Which of the following is the strongest base?
 (a) SbH_3 (b) AsH_3
 (c) PH_3 (d) NH_3
- Conc. HNO_3 reacts with iodine to give
 (a) HOIO_3 (b) HOIO_2
 (c) HOIO (d) HOI
- Ammonia gas can be dried over
 (a) CaO (b) Anhydrous CaCl_2
 (c) P_4O_{10} (d) conc. H_2SO_4
- Which one of the oxides of nitrogen is a coloured gas?
 (a) N_2O (b) NO
 (c) NO_2 (d) N_2O_4

13. One mole of calcium phosphide (or Zinc phosphide) on reaction with excess of water gives
 - (a) One mole of phosphine
 - (b) Two moles of phosphine
 - (c) Two moles of phosphorus acid
 - (d) Two moles of phosphoric acid
14. The CN^- ion and N_2 are isoelectronic. But in contrast to CN^- , N_2 is chemically inert because of
 - (a) Low bond energy
 - (b) Unsymmetrical electron distribution
 - (c) Absence of bond polarity
 - (d) Presence of more electrons in bonding orbitals.
15. Ammonium dichromate is used in some fireworks. The green coloured powder blown is
 - (a) $\text{CrO}(\text{O}_2)_2$
 - (b) CrO_3
 - (c) Cr_2O_3
 - (d) $\text{CrO}(\text{O}_2)$
16. Which of the following can separate nitric oxide from nitrous oxide?
 - (a) Ammoniacal silver nitrate
 - (b) Sodium nitroprusside
 - (c) Ferrous sulphate solution
 - (d) Lucas reagent.
17. Phosphine reacts with CuSO_4 solution to form
 - (a) Copper phosphate
 - (b) Copper phosphite
 - (c) Copper phosphide
 - (d) Copper hypophosphite
18. White phosphorus is kept in
 - (a) Alcohol
 - (b) Ether
 - (c) Kerosene
 - (d) Water
19. By the action of hot conc. H_2SO_4 , phosphorus changes to
 - (a) Phosphorus acid
 - (b) Metaphosphoric acid
 - (c) Orthophosphoric acid
 - (d) Pyrophosphoric acid
20. Nitrogen is not liberated by the thermal decomposition of
 - (a) NaN_3
 - (b) NH_4NO_3
 - (c) NH_4NO_2
 - (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
21. The number of P – O – P bonds in cyclic trimetaphosphate ion is
 - (a) One
 - (b) Two
 - (c) Three
 - (d) Four
22. Ammonium compound which on heating does not give ammonia is
 - (a) $(\text{NH}_4)\text{C}_2\text{O}_4$
 - (b) $(\text{NH}_4)_2\text{SO}_4$
 - (c) NH_4NO_2
 - (d) $(\text{NH}_4)_2\text{CO}_3$
23. Which of the following mixture is used to produce signal in oceans?
 - (a) $\text{CaCl}_2 + \text{Ca}_3\text{P}_2$
 - (b) $\text{CaO} + \text{Ca}_3\text{P}_2$
 - (c) $\text{CaC}_2 + \text{Ca}_3\text{P}_2$
 - (d) $\text{Zn}_3\text{P}_2 + \text{Ca}_3\text{P}_2$
24. Gr – 15 elements form hydride of the type MH_3 (M = N, P, As, Sb). The bond angle HMH decreases in the order
 - (a) $\text{N} > \text{P} > \text{As} > \text{Sb}$
 - (b) $\text{Sb} > \text{As} > \text{P} > \text{N}$
 - (c) $\text{N} = \text{P} > \text{As} > \text{Sb}$
 - (d) $\text{N} > \text{P} = \text{As} > \text{Sb}$
25. The hybridization of P in metaphosphate ion (PO_3^-) is
 - (a) sp^2
 - (b) sp^3
 - (c) sp^3d
 - (d) None of these

ANSWERS

- | | | | | | | | | | |
|---------|---------|---------|---------|----------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (c) | 3. (b) | 4. (d) | 5. (b) | 6. (b) | 7. (a) | 8. (b) | 9. (d) | 10. (b) |
| 11. (a) | 12. (c) | 13. (b) | 14. (c) | 15. (c) | 16. (c) | 17. (c) | 18. (d) | 19. (a) | 20. (b) |
| 21. (c) | 22. (c) | 23. (c) | 24. (a) | 25. (b). | | | | | |



17

Group – 16 (VI_A)

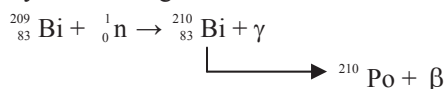
O, S, Se, Te, Po

INTRODUCTION

Elements of this group are O, S, Se, Te, and Polonium.

Oxygen, S, Se and Te are non-metallic. They are called chalcogens (ore forming, as many of the metal ores are either oxide or sulphide).

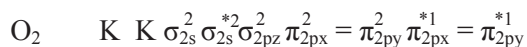
Polonium is metallic and radioactive. It was discovered by M. Curie. Its name Polonium was derived from the homeland, Poland, of M. Curie. It is found in U and Th ores as a radioactive decay product. It can be made by bombarding ^{209}Bi with neutrons in a nuclear reactor.



Polonium-210 is α -active and has a half-life of 138.4 days (i.e., $t_{1/2}$ 138.4 days).

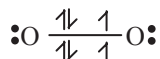
Physical state of the elements

Oxygen at s.t.p. is gas and exists as dioxygen i.e., O_2 . It is stable due to very effective $p\pi - p\pi$ bonding ($E_{0=0} = 496 \text{ KJmol}^{-1}$). Bonding in O_2 is best explained by MO model. It has MO electron configuration.



The bond order is 2 i.e., one σ and one π bond.

According to valence bond model O₃ has two three-electron bonds.



A three electron bond is equivalent to half-bond.

Both the above bonding models show that O_2 has two unpaired electrons. It is, therefore, paramagnetic ($\mu = \sqrt{8}$ BM).

Like oxygen, S is not S_2 at stp. It is because S can not form effective $(p - p)\pi$ bond. The $(p - p)\pi$ bonding in S is not effective due to large size and 8-e core in S. ordinary S is solid and exists as S_8 . The S_8 has puckered ring structure (crown structure).

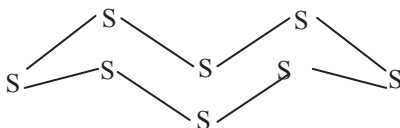


Figure 17.1

In the solid S_8 , rings are packed over one another.

Allotropy of O and S

Oxygen

It has two allotropes:

- (i) Dioxygen O_2
- (ii) Trioxygen O_3 (ozone)

The structure and bonding in O_2 is explained above.

Ozone (O_3) has bent structure.

The O–O distance in O_3 is 1.28 Å. It is intermediate between single (1.41 Å) and double bonds (1.21 Å). Thus O_3 has resonance structure,



Figure 17.3

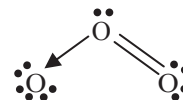


Figure 17.2

However, O_3 is polar due to coordinate bond and bent structure. The central O-atom is sp^2 hybridized.

Sulphur

Sulphur forms open and cyclic species S_n , $n = 2$ to 20 because of its ability for catenation. Solid allotropes are:

- (i) Ordinary or α -sulphur or orthorhombic-S.
- (ii) β - sulphur or monoclinic
- (iii) Cyclo- S_n $n = 6$ to 12
- (iv) Plastic – S

α -Sulphur or orthorhombic – S (a, b, c and $\alpha, \beta, \gamma = 90^\circ$)

- Common form of S at 25°C .
- It is bright yellow, mp = 112.8°C .
- Insoluble in water.
- Soluble in CS_2 .
- S_8 and has crown ring structure.

β -Sulphur or monoclinic (a, b, c; $\alpha, \gamma = 90^\circ, \beta$)

- α -S changes at 95.5°C to β -sulphur.
- It is dull yellow, mp = 119°C .
- Insoluble in water.
- Soluble in CS_2 .
- S_8 and has crown ring structure.

Cyclo –S

It contains S_n ring, $n = 6$ to 12, 18 and 20 also. The rings are similar in

- S – S distance (2.05 Å)
 - SSS angles $\sim 106^\circ$
 - S – S bond energy $\sim 265 \text{ kJ mol}^{-1}$.
- They are soluble in CS_2 , benzene etc.

Plastic – S or catena – S

- It is obtained when molten S is poured in ice cold water.
- It contains long zig – zag chain of S – atoms.
- It is insoluble in CS₂.
- It transforms slowly to S_α.

Effect of heat on S

Sulphur undergoes variety of changes on heating. They are:

- S₈ $\xrightarrow{\Delta}$ melt to a yellow transparent mobile liquid.
- Melt $\xrightarrow{> 160^\circ\text{C}}$ brown, viscosity increases and reaches its maximum at ~200°C, when it is tar like.
- Temperatures > 200°C viscosity decreases, mobility increases till the bp (444.6°C) when it is dark red liquid.
- At temperature above bp – red vapour, turning yellow as the temperature is raised. This is believed to contain S₈, S₆ etc.
- At ~1000°C, Sulphur is S₂ which is paramagnetic and has a structure similar to O₂.

Viscosity of liquid S and temperature

Viscosity of liquid S increases gradually and is maximum at around 200°C. It is believed due to the formation of long chain polymeric structure of S – atoms. As temperature increases, S₈ rings break and radical ends are generated. Then those radicals join together to produce long chain structure. The chain length is maximum at 200°C (around 8x10⁵ atoms). Therefore, the viscosity is highest. When temperature is raised beyond 200°C, the chains break leading to smaller chains. Therefore, viscosity decreases and behaviour parallels to a liquid.

Oxidation state and nature of bond**Table 17.1**

| Oxidation states | O | S |
|----------------------|--|---|
| -2 | Na ₂ O, CaO H ₂ O | Na ₂ S, CaS, H ₂ S etc |
| -1 (peroxide) | Na ₂ O ₂ , BaO ₂ H ₂ O ₂ | H ₂ S ₂ Na ₂ S ₂ |
| -1/2 (superoxide) | MO ₂ (M = K, Rb, Cs) | – |
| 0 | O ₂ , O ₃ | S ₈ |
| +1 | O ₂ F ₂ | – |
| +2 | OF ₂ | – |
| +4 | – | SF ₄ , SO ₂ |
| +6 | – | SO ₃ , SF ₆ , H ₂ SO ₄ etc. |

Note:

- Oxygen has positive oxidation state only with F because F is only more electronegative than O, (X_F = 4.0, X_O = 3.5).
- The oxidation state $\frac{-1}{2}$ for O is found only in the superoxides KO₂, RbO₂ and CsO₂.

(iii) Sulphides, except alkali metals and Ca, Sr, Ba have covalent nature because S^{2-} ion is easily polarizable.

Oxygen has high electronegativity. Therefore, it is ionic only in highly electropositive metals, Gr – 1 and Ca, Sr and Ba. i.e., M_2O or MO .

It is, however, mostly covalent, which it achieves in the following way:

- By forming two single bonds, $-O-$, (i.e., H_2O , $R-O-H$, $R-O-R$).
- By forming double bonds, $=O$, ($C=O$, $N=O$, $P=O$, $S=O$ etc).
- By forming three single bonds, H_3O^+ or 4 single bonds, which is rare, e.g., in $Be_4O(CH_3COO)_6$, the basic Be – acetate.

In addition to the above mode of bonding, O has strong ability to form H – bond. It very much distinguishes oxygen from S which has little tendency for H – bonding.

Oxygen differs in its chemistry from Sulphur. The reasons are given below:

Table 17.2

| O | S |
|--|---|
| (a) Valence orbitals are s and p only $2s^2 2p^4$. | (a) Valence orbitals are 3s, 3p and 3d, the configuration is $3s^2 3p^4 (3d^0)$. |
| (b) It can form a maximum of 4 bonds only but mainly is di and trivalent. | (b) It can form more than four bonds by the use of 3d orbitals. |
| (c) Highly electronegative, so stabilizes higher oxidation state of metals, Mn_2O_7 , CrO_3 , OsO_4 etc. | (c) No such compounds are known because S is less electronegative. |
| (d) Forms strong $p\pi - p\pi$ bonds. | (d) No $p\pi - p\pi$ bond instead forms strong $d\pi - p\pi$ bonds. |
| (e) No tendency towards catenation. | (e) Much higher catenation ability. ($E_{S-S} = 226 \text{ KJmol}^{-1}$). |

Note

Catenated compounds of S are the following:

- Polysulphides, S_n^{2-} , where $n = 2, 3, 4$ etc. They are coloured due to charge transfer, e.g., yellow ammonium sulphide generally denoted as $(NH_4)_2S_2$.
- Sulphanes of the type $X - S_n - X$, where $X = H, Cl, CN$ etc., compounds corresponding to $n = 100$ are reported.
- Polysulphonic (or sulphane disulphonic) acids. They have the general formula.



The well-established polythionate anions are for $n = 1$ to 4. However, there is evidence for anions upto $n = 22$.



General properties of the elements**Table 17.3**

| Property | O | S | Se | Te | Po |
|----------------------------|-------------------------------------|-------------------------------------|--|--|---|
| Atomic no. | 8 | 16 | 34 | 52 | 84 |
| Electronic structure | [He]2s ² 2p ⁴ | [Ne]3s ² 3p ⁴ | [Ar]3d ¹⁰ 4s ² 4p ⁴ | [Kr]4d ¹⁰ 5s ² 5p ⁴ | [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴ |
| Atomic radius (Å) | 0.74 | 1.03 | 1.17 | 1.37 | – |
| Radius X ^{2–} (Å) | 1.4 | 1.7 | 1.84 | 2.07 | – |
| Electronegativity | 3.5 | 2.5 | 2.48 | 2.01 | 1.76 |
| mp (°C) | | 119 | 221 | 450 | 254 |
| bp (°C) | | 444.6 | 684.8 | 990 | 962 |

Hydrides

All the elements of group–16 form hydrides of the type MH₂ i.e., H₂O, H₂S, H₂Se, H₂Te and H₂Po (it is prepared only in trace amounts).

Water is liquid at room temperature due to extensive association of H₂O molecules through intermolecular H – bonding (Cf Hydrogen). Other hydrides (H₂S to H₂Te) are foul smelling toxic gases. These hydrides are weak acid in aqueous solution but H₂O is amphoteric. Hydrogen sulphide (hydrosulphuric acid), H₂Se and H₂Te can be prepared as:

**General properties of hydrides****Table 17.4**

| Property | H ₂ O | H ₂ S | H ₂ Se | H ₂ Te |
|-------------------|--|------------------|-------------------|-------------------|
| ΔH _f | | | | Decreases |
| Thermal stability | | | | Decreases |
| Bond angle | | | | Decreases |
| Reducing power | | | | Increases |
| Acid strength | | | | Increases |
| Toxicity | | | | Increases |
| B.p. | H ₂ O highest due to extensive H – bonding. For H ₂ S, H ₂ Se and H ₂ Te molecular mass is controlling factor. | | | |
| | Order H ₂ Te > H ₂ Se > H ₂ S | | | |
| | Overall order H ₂ O > H ₂ Te > H ₂ Se > H ₂ S | | | |

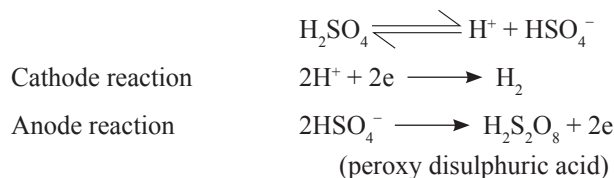
Acid strength of MH_2 **Table 17.5**

| Acid | H_2O | H_2S | H_2Se | H_2Te |
|--|---|----------|-----------|-----------|
| Conjugate base | O^{-2} | S^{-2} | Te^{-2} | Te^{-2} |
| Size of (M^{-2}) | $r_{O^{-2}} < r_{S^{-2}} < r_{Se^{-2}} < r_{Te^{-2}}$ | | | |
| Charge density on conjugate base (charge/radius) | $O^{-2} > S^{-2} > Te^{-2} > Te^{-2}$ | | | |

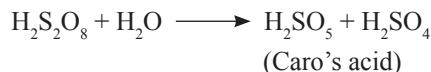
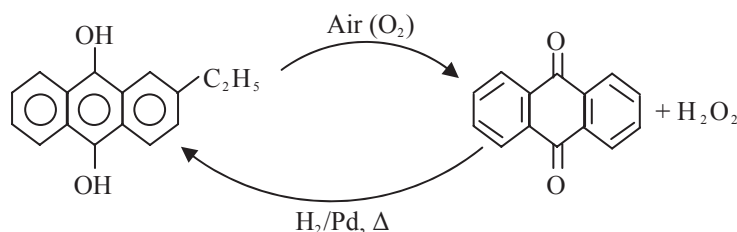
The greater the charge density on the conjugate base greater is its attraction for proton. It suppresses ionisation making the acid weak. Oxygen also forms H_2O_2 , the hydrogen peroxide (details in compound section). It is prepared in the laboratory by the action of dil. acid on a metal – peroxide.

**Industrial preparation of H_2O_2**

- (i) By the electrolysis of conc. H_2SO_4 or $(NH_4)_2HSO_4$.
- (ii) By auto oxidation of 2 ethylanthraquinol.

Electrolysis of conc. H_2SO_4 

Anode solution is hydrolyzed by water to give H_2O_2 . Fractional distillation of hydrolyzed anode solution produces H_2O_2 upto 90–98%.

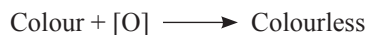
**Auto oxidation of 2 – ethylanthraquinol****Figure 17.4**

H₂O₂ is a bluish viscous liquid, i.e., denser than H₂O. It is due to the fact that H₂O₂ is more associated through H – bonding than water. However, pure H₂O₂ is colourless liquid (bp 150.2°C, mp – 0.43°C).

H₂O₂ decomposes even at room temperature to give oxygen,



It is, therefore, a bleaching agent.



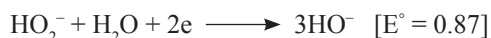
As bleaching is oxidative, it is permanent.

Aqueous (an 30%) solution of H₂O₂ is used as or oxidant. It is a reducing agent also. The oxidation number of oxygen in H₂O₂ is –1, which is intermediate for oxygen. Therefore, it is oxidant and reductant both.

H₂O₂ as oxidant



In this reaction H₂O₂ is reduced (O^{–1} to O^{–2}). So it is oxidant. As pot (E°) is high, it is a strong oxidant. It is oxidizing agent in basic medium also,



The reaction in basic medium is fast.

It oxidizes Fe²⁺ → Fe³⁺, I[–] → I₂, NO₂[–] → NO₃[–], AsO₃^{3–} → AsO₄^{3–}, S^{2–} → SO₄^{2–} etc.

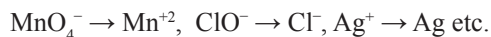


H₂O₂ is used to clean blackened old paintings (due to oxidation of PbS to PbSO₄).

H₂O₂ as reductant



It is not a strong reducing agent. It reduces



Strength of H₂O₂

The strength of H₂O₂ is denoted as volume strength, e.g., 10V, 20V etc. H₂O₂.

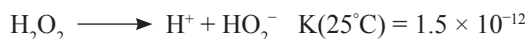
The volume strength denotes the volume of O₂ produced at s.t.p. For example, a 10V H₂O₂ means a solution of which 1ml produces 10 ml O₂ at s.t.p.

The other units are:

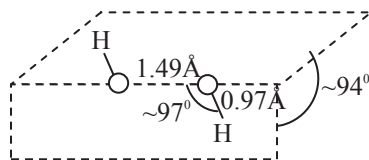
- (i) g/l strength of H₂O₂ = (68/22.4)Xv
- (ii) Normality of H₂O₂ = V/5.6
- (iii) Mol/l or Molarity = V/11.2

Acid strength of H₂O₂ and H₂O

Acid strength of H₂O₂ is greater than H₂O.



It is because oxidation number of oxygen in H₂O is –2 and in H₂O₂ is –1.

Structure of H_2O_2 **Figure 17.5**

This structure is like an open book.

Halides

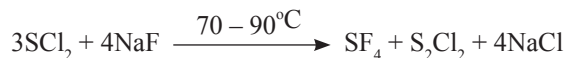
As fluorine is more electronegative than oxygen the binary compound of O and F is called oxygen fluoride not fluorine oxide. Sulphur forms variety of halides in +1, +2, +4 and +6 oxidation states.

Common halides of O and S**Table 17.6**

| Oxidation states | O | S |
|------------------|------------------------|---|
| +1 | O_2F_2 | S_2X_2 (X = F, Cl, Br, I) |
| +2 | OF_2 | SX_2 (X = F, Cl, Br) |
| +4 | — | SX_4 (X = F, Cl) |
| +6 | — | SF_6 |

In addition to the above, S also forms some very important oxohalides. They are SOX_2 , (X = F, Cl, Br) i.e., SOF_2 , SOCl_2 , SOBr_2 .

The sulphur tetrafluoride (SF_4) can be prepared by the reaction.



It is highly reactive and is hydrolyzed by water



The SF_6 is produced by direct fluorination of sulphur. Traces of SF_4 and S_2F_{10} are also formed.



Sulphur hexafluoride is chemically very inert. It is used as an insulating medium for high voltage electrical equipment. However, the break down product of SF_6 , SF_5CF_3 (trifluoromethyl sulphur pentafluoride) has green house effect. It is very stable and expected to remain in the atmosphere for about 1000 years (CH_4 lasts for 10 years and CO_2 for 100 years).

 SOCl_2

Thionyl chloride is most important oxohalide of S. It can be prepared by the reaction.



It is a colourless fuming liquid (bp 80°C). It is readily hydrolyzed by water,



The products are gaseous and easily removed. Therefore, SOCl_2 is often used to prepare anhydrous metal chlorides.

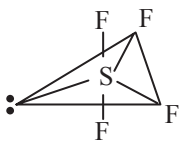
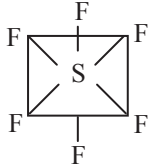
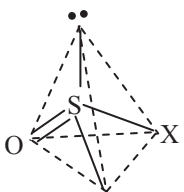


It is also used to replace $-\text{OH}$ gr by $-\text{Cl}$ form an alcohols (or acid).



Structure of SF_4 , SF_6 and SOX_2

Table 17.7

| Molecule | Structure | Shape |
|----------------|---|--------------|
| SF_4 | tbp  | Distorted Td |
| SF_6 | Oh  | Oh |
| SOX_2 | Td  | Δ Py. |

The S – O bond in SOX_2 has multiple bond nature. Its bond order depends on the electronegativity of the halogen. The S – O bond has highest bond order in SOF_2 . It is because the high electronegativity of F causes larger contraction of 3d orbitals of S. Which facilitates $d\pi - p\pi$ bonding (O has filled p – orbitals).

Molecular parameters in SOX_2

Table 17.8

| Parameter | OSF_2 | OSCl_2 | OSBr_2 |
|-----------------------|----------------|-----------------|-----------------|
| Bond order (S – O) | —————→ | | Decreases |
| Bond distance (S – O) | —————→ | | Increases |

Oxides

The binary compounds of oxygen are called oxides. They are formed by almost every element. The bond nature in oxides ranges from ionic (Na_2O , CaO etc) to covalent (CO_2 , B_2O_3 , SiO_2 etc.).

The formation of O^{2-} ion from dioxygen is highly endothermic, that is, requires a large amount of energy,



However, many ionic oxides are formed due to high lattice energy of the compound, e.g., CaO , ZnO etc.

Non-metal oxides are covalent. Some are discrete molecular species (CO_2 , SO_2 , CO , NO_2 , etc) whereas some are macromolecular (B_2O_3 , SiO_2 etc.).

Classification of oxides

On the basis of

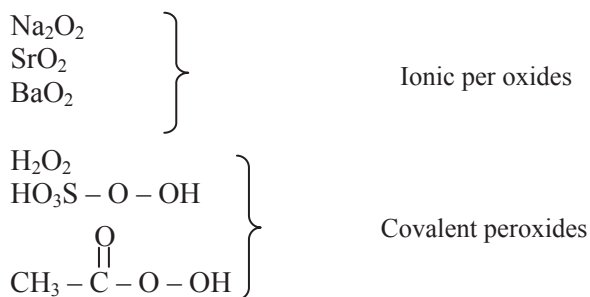
- (i) The oxidation state of oxygen.
- (ii) The acid–base nature.

Oxidation states of oxygen and oxides

Three types are found

- (i) *Normal oxides* (O^{2-}): They have oxygen in -2 oxidation states, e.g., CaO , Na_2O , FeO , MnO_2 etc.
- (ii) *Peroxides* (O_2^{2-} unit): They have the unit O_2^{2-} i.e., oxygen in -1 oxidation state.

Ionic as well as covalent peroxides are formed.



Peroxides are oxidizing agents and ionic peroxides give H_2O_2 with water or dil. acid.



- (iii) *Superoxides* (O_2^-): They contain the unit (O_2^-) i.e., oxygen in $-1/2$ oxidation state.

The ion O_2^- has 17 electrons (odd number). Therefore, superoxides are paramagnetic and coloured (due to unpaired electron). Superoxides are formed by K, Rb and Cs only.



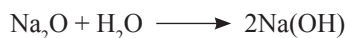
Superoxides are stronger oxidant than peroxides. They are decomposed by water or dil. acids to H₂O₂ and O₂.



Acid–Base nature and oxides

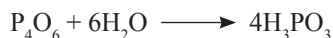
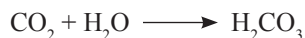
Basic oxides contain O²⁻ discrete ion in solid state. They are formed by metals in their low oxidation state (+1, +2, +3), e.g., Na₂O, CaO, FeO, Cr₂O₃ (Cr⁺³ and O²⁻).

Soluble metal oxides produce hydroxide with water due to hydrolysis of O²⁻ ion.

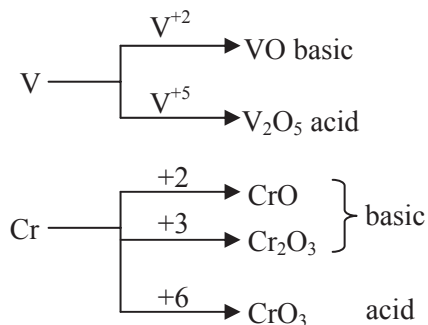


Acid oxides

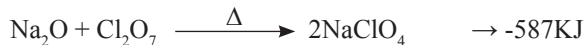
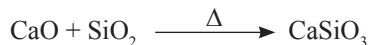
An oxide which forms an acid with water is termed as acidic oxide. They are mainly formed by non-metals and are covalent (CO₂, SO₂, NO₂, P₄O₆ etc.).



Transition metals in their high oxidation state form acidic oxides,



Acidic and basic oxides combine to form salt.



The stability of the salt depends on the gap in acidic and basic nature of the oxides. The larger the gap stabler is the salt. It is seen in the above reaction (values of ΔG).

So,



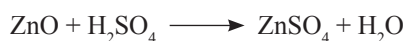
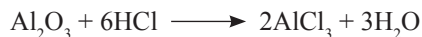
Similarly,



Amphoteric oxides

Elements having relatively less metallic nature form amphoteric oxide (Al, Sn, Pb, Zn etc.) Example, Al_2O_3 , SnO , PbO , ZnO etc.

They behave as bases towards strong acids and acidically towards strong bases.



The only non-metal oxide, H_2O , is amphoteric.

Neutral oxides

The non-metal oxides N_2O , NO and CO are neutral.

In addition to the above types there are

- (i) Non-stoichiometric oxides, and
- (ii) Mixed metal oxides.

Non-stoichiometric oxides

Oxides in which metal and oxygen do not maintain whole number ratio are called non-stoichiometric oxides. They are formed by transition metals and some lanthanides. For example, Fe (II) oxides is generally $\text{FeO}_{0.9}$ to $\text{FeO}_{0.95}$.

Mixed metal oxide

They contain different metal ions or the same metal in different oxidation states. Some common types are

- (i) Spinel: $\text{M}^{+2}, \text{M}_2^{+3}\text{O}_4$, Example,



- (ii) Ilmenite: FeTiO_3

It is $\text{FeO} \cdot \text{TiO}_2$ and is a mineral of Ti.

- (iii) Perovskite: CaTiO_3

It is also a mineral of Ti. It is $\text{CaO} \cdot \text{TiO}_2$.

All the oxides of the above type adopt specific crystal structure.

- (iv) Some mixed oxides containing Al_2O_3 and traces of some transition metals are very important, e.g., Ruby – $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, Blue sapphire – Al_2O_3 (Fe^{2+} , Fe^{3+} , Ti^{4+}) oxides.

Oxides of group – 16

Common oxides formed by the elements of this group are M O_2 and M O_3 .

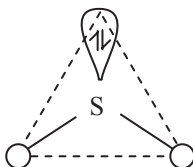
Table 17.9

| Oxides | Oxidation state of M | S | Se | Te |
|-----------------|----------------------|-----------------|------------------|------------------|
| MO ₂ | +4 | SO ₂ | SeO ₂ | TeO ₂ |
| MO ₃ | +6 | SO ₃ | SeO ₃ | TeO ₃ |

Sulphur dioxide (SO₂) can be prepared by a number of methods viz.,

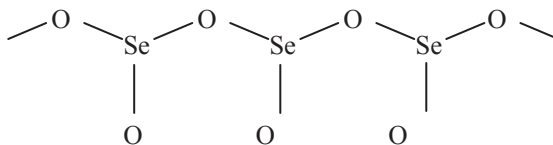
- (i) $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$
- (ii) Metal – sulphite + dil. acid $\longrightarrow \text{SO}_2$
- $$\text{Na}_2\text{SO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2\uparrow$$
- (iii) Metal – thiosulphate + dil. acid $\longrightarrow \text{SO}_2 + \text{S}$
- $$\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{S}\downarrow + \text{SO}_2\uparrow$$
- (iv) By roasting M – sulphide
- $$\text{ZnS} + \frac{3}{2}\text{O}_2 \longrightarrow \text{ZnO} + \text{SO}_2\uparrow$$
- $$\text{PbS} + \frac{3}{2}\text{O}_2 \longrightarrow \text{PbO} + \text{SO}_2$$

Sulphur dioxide is a triangular planar molecule with S in sp² hybrid state.

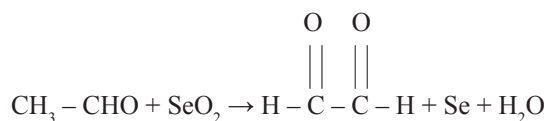
**Figure 17.6**

The SO₂ molecule is angular in shape with OSO angle of ~119°. Both the S – O bonds are equal (1.43 Å). The bond is short which suggests pπ – π as well as pπ – dπ bonding. The vacant d – orbitals at S and filled p – orbital at O – atom overlap to form pπ – dπ bond.

Selenium dioxide (SeO₂) is solid and has polymeric zig-zag chain structure,

**Figure 17.7**

SeO₂ is used as an oxidizing agent in organic chemistry.



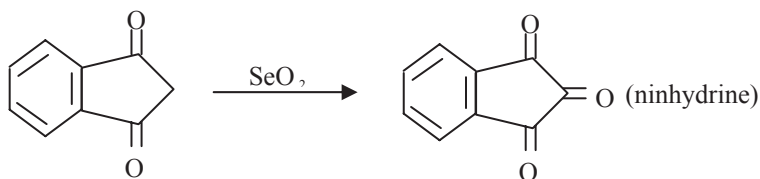
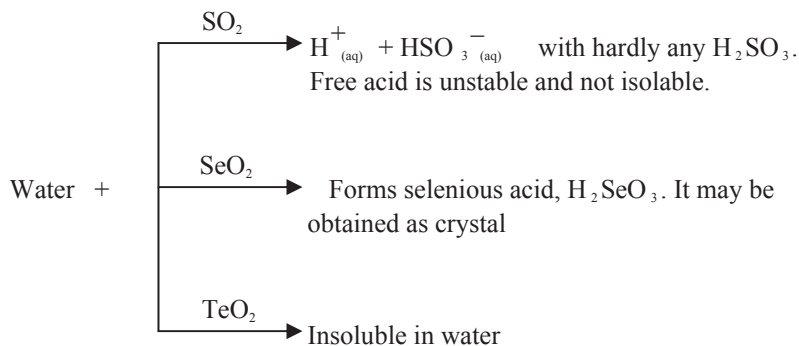
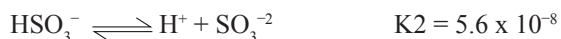


Figure 17.8

TeO_2 forms an ionic crystal. The dioxides differ in their reactions with water,



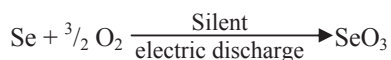
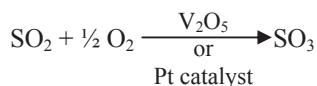
The aq. solution of SO_2 has the following equilibria.



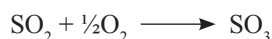
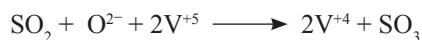
Although H_2SO_3 does not exist, two series of salts, the bisulphites (NaHSO_3) and sulphites Na_2SO_3 are known. Only NH_4^+ and alkali metal (except Li) bisulphites are known in solid state. All bisulphites are water soluble.

Trioxides (MO_3)

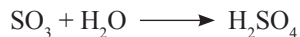
The MO_3 are prepared as:



The conversion of SO_2 to SO_3 is favored thermodynamically ($\Delta G^\circ = -6.7 \text{ mol}^{-1}$) but the reaction is very slow due to high activation energy. Therefore, catalytic oxidation is required. The reaction, with V_2O_5 as catalyst, proceeds as:



The trioxides are acid anhydrides.



The formula of telluric acid is Te(OH)_6 . It is due to large size of Te. The acid, Te(OH)_6 has octahedral structure.

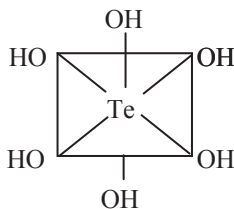


Figure 17.9

Gaseous SO_3 has triangular planar structure with sp^2 S – atom.

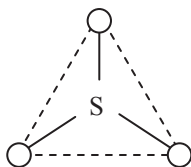


Figure 17.10

All S – O bonds are equal (1.41\AA), intermediate between S – O single and S – O double bonds. The S – O bond has contribution from $\text{p}\pi - \text{p}\pi$ as well as $\text{d}\pi - \text{p}\pi$ bonding. At room temperature SO_3 is solid. Solid SO_3 has either linear chain structure or cyclic trimeric structure.

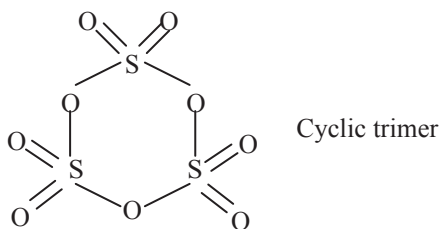
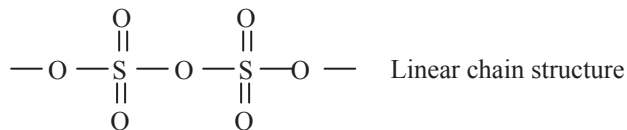


Figure 17.11

Oxo acids

Sulphur, Se and Te form oxo acids. But S acids are important and numerous.

Oxo-acids of S.

Table 17.10

| Name | Formula | Structure |
|---|--|--|
| Acids having no S – S bond | | |
| Pyrosulphuric acid | $\text{H}_2\text{S}_2\text{O}_7$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{O} - \text{S} - \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ |
| Acids having S – S bond | | |
| Thiosulphuric acid | $\text{H}_2\text{S}_2\text{O}_3$ | $\begin{array}{c} \text{OH} \\ \\ \text{HO} - \text{S} = \text{S} \\ \parallel \\ \text{O} \end{array}$ |
| Dithionous acid | $\text{H}_2\text{S}_2\text{O}_4^{\text{a}}$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \end{array}$ |
| Pyrosulphurous acid | $\text{H}_2\text{S}_2\text{O}_5^{\text{a}}$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \\ \parallel \\ \text{O} \end{array}$ |
| Dithionic | $\text{H}_2\text{S}_2\text{O}_6$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S} - \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ |
| Polythionic acid | $\text{HO}_3\text{S}(\text{S})_x\text{SO}_3\text{H}$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{S}_x - \text{S} - \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ |
| Peroxo acids (i.e., O – O bond) | | |
| Peroxomono sulphuric acid (Caro's acid) | H_2SO_5 | $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} - \text{S} - \text{O} - \text{O} - \text{H} \\ \parallel \\ \text{O} \end{array}$ |
| Peroxodisulphuric acid (Marshall's acid) | $\text{H}_2\text{S}_2\text{O}_8$ | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO} - \text{S} - \text{O} - \text{O} - \text{S} - \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ |

Note:

- (i) Acids marked 'a' are not known in free state.
- (ii) All S – oxoacids are diprotic.
- (iii) All acids have Td structure.
- (iv) In peroxo acids O – atoms forming peroxide link are in –1 oxidation state i.e., central O – atoms in Marshall's acids have –1 oxidation state.
- (v) In peroxo acids oxidation number of S is +6.

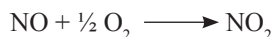
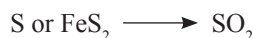
Sulphuric acid

It is most important acid of S. It is manufactured by

- (i) Lead chamber process,
- (ii) Contact process.

Lead chamber process

In this process SO₂ is oxidized to SO₃ in the presence of NO catalyst. SO₃ is then dissolved in water to form H₂SO₄.

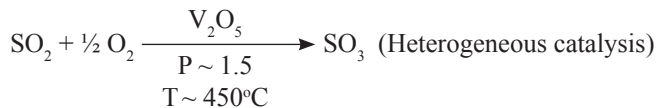


This method produces dil. H₂SO₄, ~65% H₂SO₄. It is concentrated by Cascade process. This method has many difficulties:

- (i) In low concentration of water, SO₃ forms a mist like material which is difficult to dissolve.
- (ii) In case of low concentration of water vapour, chamber crystals are formed, HO – SO₂ – ONO i.e., nitrososulphuric acid. This method is now obsolete.

Contact process

This method is now widely used. SO₂ is oxidized to SO₃ in the presence of V₂O₅ catalyst. SO₃ is dissolved in conc. H₂SO₄ to form pyrosulphuric acid H₂S₂O₇. It is called fuming sulphuric acid or oleum. It is diluted with water to prepare conc. H₂SO₄.

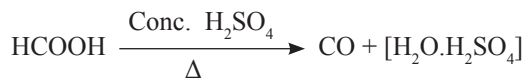


- Pure acid is colourless liquid.
- It is highly viscous liquid due to extensive intermolecular H – bonding.
- Conc. H₂SO₄ is called 'Oil of Vitriol'.
- It self ionizes as



Therefore, the acid is good conductor of electricity.

- Conc. acid is a powerful dehydrating agent, and dehydrates variety of substances.



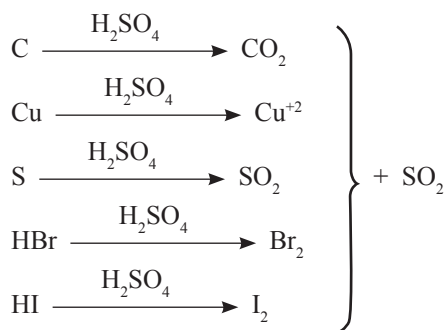
- This reaction may be used to prepare CO.



Sugars and organic hydroxy acid are charred by conc. H_2SO_4



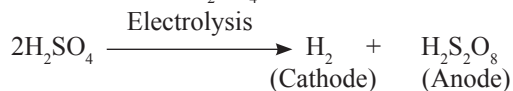
- Conc. H_2SO_4 acts as an oxidizing agent (not strong). It oxidizes



In all the above reactions H_2SO_4 is reduced to SO_2 i.e., SO_4^{-2} is actual oxidant.



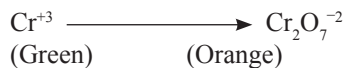
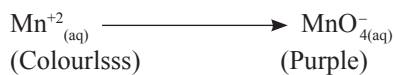
- Electrolysis of conc. H_2SO_4 gives peroxydisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ at anode.



The persulphate ion $\text{S}_2\text{O}_8^{-2}$ ion is a powerful oxidant.



It oxidizes



- Conc. H₂SO₄ forms chlorosulphonic acid and sulphuryl chloride with PCl₅.

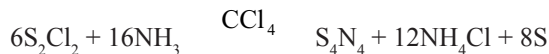


This reaction shows that the two OH groups are attached to SO₂ in H₂SO₄.

Main use of H₂SO₄ is as reagent and in industry.

S – N compounds

Many chain and ring compounds containing S and N are known, such as S₄N₄, tetrasulphur tetranitride.



The molecule S₄N₄ has cradle like structure.

$$d_{\text{S} \cdots \text{S}} = 2.58 \text{ \AA}$$

$$d_{\text{S} \cdots \text{N}} = 1.78 \text{ \AA}$$

The weak S – S bonding makes S₄N₄ a cage type molecule.

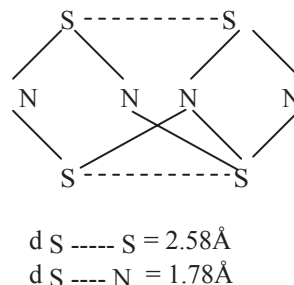


Figure 17.12

PRACTICE QUESTIONS

A. Explain the following.

- Although O₂ has even number of electrons it is paramagnetic.
- There is colour change when S is heated at different temperatures.
- Sodium sulphite decolourizes bromine water.
- SF₄ is hydrolyzed in water but not SF₆.
- The bond angle in H₃O⁺ (~115°) is much larger than NH₃ (~107°).
- The bond angle in (CH₃)₂O (~111°) is much smaller than in (SiH₃)₂O (~150°).
- Oxidation and oxygenation reactions.
- Oxygen is diatomic (O₂) gas and sulphur is S₈ and solid.
- Unlike SO₂, SeO₂ is a solid that has chain structure.
- The bond multiplicity of S – O bond decreases in the series OSF₂ > OSeCl₂ > OSBr₂.
- The bond angle in H₂O (~105°) is greater than in H₂S (~92°).
- H₂S is stronger acid than H₂O.
- Gaseous and solid SO₃ differ in structure.

- Sulphuric acid (H₂SO₄) and telluric acid [Te(OH)₆] differ in stoichiometry, acidity and structure.

- Viscosity of liquid sulphur is maximum at around 200°C.

B. Fill in the blanks.

- For the preparation of H₂S in the laboratory _____ apparatus is used.
- The manufacture of H₂SO₄ by the contact process uses _____ as catalyst.
- Sulphur acts as _____ agent in vulcanization of rubber.
- Oxygen gas is absorbed by _____.
- The bleaching action of O₃ is due to _____ and that of SO₂ is due to _____.
- The structure of solid SO₃ is either _____ or _____.
- Ozone has dipole moment due to _____ and _____.
- The viscosity of liquid S at 200°C is _____ due to _____.
- Passing H₂S through dil. HNO₃ produces _____ form of sulphur.

- (j) Viscous nature and high boiling point of conc. H_2SO_4 is due to _____.

C. What happens when?

- (a) SO_2 is passed through aq. solution of copper sulphate in the presence of potassium thiocyanate.
 (b) SO_2 , water vapour and air are passed over heated sodium chloride.
 (c) Sulphur is heated with conc. H_2SO_4 .
 (d) Sulphur is boiled with lime water.
 (e) H_2S is passed in conc. H_2SO_4 .
 (f) Sodium thiosulphate is added slowly to AuCl_3 .
 (g) Ammonium sulphate is heated with a mixture of NO and NO_2 .
 (h) Ammonium persulphate, $(\text{MH}_4)_2\text{S}_2\text{O}_8$, is treated with MnSO_4 in water.

OBJECTIVE-TYPE QUESTIONS

- Sodium thiosulphate is prepared by
 - Boiling Na_2SO_3 solution with S in alkaline medium.
 - Boiling Na_2SO_3 solution with S in acid medium.
 - Neutralizing $\text{H}_2\text{S}_2\text{O}_3$ solution with NaOH.
 - Reducing Na_2SO_4 with H_2S .
- Marshall's acid is
 - $\text{H}_2\text{S}_2\text{O}_5$
 - $\text{H}_2\text{S}_2\text{O}_8$
 - H_2SO_4
 - $\text{H}_2\text{S}_2\text{O}_7$
- Which of the following give SO_2 and S with dil. acid?
 - Na_2SO_3
 - $\text{Na}_2\text{S}_2\text{O}_3$
 - Na_2S
 - Na_2SO_4
- Shape of O_3 is
 - Angular
 - Triangular planar
 - Linear
 - Tetrahedral
- Catalyst now used in contact process is
 - Oxides of nitrogen
 - Vanadium pentaoxide
 - Finely divide nickel
 - Vanadium monoxide
- Group-16 elements form hydrides of the type MH_2 , ($\text{M} = \text{O}, \text{S}, \text{Se}, \text{Te}$). Their correct stability order is
 - $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
 - $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$
 - $\text{H}_2\text{Te} > \text{H}_2\text{O} > \text{H}_2\text{Se} > \text{H}_2\text{S}$
 - $\text{H}_2\text{S} > \text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se}$
- The correct order of electron attachment enthalpy of O, S and Se is
 - $\text{O} > \text{S} > \text{Se}$
 - $\text{S} > \text{Se} > \text{O}$
 - $\text{S} > \text{O} > \text{Se}$
 - $\text{Se} > \text{S} > \text{O}$
- Chlorine gas is passed in an aq. solution of $\text{Na}_2\text{S}_2\text{O}_3$, the product is
 - Na_2SO_3 , S, HCl
 - Na_2O_4 , S, HCl
 - NaClO_2 , S, HCl
 - Na_2S , S, HCl
- The geometry and dipole moment of O_3 are
 - Linear and zero
 - Angular and zero
 - Angular and non-zero
 - Linear and non-zero
- In the persulphate dianion ($\text{S}_2\text{O}_8^{2-}$)
 - All S – O bonds are non – equivalent
 - Four S – O bonds are equivalent
 - Six S – O bonds are equivalent
 - All S – O bonds are equivalent
- Which of the following reactions should be most favoured thermodynamically?
 - $2\text{Na}_2\text{O} + \text{SiO}_2 \rightarrow \text{Na}_4\text{SiO}_4$
 - $\text{Na}_2\text{O} + \text{P}_4\text{O}_{10} \rightarrow \text{Na}_3\text{PO}_4$
 - $\text{Na}_2\text{O} + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4$
 - $\text{Na}_2\text{O} + \text{Cl}_2\text{O}_7 \rightarrow \text{NaClO}_4$
- There is O – O bond in
 - $\text{S}_2\text{O}_3^{2-}$
 - $\text{S}_2\text{O}_4^{2-}$
 - $\text{S}_2\text{O}_7^{2-}$
 - $\text{S}_2\text{O}_8^{2-}$
- When chlorosulphonic acid is treated with 100% H_2O_2 , the product is

- (a) $\text{H}_2\text{S}_2\text{O}_8$ (b) $\text{H}_2\text{S}_2\text{O}_7$
 (c) $\text{H}_2\text{S}_2\text{O}_5$ (d) H_2SO_5
14. There is no S – S bond in
 (a) $\text{S}_2\text{O}_7^{2-}$ (b) $\text{S}_2\text{O}_5^{2-}$
 (c) $\text{S}_2\text{O}_4^{2-}$ (d) $\text{S}_2\text{O}_3^{2-}$
15. The oxidation number of S in H_2S , S_2F_2 and S_8 respectively are
 (a) 0, +1 and –2 (b) –2, +1 and 0
 (c) 0, + and +2 (d) –2, +1 and +2
16. Hydrolysis of one mole of peroxydisulphuric acid produces
 (a) Two types of peroxymonosulphuric acid
 (b) Two moles of sulphuric acid
 (c) One mole of peroxymonosulphuric acid and one mole of sulphuric acid.
 (d) One mole H_2O_2 , one mole sulphuric acid and one mole peroxymonosulphuric acid
17. Number of atoms in α -sulphur is
 (a) 6 (b) 8
 (c) 4 (d) Infinite
18. Which of the following has peroxy bond?
 I H_2SO_5
 II $\text{H}_2\text{S}_2\text{O}_3$
 III $\text{H}_2\text{S}_2\text{O}_7$
 IV $\text{H}_2\text{S}_2\text{O}_8$
 (a) I, II (b) II, III
 (c) III, IV (d) I, IV
19. Molecular iodine oxidizes $\text{S}_2\text{O}_3^{2-}$ ion into
 (a) SO_3^{2-} (b) SO_4^{2-}
 (c) $\text{S}_4\text{O}_6^{2-}$ (d) $\text{S}_2\text{O}_5^{2-}$
20. The number of S – S bonds in SO_3 trimer, S_3O_9 is
 (a) Zero (b) One
 (c) Two (d) Three
21. Identify the correct order of increasing solubility.
 (a) $\text{Na}_2\text{S} < \text{ZnS} < \text{CuS}$
 (b) $\text{CuS} < \text{ZnS} < \text{Na}_2\text{S}$
 (c) $\text{ZnS} < \text{CuS} < \text{Na}_2\text{S}$
 (d) $\text{Na}_2\text{S} < \text{CuS} < \text{ZnS}$
22. Two salts M and N are treated separately with dil HCl. They liberated two gases A and B respectively. The gas A turns lead acetate paper black and B decolourises acidic KMnO_4 . The salts M and N respectively are
 (a) Na_2SO_4 and Na_2SO_3
 (b) Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$
 (c) $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2S
 (d) Na_2S and Na_2SO_4
23. The gaseous mixture N_2O and O_2 is used as
 (a) Anesthetic
 (b) Fuel
 (c) Oxidizing agent
 (d) None of these
24. H_2S acts as
 (a) Oxidizing agent
 (b) Reducing agent
 (c) Both oxidizing and reducing agent
 (d) None of these
25. The oxidation states of S in H_2SO_5 , H_2SO_3 and $\text{H}_2\text{S}_2\text{O}_8$ respectively are
 (a) +5, +3 and +6
 (b) +6, +3 and +6
 (c) +6, +4 and +6
 (d) None of these
26. The correct order of $\text{S}=\text{O}$ in (I) SO_2 , (II) SO_3 , (III) SO_4^{2-} is
 (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{I} > \text{II}$
 (c) $\text{II} > \text{III} > \text{I}$ (d) $\text{I} > \text{III} > \text{II}$

ANSWERS

1. (a) 2. (b) 3. (b) 4. (a) 5. (b) 6. (a) 7. (b) 8. (b) 9. (c) 10. (c)
 11. (d) 12. (d) 13. (d) 14. (a) 15. (b) 16. (c) 17. (b) 18. (d) 19. (c) 20. (a)
 21. (b) 22. (b) 23. (a) 24. (b) 25. (c) 26. (b)

18

Group 17 (VIIA) Halogens F, Cl, Br, I and At



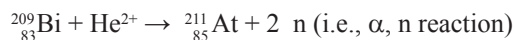
INTRODUCTION

The elements F, Cl, Br, I and At (Astatine) are called halogens (Greek, ‘Halos’—salt and ‘gene’ – born, i.e., salt forming).

Table 18.1

| Elements | Atomic Number | Electron Configuration |
|---------------|---------------|--|
| Fluorine (F) | 9 | ${}_2[\text{He}] 2s^2 2p^5$ |
| Chlorine (Cl) | 17 | ${}_{10}[\text{Ne}] 3s^2 3p^5$ |
| Bromine (Br) | 35 | ${}_{18}[\text{Ar}] 3d^{10} 4s^2 4p^5$ |
| Iodine (I) | 53 | ${}_{36}[\text{Kr}] 4d^{10} 5s^2 5p^5$ |
| Astatine (At) | 85 | ${}_{54}[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^5$ |

All the elements of this group are non-metallic. Iodine is solid and has some metallic lustre. Astatine (At) is radioactive and does not occur in nature. It can be made by nuclear reaction,



The $t_{1/2}$ of ${}^{211}\text{At}$ is 7.5 hrs. The longest lived isotope is ${}^{210}\text{At}$ ($t_{1/2} \approx 8.3\text{h}$).

Physical state

All elements exist as diatomic molecules, F_2 , Cl_2 , Br_2 and I_2 and are coloured. But the elements differ in physical states at room temperature.

Table 18.2

| Molecule | Physical state | Colour |
|---------------|----------------|--------------------------------|
| F_2 | Gas | Light yellow |
| Cl_2 | Gas | Greenish yellow |
| Br_2 | Liquid | Red brown |
| I_2 | Solid | Black solid Violet (vapour) |

The change in physical state gas \rightarrow liquid \rightarrow solid is due to increase in van der Waals force. This weak force depends on the number of electrons in a chemical species. As atomic number increases from F(9) to I(53), the number of electrons also increases. This increase causes increase in van der Waals force from fluorine to iodine. Therefore, F and Cl are gases, Br is liquid and iodine is solid.

The colour of halogens is due to charge transfer, $\cdot\ddot{X}-\ddot{X}\cdot$ (actually the electro transition is $n \rightarrow \pi^*$ transition).

Table 18.3

| Property | Fluorine | Chlorine | Bromine | Iodine |
|---|----------|----------|---------|--------|
| Atomic radius (Å) | 0.72 | 0.99 | 1.14 | 1.33 |
| Ionic radius, X^- (Å) | 1.36 | 1.84 | 1.95 | 2.16 |
| Ionization energy | | | | |
| ev. | 17.4 | 13.01 | 11.8 | 10.44 |
| KJmol^{-1} | 1681 | 1256 | 1143 | 1009 |
| Electron affinity | 333 | 349 | 325 | 296 |
| Electronegativity | 4.0 | 3.0 | 2.8 | 2.5 |
| Bond length, $(X-X)$ (Å) | 1.43 | 1.99 | 2.28 | 2.66 |
| Heat of dissociation, $X-X$ i.e., bond energy, KJmol^{-1} | 126 | 210 | 158 | 118 |
| Std. electrode Pot, E° (V) | +2.87 | +1.4 | +1.09 | +0.62 |
| $\frac{1}{2}X_2 + e \rightarrow X^-$ | | | | |

The above table shows that the general properties vary regularly in this group (like group 1).

(i) Properties which decrease down the group:

Table 18.4

| Property | F | Cl | Br | I |
|-------------------|-----------------------------|----|----|---|
| Ionization energy | \longrightarrow Decreases | | | |
| Electronegativity | \longrightarrow Decreases | | | |
| E° | \longrightarrow Decreases | | | |
| Oxidizing power | \longrightarrow Decreases | | | |

(ii) Properties which increase down the group:

Table 18.5

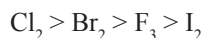
| Property | F | Cl | Br | I |
|-----------------------|-----------------------------|--------|--------|-------|
| Atomic radius | \longrightarrow Increases | | | |
| Ionic radius | \longrightarrow Increases | | | |
| Bond length $(X-X)$ | \longrightarrow Increases | | | |
| mp | \longrightarrow Increases | | | |
| bp | \longrightarrow Increases | | | |
| Reducing power, X^- | \longrightarrow Increases | | | |
| | F^- | Cl^- | Br^- | I^- |

(iii) Electron affinity does not vary regularly. The order is $Cl > F > Br > I$.

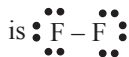
Lower E_a of F is due to its small size. In F the electron is added in 2p orbital. As the shell is small, electron-electron repulsions in it is relatively large. Therefore, the electron being added to F experiences great repulsion and so E_a is smaller than Cl. The degree of repulsion is seen in the expansion of size of F^- compared to F,

$$r_F \sim 0.71 \text{ \AA} \text{ and } r_{F^-} \approx 1.33 \text{ \AA} \text{ i.e., an increase of about 87\%.$$

(iv) The X – X bond energy also does not vary regularly. The order is



In spite of shortest bond in F_2 its dissociation energy is low. It is due to small size of F – atom. the F_2 molecule



i.e., three lps at each F – atom

As size of F is small, repulsion between lps at two F – atoms is very large. This repulsion weakens the bond and dissociation energy is low.

Special properties of Fluorine

Fluorine is peculiar in its properties.

- (i) It is chemically most reactive of all the elements and combines directly with all the elements except O_2 , He, Ne and Ar. It is due to:
 - (a) Low F – F bond energy
 - (b) High bond energy of F with other elements

Table 18.6 Some bond energies. KJmol^{-1}

| X | B – X | C – X | N – X | Si – X | P – X | S – X |
|----|-------|-------|-------|--------|-------|-------|
| F | 645 | 439 | 272 | 582 | 490 | 326 |
| Cl | 444 | 347 | 201 | 391 | 319 | 255 |
| Br | 368 | 276 | - | 310 | 264 | 213 |
| I | 272 | 238 | - | 234 | 184 | - |

- (c) The high hydration energy of F^- due to smallest size of F^- . AgF is soluble in water due to high hydration energy of F^- . Other silver halides (AgX , X = Cl, Br, I) are insoluble in water.
- (d) Reaction of F with chemical substances is highly exothermic.



- (ii) Presence of very strong H – bond in HF, - - - H – F - - - H – F - - -.
- (iii) Fluorinated hydrocarbons are very inert, e.g., polytetrafluoroethene (PTFE). It is used as a coating for non-stick cook wares.

Oxidation state and bonding

Fluorine is the most electronegative element ($X_F = 4.0$) and so it shows only oxidation state of – 1, (not positive oxidation state). Other halogens show oxidation states from –1 to +7.

Chlorine shows ⊕ive oxidation with F and O, Bromine with Cl, F, O and N and I with F, Cl, Br, N and O. The common oxidation states are 0, +1, +3, +5 and +7.

Table 18.7

| Oxidation state | F | Cl | Br | I |
|-----------------|----------------|--------------------|--------------------|-------------------|
| -1 | NaF HF | NaCl HCl | NaBr HBr | NaI HI |
| 0 | F ₂ | Cl ₂ | Br ₂ | I ₂ |
| +1 | | HOCl | HOBr | HOI |
| +3 | – | HOClO | HOBrO | HOIO |
| +5 | – | HOClO ₂ | HOBrO ₂ | HOIO ₂ |
| +7 | – | HOClO ₃ | HOBrO ₃ | HOIO ₃ |

Halogens are one electron short than noble gas configuration. Therefore, they can achieve stable configuration:

- (i) By gain of one electron to form X⁻
 $\frac{1}{2} \text{F}_2 + \text{e} \longrightarrow \text{F}^- (\equiv \text{Ne})$
 $\frac{1}{2} \text{Cl}_2 + \text{e} \longrightarrow \text{Cl}^- (\equiv \text{Ar})$ etc.
 In the above situation ionic compounds are formed.
- (ii) By sharing an electron with other elements i.e., monocovalency,



Figure 18.1

Such compounds are polar covalent.

Formation of X₂ (X = F, Cl, Br, I)

F₂

- (i) Fluorine is most oxidizing and therefore, common oxidizing agents fail to oxidize F⁻ to produce F₂. However, the following reaction can produce F₂.



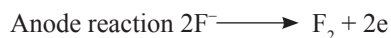
In this reaction the stronger Lewis acid SbF₅ displaces weak acid (MnF₄) from its salt (K₂MnF₆). But MnF₄ is unstable and decomposes into MnF₃ and F₂.

- (ii) Fluorine is generally prepared in large quantity by electrolysis of a mixture of fused anhydrous HF and KF. The liquid contains K⁺. HF₂⁻ (HF₂⁻ is stable due to H – bonding).
 The electrolytic cell is made of steel or monel metal.

The electrodes are:

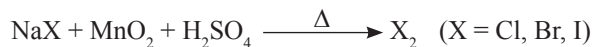
Anode – copper impregnated graphite.

Cathode – Fe



Chlorine (Cl₂), Bromine (Br₂) and Iodine (I₂)

- (i) All these three halogens can be prepared by heating respective halides with MnO₂ and conc. H₂SO₄. This is laboratory method for X₂.



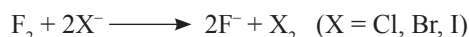
or



- (ii) Lower atomic number halogen oxidizes halide ion having higher atomic number to form X₂.

Thus,

- (a) F₂ oxidizes Cl⁻ to Cl₂, Br⁻ to Br₂ and I⁻ to I₂



- (b) Cl₂ oxidizes Br⁻ to Br₂ and I⁻ to I₂

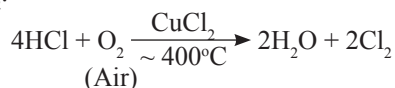


- (c) Br₂ oxidizes I⁻ to I₂

**Manufacture of Cl₂**

There are many methods:

- (i) As a by-product in the manufacture of NaOH by the electrolysis of brine.
 (ii) As a by-product in the isolation of Na by the electrolysis of fused NaCl.
 (iii) **Deacon's process:** In this method HCl is oxidized with air in the presence of CuCl₂ catalyst to produce Cl₂.

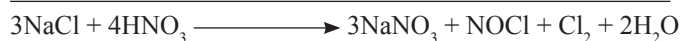


- (iv) **Weldon's process:** This process involves oxidation of conc. HCl with pyrolusite (MnO₂). The reaction takes place on heating.



This method is inferior to Deacon's process.

- (v) **Nitrosyl chloride process:** When NaCl is treated with conc. HNO₃, Cl₂ and NOCl are formed.



The gaseous mixture Cl₂ + NOCl is oxidized with O₂



The product (NO_2 and Cl_2) is liquefied and Cl_2 is distilled out. The NO_2 is converted into HNO_3 which is used again.



Manufacture of Br_2

(i) From carnalite

Carnalite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) contains MgBr_2 in small quantities. Fractional crystallization of a solution of carnalite produces crystal of KCl . The mother liquor contains MgCl_2 and MgBr_2 . When Cl_2 is passed in this hot solution vapours of Br_2 are produced. It is carried up by steam into condensers, where liquid bromine is obtained.

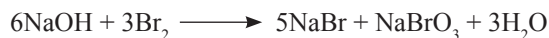
Any uncondensed bromine is absorbed in iron filings forming ironbromide.



(ii) From sea water

Sea water, the most important source of Br_2 , contains MgCl_2 and MgBr_2 in minute quantities.

Brine is acidified and saturated with Cl_2 gas. Bromine is set free. It is absorbed in NaOH . When this solution is acidified, bromine is liberated.



Manufacture of iodine

(i) From sea weed

Sea weeds contain iodine (~0.5%) in the form of iodide. Dried sea weeds are burnt to ash. This ash is called 'Kelp'. It contains iodine as iodide.

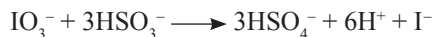
Kelp is extracted with water and filtered. When the filtrate is evaporated chlorides, carbonates and sulphates of alkalimetals crystallize out. The mother liquor is distilled with MnO_2 and H_2SO_4 . The iodine is collected in aludels (stoneware receivers).



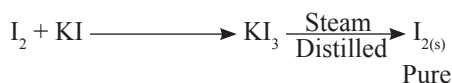
(ii) From caliche (chile salt petre) ($\text{NaNO}_3 \cdot \text{NaIO}_3$)

It is the main source of iodine. It contains iodine as NaIO_3 .

Calich solution on fractional crystallization gives ppt. of NaNO_3 . When it is heated with calculated amount of NaHSO_3 , I_2 separates out in vapour state.



Iodine vapour is absorbed in KI solution. It is steam distilled to get pure iodine.



Reactions of X_2 ($X = F, Cl, Br, I$)

- Fluorine is most reactive of all the elements.
- It combines with all elements directly except He, Ne and Ar.
- It does not show positive oxidation state as it is the most electronegative element ($\chi_F = 4.0$).
- It is an extremely strong oxidizing agent ($E^\circ = 2.87$), such strong that it can cut through a wall like a hot knife through butter.
- Cl and Br are very comparable in their reaction.
- Iodine is less reactive.
- Reactivity order $F > Cl > Br > I$.

Important reactions**Table 18.8**

| Reactants | Reaction | Comment |
|-------------------------------------|---|---|
| Water + F_2 | $H_2O + F_2 \rightarrow 2HF + \frac{1}{2}O_2$ | F oxidizes water to O_2 . This reaction is also possible with Cl but is extremely slow (activation energy factor). |
| Water + X_2 ($X = Cl, Br$) | $H_2O + X_2 \rightarrow HX + HOX$ | It is disproportionation of halogen, occurs to a very small extent, Cl and Br are actually hydrated in water, $Cl_2 \cdot 8H_2O$, $Br_2 \cdot 8H_2O$. |
| Water + I_2 | -- | Practically no reaction iodine is insoluble in water. I_2 is soluble in KI solution due to the reaction $KI + I_2 \rightarrow KI_3$ |
| $NaOH + F_2$ | $2NaOH + 2F_2$ \downarrow $2NaF + H_2O + OF_2$ | OF_2 is strong oxidizing agent and used as rocket fuel. |
| $NaOH + X_2$ ($X = Cl, Br, I$) | (i) dil. and cold $NaOH$ $2NaOH + X_2$ \downarrow $NaX + NaOX + H_2O$ (ii) hot conc. $NaOH$ $6NaOH + X_2$ \downarrow $5NaX + NaO_3X + 3H_2O$ or $XO^- + H_2O + 2e \rightarrow X^- + 2HO^-] \times 2$ $XO^- + 4HO^- \rightarrow XO_3^- + 4e + 2H_2O$ | Both are disproportionation reactions. |
| $NH_3 + X_2$ ($X = F, Cl, Br$) | (i) with excess NH_3 $8NH_3 + 3X_2 \rightarrow N_2 + 6NH_4X$ (ii) with excess X_2 $NH_3 + 3X_2 \rightarrow NX_3 + 3HX$ | NF_3 is stable. NCl_3 is explosive and unstable. NBr_3 does not exist at room temperature. |

(Continued)

| Reactants | Reaction | Comment |
|-----------------------------------|---|---|
| $H_2 + X_2$ (X = F, Cl, Br, I) | $H_2 + X_2 \rightarrow 2HX$ | Reaction with F is explosive. Cl reacts in sun light. Br reacts on heating. I reacts in the presence of a catalyst (Pt.) |
| $SO_2 + X_2$ (X = F, Br, I) | $SO_2 + X_2 + 2H_2O$ \downarrow $H_2SO_4 + 2HX$ or $X_2 + 2e \rightarrow 2X^-$ $SO_2 + 2H_2O \rightarrow SO_4^{-2} + 2e + 4H^+$ | X_2 is oxidizing agent and SO_2 is reducing agent in this reaction. |
| | $X_2 + SO_2 + 2H_2O \rightarrow 2X^- + SO_4^{-2} + 4H^+$ | |
| $SO_2 + X_2$ (X = F, Cl) | $SO_2 + X_2 \rightarrow SO_2X_2$ Sulphuryl halide | It is a colourless liquid fuming in moist air. |
| $H_2S + X_2$ X = Cl, Br, I) | $H_2S + X_2 \rightarrow 2HX + S$ | H_2S is reducing agent and X_2 is oxidizing agent. |
| Metal + X_2 | $M + X_2 \rightarrow M - \text{halide}$ | Metal halides are ionic to covalent. |
| Conc. $H_2SO_4 + I_2$ | $I_2 + 5H_2SO_4$ $\downarrow(\text{boil})$ $2HIO_3 + 5SO_2 + 4H_2O$ or $I_2 + 6H_2O \rightarrow 2IO_3^- + IO_3^- + 12H^+$ $SO_4^{-2} + 2e + 4H^+ \rightarrow SO_2 + 2H_2O] \times 5$ | Cl and Br are not oxidized. |
| | $I_2 + 5SO_4^{-2} + 8H^+ \rightarrow 2IO_3^- + 5SO_2 + 4H_2O$ | |
| Conc. $HNO_3 + I_2$ | $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$ | Cl and Br are not oxidized. |
| $Na_2S_2O_3 + I_2$ (hypo) | $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$ or $I_2 + 2e \rightarrow 2I^-$ $2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2e$ | I_2 (brown sol.) is decolorized by hypo. This reaction is used in volumetric analysis, iodometry (estimation of Cu in $CuSO_4$). |
| | $I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^-$ | |

Hydrogen halides, HX (X = F, Cl, Br, I)

Hydrogen halides are covalent diatomic molecules in the gas phase. Hydrogen fluorides in highly associated molecules through hydrogen bonding. It has effect on its mp, bp and ionization constant in water. All the halides are acidic in aqueous solution and are hydra acids.

Common properties**Table 18.9**

| Property | HF | HCl | HBr | HI |
|--------------------------------------|----------------------|--------|--------|-----------|
| Physical state | Liquid | Gas | Gas | Gas |
| ΔG_f Kcal | 65 | 23 | 13 | 6.2 |
| Bond energy (KCalmol ⁻¹) | 135 | 103 | 86 | 71 |
| Thermal stability | Decreases → | | | |
| mp °C | -83 | -114.8 | -87 | -50.7 |
| bp °C | 19.5 | -85 | -66.8 | -35.4 |
| Acidity of aq. sol. | Increases → | | | |
| Ka in water | 7.0×10^{-4} | 10^7 | 10^9 | 10^{11} |

Note

- (i) HF is liquid due to extensive hydrogen bonding and so has highest bp.
- (ii) ΔG_f decreases due to long weaker H – X bond.
- (iii) Bond energy decreases from HF to HI due to longer H – X bond with increase in the size of X.
- (iv) Bond energy is lowest in H – I. So, it ionizes most and is strongest acid.
Acidity order HF < HCl < HBr < HI

HF

It is prepared by heating CaF₂ with conc. H₂SO₄.



Successive washing, cooling and fractional distillation give 99.9% HF.

Properties

- (i) Gaseous HF is very toxic substance.
- (ii) It is highly fuming liquid (bp = 19.5°C).
- (iii) It is very soluble in water but the aq. solution is weakly acidic. It is due to high H – F bond strength.



- (iv) It is very corrosive and attacks glass



Therefore, HF is handled in Cu or Monel metal apparatus.

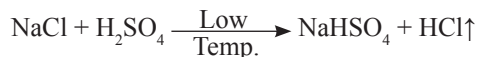
Uses

- (i) In the production of fluorides.
- (ii) For etching glass and metals.

- (iii) To produce freons.
- (iv) In uranium processing (separation of ^{235}U from ^{238}U , UF_6 is used as it is volatile).
- (v) To produce synthetic cryolite.
- (vi) Aqueous HF is used for pickling steel.

HCl

It can be prepared by heating a soluble chloride with conc. H_2SO_4 .



A coating of insoluble NaHSO_4 develops on NaCl which prevents further reaction. But at high temperature ($\sim 550^\circ\text{C}$) Na_2SO_4 is formed and reaction proceeds.



In laboratory HCl can be prepared by treating NH_4Cl with conc. H_2SO_4 .

This reaction is smooth as NH_4HSO_4 soluble.



On large scale HCl is produced by burning H_2 in Cl_2 .

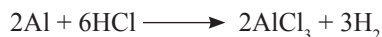


This HCl is of high purity.

It is also produced in large quantity in the chlorination of organic compounds.

Properties

- (i) Pure dry HCl gas is covalent and shows no acidic property.
- (ii) HCl is very soluble in water and solution is strong acid. Pure acid is colourless but common grade is yellowish due to the presence of Fe(III) .
- (iii) Hydrochloric acid forms a constant boiling mixture (bp 110°C) containing 20% acid by weight.
- (iv) Many metals dissolve in HCl and form chlorides.



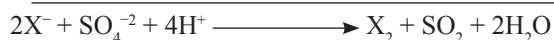
All of the chlorides are soluble except AgCl , PbCl_2 and Hg_2Cl_2 .

Uses

- (i) In the production of Cl_2 and chlorides.
- (ii) In the preparation of aquaregia, ($3\text{HCl} + \text{HNO}_3$).
- (iii) As a lab reagent.
- (iv) The largest use is for pickling metals, (i.e., removing oxide film from the surface).
- (v) In the production of dyestuffs and in the sugar industry.

HBr and HI

HBr and HI can not be prepared like HCl . It is because conc. H_2SO_4 is strong enough an oxidizing agent to oxidize HBr to Br_2 and HI to I_2 .



HBr

- (i) It can be prepared by the hydrolysis of
- PBr_3
- .



This reaction is brought about by adding bromine, dropwise to a paste of red P and water.

- (ii) A bromide on reaction with
- H_3PO_4
- (a non-oxidizing acid) forms HBr.



(H_3PO_4 is not an oxidizing agent so HBr is not oxidized to Br_2).

HI

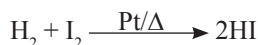
- (i) It is prepared by heating red P,
- I_2
- and water.



- (ii) It is also prepared by heating KI and
- H_3PO_4
- (a non-oxidizing acid)



- (iii) When a mixture of
- H_2
- and
- I_2
- is heated in the presence of Pt – catalyst, HI is formed.

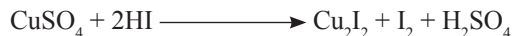
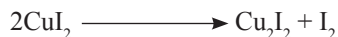
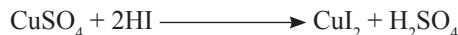
**Properties**

- (i) Strongest acid among HF, HCl, HBr and HI.

Acidity order $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

- (ii) It is strongest reducing agent among HX.

HI reduces Cu^{2+} to Cu^+ , e.g.,



This reaction takes place because I^- is reducing and reduces Cu^{+2} to Cu^+ . This reaction does not take place with HCl and HBr because Cl^- and Br^- are not so reducing that they can reduce Cu^{+2} (CuCl_2 and CuBr_2 are stable and CuI_2 does not exist).

Uses

- (i) In pharmaceutical industry.
- (ii) In photography.
- (iii) As a reducing agent.

Tests of HI

- (i) Forms yellow ppt. with
- AgNO_3
- solution



This ppt. is insoluble in NH_4OH solution.

- (ii) HI forms violet vapours when wormed with conc. H_2SO_4 .
- (iii) When Cl_2 gas is passed in starch +HI, blue solution results. It is due to oxidation of I^- to I_2 and adsorption of I_2 in starch channel.

Halides

Binary compounds of halogens are known as halides. Metals and non-metals both form halides.



They form the following classes:

- (i) Ionic halides
- (ii) Molecular (or covalent) halides.
- (iii) Complex halides.

Ionic halides

Most halides of metals in +1, +2 and +3 oxidation states are mainly ionic. Thus,

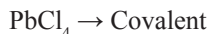
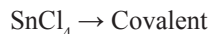
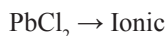
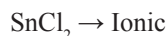
- (i) Alkali metals,
 - (ii) Alkaline earth metals (except Be)
 - (iii) Some d – elements and
 - (iv) Most of the lanthanides
- form ionic halides.

Covalent nature in ionic halides

As the charge to radius ratio of M^{n+} increases, covalent nature develops in the halides.

For example,

- (i) Among KCl , CaCl_2 , SeCl_3 and TiCl_4 , KCl is completely ionic whereas TiCl_4 is a covalent halide.
- (ii) For metals which show variable oxidation states, halides in lower oxidation state are more ionic and in higher oxidation state are more covalent,



- (iii) Chlorides, bromides and iodides of Ag^+ , Cu^+ , Hg^+ have enough covalent nature. It is because these metal ions are small and more polarizing (18e core).
- (iv) For halides of a metal covalent bond nature follows the order:
Iodide > Bromide > Chloride > Fluoride
It is because large anions are more polarizable.
So, $\text{CaI}_2 > \text{CaBr}_2 > \text{CaCl}_2 > \text{CaF}_2$ Covalent nature decreases.

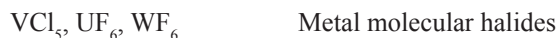
Solubility of ionic halides

- (i) Most of the ionic halides are water soluble. The solubility order being
Iodide > Bromide > Chloride > Fluoride
It is because solubility controlling factor (for ionic halides) is lattice energy which increases as the ionic radii decrease. The above solubility order is true for alkali, alkaline earth and lanthanide halides.

- (ii) The chlorides, bromides and iodides of Ag^+ , Cu^+ , Hg^+ and Pb^{+2} are insoluble in water (AgF is soluble due to very high hydration energy of small F^- ion).
- (iii) Fluorides of Li, Ca, Sr and Ba are sparingly soluble.

Molecular halides

Non-metals and metals in high oxidation states (+5 and +6) form molecular halides.



They are basically covalent and are gases, liquids or volatile solids.

| | | | | |
|----------------|---------------|----------------|----------------|---------------|
| Halide | BF_3 | PCl_3 | PCl_5 | UF_6 |
| Physical state | Gas | Liquid | Solid | Solid |

Within the molecule there is covalency (strong force) but between the molecules weak van der Waals forces exist (hence gas, volatile liquid or solid).

Stability order found in such halides is:



Molecular fluorides

Fluorine is most oxidizing. Therefore, highest oxidation states of elements are found in fluorides, e.g., SF_6 , IF_7 , WF_6 , OsF_6 , UF_6 etc., these are generally gases, volatile liquids or solids. The intermolecular forces in such compounds are only weak van der Waals forces. It is because polarizability of fluorine is very low (F is very small) and no other suitable outer vacant orbitals exist for other type of bonding.

The $\text{M} - \text{F}$ bonds are very strong and short. Two factors are responsible,

- Polarity of the bond and
- Back bonding, when the central atom has vacant p or d – orbital (B, Si, P, S etc.).

Reactivity

- Fluorides are generally less reactive (strong $\text{M} - \text{F}$ bond, NF_3 , CF_4 , SF_6 etc).
- A very common reaction of molecular halides is their easy hydrolysis.



- When the central atom has its maximum covalency, the halide is inert, (CCl_4 , SF_6).

Structural feature

Many molecular halides are polymeric. It is due to the formation of halide bridges. Al_2Cl_6 , $(\text{BeF}_2)_x$, $(\text{BeCl}_2)_x$ etc.

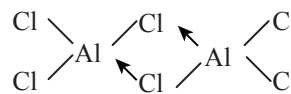
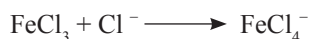


Figure 18.2

Halide complexes

All the halide ions are ligands. They are formed by reaction between a halide acting as a Lewis acid with a halide ion acting as a ligand.



They are known in solution as well as in crystalline salts. For example, BF_4^- is stable in solution whereas BCl_4^- and BBr_4^- are stable in crystalline salts of large cations (lattice energy is responsible).

General order of stability is $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

Many complex halogeno anions are known only in dry state or in non-aqueous medium (e.g., NiCl_4^{2-}).

In many cases steric factor decides stability e.g.,

FeCl_4^- , CoCl_4^{2-} , SiCl_4 are stable whereas the stable fluoro species are FeF_6^{3-} , CoF_6^{3-} , SiF_6^{2-} etc.

Halogeno anions are important in many ways:

- (i) They are intermediates in many organic reactions where Lewis acids take part e.g., in Friedel–Crafts reaction AlCl_3 , BF_3 are catalyst and AlCl_4^- is intermediate.
- (ii) Halide complex formation can be used for the separation of metal ions, (Co^{2+} and Ni^{2+}). They can be separated by passing a strong HCl solution through an ion-exchange resin. Co^{2+} forms chlorocomplex in aq. medium but not Ni^{2+} .
- (iii) Large complex halo anions can be used to precipitate salts, e.g., $\text{NO}_2^+\text{BF}_4^-$, $\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ etc.
- (iv) They can be common source material for many elements to prepare their compounds, e.g., chloroplatinic acid, H_2PtCl_6 .

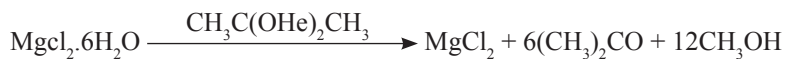
Preparation of Anhydrous halides

- (i) Direct reaction of element with halogen.



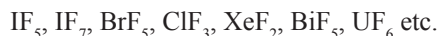
Reactivity order of halogen, $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

- (ii) **Dehydration of halide hydrate.** The hydrates can be dehydrated by thionyl chloride (SOCl_2) or with 2,2 – dimethoxy propane.



- (iii) Anhydrous fluorides

Fluorine is most oxidizing and it is difficult to work with elemental F many times. Therefore, many fluorinating agents are used. Example,



Halogen oxides

The halogen oxides are the binary X_mO_n compounds in which $\text{X} = \text{Cl}, \text{Br}, \text{I}$.

Fluorine is more electronegative than oxygen. Therefore, the binary oxygen compounds of fluorine are oxygen fluorides not fluorine oxides. So, not discussed here. Important oxides of halogens are given below:

Table 18.10

| Halogen | +1 | +4 | +5 | +7 |
|---------|-------------------|------------------|-------------------------------|--------------------------------|
| Cl | Cl ₂ O | ClO ₂ | -- | Cl ₂ O ₇ |
| Br | Br ₂ O | BrO ₂ | -- | -- |
| I | -- | -- | I ₂ O ₅ | -- |

Dichlorine monoxide (Cl₂O)

It is prepared on a laboratory scale (or commercially) by heating fresh yellow HgO with Cl₂ gas (or Cl₂ dissolved in CCl₄).



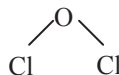
Cl₂O is a yellow-brown gas (25°C). It is endothermic compound and explodes on heating. It dissolves readily in water forming an orange solution,



Most of the Cl₂O is used to produce hypochlorites [NaOCl or Ca(OCl₂)₂]. These are used as:

- (i) Bleaching agent for wood pulp and fabrics.
- (ii) Disinfectants.

The Cl₂O molecule is bent (111°) with Cl – O = 1.71 Å

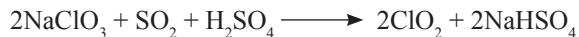


Chlorine dioxide (ClO₂)

It is highly reactive and can explode violently. Therefore, it is prepared where and as required (i.e., insitu). It is produced by reducing KClO₃ with moist oxalic acid at 90°C.



Commercially, ClO₂ is made by reduction of NaClO₃ with SO₂ in H₂SO₄ (in the presence of Cl[–] ions)



ClO₂ is yellowish gas at room temperature. It is used to produce NaClO₂ which is used for bleaching textile and paper.

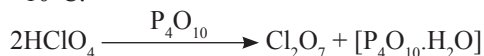


Structure

The molecule, ClO₂ is angular (118°) with Cl – O = 1.47 Å. It is odd electron molecule (19 electrons) but has no tendency to dimerize like NO₂. It may be due to delocalization of the odd electron.

Dichlorine heptoxide, Cl₂O₇

It is the most stable and is the only exothermic oxide of chlorine. It is formed by dehydration of HClO₄ with P₄O₁₀ at –10°C.



Cl_2O_7 is a colourless liquid. It dissolves in water forming HClO_4 . It has the structure $\text{O}_3\text{Cl}-\text{O}-\text{ClO}_3$ with a ClOCl angle 118.6° at the central oxygen.

Bromine oxides are not well characterized.

Iodine pentaoxides I_2O_5

It is white crystalline hygroscopic solid. It is produced by heating HIO_3 at $\sim 170^\circ\text{C}$.



I_2O_5 is most stable of the halogen oxides (stable upto $\sim 300^\circ\text{C}$). I_2O_5 reacts as an oxidizing agent ($\text{H}_2\text{S} \rightarrow \text{SO}_2$, $\text{NO} \rightarrow \text{NO}_2$, $\text{CO} \rightarrow \text{CO}_2$). The redox reaction with CO is quantitative.



The liberated iodine is determined volumetrically with standard sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$).

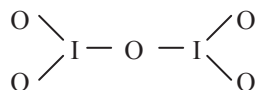
This method finds use in analyzing exhaust gas from car engines or gases from blast furnaces.

With F_2 , it forms IF_5 ,



Structure

I_2O_5 has IO_3 pyramids sharing one O-atom, i.e., O_2IOIO_2 .



It has strong intermolecular I - - O interactions leading to three-dimensional structure.

Oxo acids

The known oxo acids of halogens are given below:

| Fluorine | Chlorine | Bromine | Iodine | Oxidation state of halogen |
|---------------|--|---|---|----------------------------|
| HO F | HO Cl a \leftarrow HO ClO HO ClO_2 HO ClO_3 | HO Br HO BrO HO BrO_2 HO BrO_3 | HO I -- HO IO_2 HO IO_3 , (HO) $_5\text{IO}$ | +1 3+ +5 +7 |

Note

- The oxidation number of +1 can not be assigned to F in HOF as F is most electronegative of all the elements.
- Acids marked 'a' are known only in solution.
- Perchloric acid (HOClO_3) can be prepared anhydrous.
- Iodic (HOIO_2) and periodic (HOIO_3) acids are known in solid state.

Acid strength

- (i) **Acid strength of HOX, HOXO, HOXO₂ and HOXO₃** As the number of free O – atoms increases, acid strength increases. Thus increasing order of acid strength is $\text{HOX} < \text{HOXO} < \text{HOXO}_2 < \text{HOXO}_3$ (X = the same halogen).

It can be explained considering effective negative charge per O – atom on the conjugate bases.

Table 18.11

| Acid | HOX | HOXO | HOXO ₂ | HOXO ₃ |
|------------------------------|---------------|-----------------|-------------------|-------------------|
| Conjugate base | XO^- | XO_2^- | XO_3^- | XO_4^- |
| Negative charge per O – atom | –1 | –1/2 | –1/3 | –1/4 |

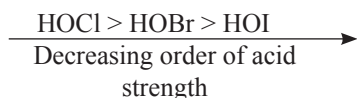
The extent of negative charge on each O – atom shows that H^+ is strongly attracted by XO^- and least strongly attracted by XO_4^- . So, the acid strength order is $\text{HOX} < \text{HOXO} < \text{HOXO}_2 < \text{HOXO}_3$. This order shows that as oxidation number of halogen increases, acid strength increases (for the same halogen).

| | | | | |
|-------------------------|------|-------|--------------------|--------------------|
| P^{K_a} | HOCl | HOClO | HOClO ₂ | HOClO ₃ |
| | 7.5 | 1.97 | ~ –1 | ~ –10 |

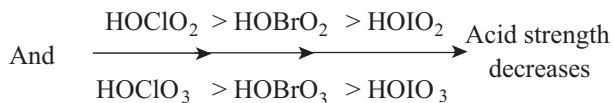
- (ii) Strength of paraperiodic acid $[(\text{HO})_5\text{IO}]$. The oxidation state of iodine in this acid is +7 but it is a very weak acid. It is because negative charge per O – atom in IO_6^{-5} is $-5/6$ (– 1).
- (iii) Acid strength of

(a) HOCl, HOBr and HOI

As X – O bond polarity increases H – O bond becomes stronger and ionisation of the acid is suppressed. Therefore, with decrease in the electronegativity of the halogen acid strength decreases.



Similar trend is followed by HOXO₂ and HOXO₃ (X = Cl, Br, I) series. That is,

**Oxidizing power**

(i) *HOX acids (X = Cl, Br, I)*

These acids are good oxidizing agents, and oxidizing power decreases as $\text{HOCl} > \text{HOBr} > \text{HOI}$. It can be seen in their std potentials.

| | | | |
|---|------|------|------|
| $\text{HOX} + \text{e} + \text{H}^+ \rightarrow \frac{1}{2}\text{X}_2 + \text{H}_2\text{O}$ | Cl | Br | I |
| $E^\circ (\text{V})$ | 1.63 | 1.59 | 1.45 |

(ii) *HOXO₃ acids*

These acids are strong oxidizing agents and oxidizing power follow the order $\text{HOBrO}_3 > \text{HOIO}_3 > \text{HOClO}_3$. It is clear from their E° for the given reaction E° (volts).

| | | | |
|--|------|------|------|
| $\text{XO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{XO}_3^- + \text{H}_2\text{O}$ | Cl | Br | I |
| $E^\circ (\text{V})$ | 1.23 | 1.76 | 1.64 |

The high oxidizing power of BrO_4^- may be related to its being thermodynamically less stable than either ClO_4^- or IO_4^- . Lesser thermodynamic stability of BrO_4^- may be related with weaker Br–O bonds. The Cl–O bond is stronger due to (d–p) π bonding and I–O bonds gets strength due to (f–p) overlap contribution. For BrO_4^- (d–p) π bonding is less effective due to large size of 4d orbitals of Br.

Comparison of ClO_n^- anions

The ClO_n^- ($n = 1, 2, 3, 4$) ions are not similar.

Bond properties

Table 18.12

| Anion | Bond length (Å) | Bond energy KJmol^{-1} | Bond angle |
|------------------|-----------------|---------------------------------|-----------------|
| ClO^- | 1.70 | 209.0 | -- |
| ClO_2^- | 1.64 | 245.0 | 111° |
| ClO_3^- | 1.57 | 243.0 | 106° |
| ClO_4^- | 1.45 | 364.0 | $109^\circ 28'$ |

Note:

- The stability increases in the order, $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$, as bond energy increases.
- Oxidizing power decreases in the order $\text{ClO}^- > \text{ClO}_2^- > \text{ClO}_3^- > \text{ClO}_4^-$. The ClO_4^- ion shows hardly any oxidizing activity in solution.
- Hypochlorites show redox reaction in any medium.
- Chlorates in solution oxidize only in acid medium



However, strong oxidants in melts, in alkaline medium also



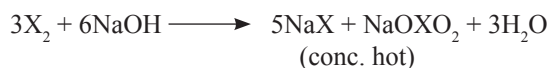
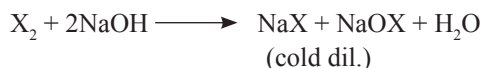
- The acid strength and oxidizing power of HClO_n ($n = 1, 2, 3, 4$) acids are in opposite order.

Table 18.13

| Property | HOCl | HOClO | HOClO_2 | HOClO_3 |
|-----------------|----------------|----------------|------------------|------------------|
| Acid strength | Increases → | | | |
| Oxidizing power | Decreases → | | | |

Preparations of oxo acids

Most of the oxo acids and acid anions of halogens are known only in solution. They can be obtained by reaction of the free halogens with (i) water or (ii) aq. bases.



All the above reactions are rapid disproportionation of halogens.

The water solution of halogens contains solvated X_2 as well as species produced due to a disproportionation reaction.

Concentration of X_2 in water at 25°C (mol l^{-1})

Table 18.14

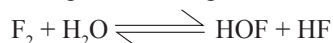
| Halogen | Cl_2 | Br_2 | I_2 |
|-----------------------|--------|-----------------------|----------------------|
| Total solubility | 0.091 | 0.21 | 0.0013 |
| conc. X_2 (aq) | 0.061 | 0.21 | 0.0013 |
| $H^+ = [X^-] = [HOX]$ | 0.030 | 1.15×10^{-3} | 6.4×10^{-6} |

Note:

- (i) There is very small concentration of HOBr.
- (ii) There is appreciable concentration of HOCl.
- (iii) The HOI is negligible in a saturated solution of iodine.

HO_F

It is a low temperature compound. It can be prepared by passing F_2 over ice and collecting the gas in a trap.



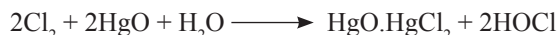
HO_F is a colourless solid, melts at -117°C . It is unstable and decomposes to HF and O_2 .

HOX ($X = Cl, Br, I$)

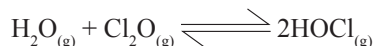
They can be prepared by the interaction of X_2 with HgO in water.



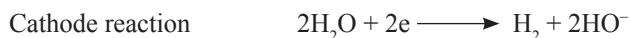
HOCl is most stable in this group. It can be prepared as:



In the vapour phase HOCl is formed in the reaction



Sodium chlorate (i), NaOCl, is used for bleaching cotton fabric and as domestic bleach (the trade name of NaOCl is Parazone or Lanry). It is produced commercially by the electrolysis of cold brine, while stirring vigorously. The reactions are:



The stirring mixes HO^- , formed at the cathode with Cl_2 formed at the anode to produce OCl^- .

HOClO (Chlorous acid)

In the series HOXO, HOClO is known but only in solution. It can be made by the reaction



Sodium chlorite may be produced by the reaction



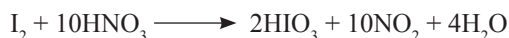
Sodium chlorite is stable in alkaline solution even when boiled. But in acid medium it disproportionates when heated.



Chlorites are used as bleaching agents.

Halic acids HOXO₂ (X = Cl, Br, I)

All the three halic acids are known. The acids HOClO₂ and HOBrO₂ are known only in solution and as salts. Only iodic acid (HOIO₂) is stable out of aq. solution. It is a white solid. It can be prepared by oxidizing I₂ with conc. HNO₃ or O₃.

***HOClO₂ and HOBrO₂***

They can be made by treating barium halates with H₂SO₄.



Ba(ClO₃)₂ can be prepared by passing Cl₂ in Ba(OH)₂ solution.

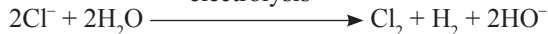


They can also be produced by reactions of X₂ with hot aq. base (NaOH)

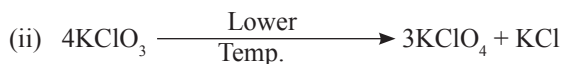
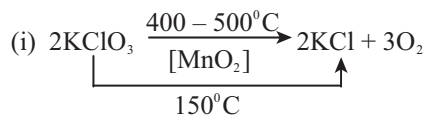


This reaction is, however, unsuitable for large scale preparations of NaClO₃ as only one sixth of the Cl₂ can be converted. Therefore, electrolytic oxidation of brine is used (yield up to 90%).

In practice, electrolysis is followed with vigorous stirring. The reactions are



KClO₃ decomposes on heating. The reaction is easy in the presence of the catalyst MnO₂



Chlorates are used in matches and fireworks. Sodium chlorate is used as a powerful weed killer.

Perhalic acids HOXO_3 ($X = \text{Cl}, \text{Br}, \text{I}$)

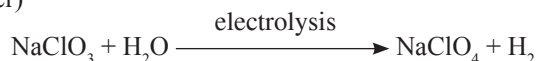
Now all the three perhalic acids are known.

Perchloric acid HOCIO_3

It can be made by treating anhydrous NaClO_4 with conc. HCl



Commercially NaClO_4 is prepared by the electrolysis of aq. NaClO_3 (Anode – Pt., Cathode – steel container)



Ammonium perchlorate (NH_4ClO_4) is an important compound. It is used as an oxidizer in solid rocket propellants (in missile and space shuttles).

It can be prepared by the reaction



Except KClO_4 , RbClO_4 and CsClO_4 all other metal perchlorates are water soluble.

Perbromic acid HOBRO_3

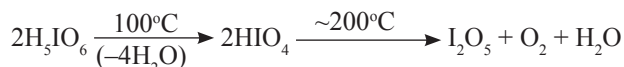
It is best prepared by oxidation of BrO_3^- by F_2 in 5M NaOH solution.



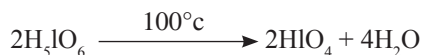
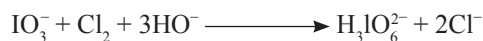
Solution of HBrO_4 can be concentrated upto 55% (6M), without decomposition. The hydrates $\text{HBrO}_4 \cdot 2\text{H}_2\text{O}$ can be crystallized.

Periodic acid HOIO_3

The common form in aq. solution of this acid is HIO_4 and also H_5IO_6 . H_5IO_6 is called paraperiodic acid (or orthoperiodic acid). It is a white crystal. It decomposes on heating as



The IO_4^- ion is tetrahedral while $(\text{OH})_5\text{IO}$ is octahedral. Periodates can be made by oxidizing iodate with Cl_2 in alkaline solution.



The white crystalline acid can be obtained from strongly acid solution. This strong acid can oxidize Mn^{+2} to MnO_4^- rapidly and quantitatively. It is a good reagent to oxidize vicinal polyols to carbonyl compounds.

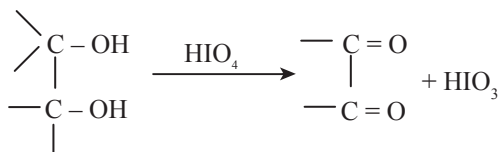
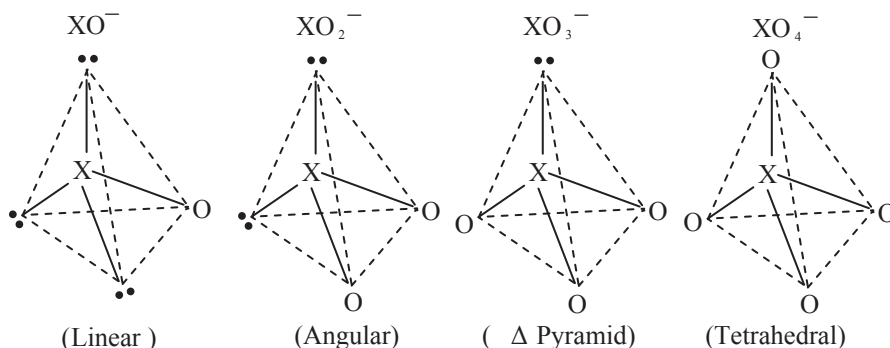


Figure 18.3

Structure of oxo anions**Table 18.15**

| Anions | XO^- | XO_2^- | XO_3^- | XO_4^- |
|-----------------------------|---------------|-----------------|--------------------|-----------------|
| Total valence electrons | 14 | 20 | 26 | 32 |
| No. of bonds (= no. of bps) | 1 | 2 | 3 | 4 |
| Electrons for bonds | 8 | 16 | 24 | 32 |
| Lone pairs | $(14-8)/2=3$ | $(20-16)/2=2$ | $(26-24)/2=1$ | 0 |
| Total electron pairs | $1+3=4$ | $2+2=4$ | $3+1=4$ | $4+0=4$ |
| Structure | Td | Td | Td | Td |
| Shape | Linear | Angular | Δ pyramidal | Td |

**Figure 18.4****Interhalogen compounds**

Halogens form many compounds between themselves. They are called interhalogen compounds. The following types are known:

1. **Neutral molecules:** These are all binary compounds of the type XX'_n . Where X and X' are different halogen atoms, X' being more electronegative and n is 1, 3, 5 or 7. Most of these compounds contain F but IF is not stable.

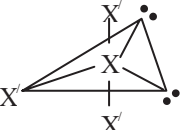
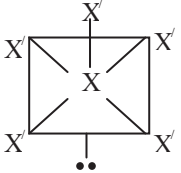
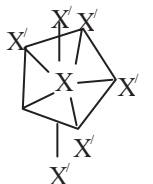
Table 18.16

| XX' | $\text{ClF}_{(g)}$ | $\text{BrF}_{(g)}$ | $\text{BrCl}_{(g)}$ | $\text{ICl}_{(s)}$ | $\text{IBr}_{(s)}$ |
|----------------|---------------------|---------------------|---------------------|--------------------|--------------------|
| XX'_3 | $\text{ClF}_{3(g)}$ | $\text{BrF}_{3(l)}$ | $\text{ICl}_{3(s)}$ | $\text{IF}_{3(s)}$ | |
| XX'_5 | $\text{ClF}_{5(g)}$ | $\text{BrF}_{5(l)}$ | $\text{IF}_{5(l)}$ | | |
| XX'_7 | | | $\text{IF}_{7(g)}$ | | |

(g = gas, l = liquid, s = solid)

As all valence electrons are paired either as bond pairs or lone-pairs, these compounds are diamagnetic.

Structure and shape**Table 18.17**

| Molecules | Bond pairs | Lone pairs | Total electron pairs | Structure | Shape |
|-----------|------------|------------|----------------------|--|----------------------|
| XX'_3 | 3 | 2 | 5 |  (tbp) | T – shaped |
| XX'_5 | 5 | 1 | 6 |  (Oh) | Square pyramid |
| XX'_7 | 7 | 0 | 7 |  (pbp) | Pentagonal bipyramid |

2. **Interhalogen cations:** These compounds are either homonuclear, e.g., I_2^+ , Cl_3^+ or heteronuclear ClF_2^+ , BrF_4^+ etc. There is one ternary cation $IBrCl^+$.

Table 18.18 Interhalogen cations

| Triatomic | | Pentaatomic | Heptaatomic |
|-----------|-----------|-------------|-------------|
| ClF_2^+ | I_2Cl^+ | ClF_4^+ | ClF_6^+ |
| | IBr_2^+ | BrF_4^+ | BrF_6^+ |
| BrF_2^+ | I_2Br^+ | IF_4^+ | IF_6^+ |
| | ICl_2^+ | | |

Structure and shape**Table 18.19**

| Cations | Bond pairs | Lone pairs | Total electron pairs | Structure | Shape |
|-------------------------|------------|------------|----------------------|-----------|----------|
| Triatomic $[XX'_2]^+$ | 2 | 2 | 4 | Td | Angular |
| Pentaatomic $[XX'_4]^+$ | 4 | 1 | 5 | tbp | T-shaped |
| Heptaatomic $[XX'_6]^+$ | 6 | 0 | 6 | Oh | Oh |

The cations may be either paramagnetic (I_2^+ , 13 valence electrons) or diamagnetic (ICl_2^+ , 20 valence electrons) depending upon valence electrons.

3. **Interhalogen anions:** Many anions are known, homo and heteronuclear both. The classical anion is triiodide ion, I_3^- . Anions are mostly ternary combinations, e.g., $IBrCl^-$, $IBrCl_3^-$, ICl_3F^- etc. The anions are generally found in crystalline solids with large cations, $Tl^+(I_3^-)$.

Structure and shape**Table 18.20**

| Anions | Bond pairs | Lone pairs | Total electron pairs | Structure | Shape |
|--------------------------|------------|------------|----------------------|-----------|---------------|
| Triatomic $I_3^-(IBrCl)$ | 2 | 3 | 5 | tbp | Linear |
| Pentaatomic $(ICl_4)^-$ | 4 | 2 | 6 | Oh | Square planar |

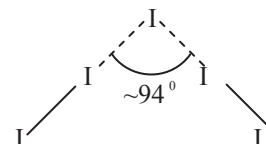
Note:

The I_5^- , I_4Cl^- and I_4Br^- ions are not octahedral. The I_5^- ion is angular.

Pseudohalogens and Pseudohalides

Many substances have properties either like X_2 or X^- (X = halogen). They are called pseudohalogens and pseudohalides. They contain two or more atoms in which one at least is N – atom, such as $(CN)_2$, CN^- , SCN^- etc.

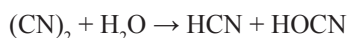
Some pseudohalogens and pseudohalides

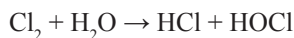
**Figure 18.5****Table 18.21**

| Pseudohalogens | Pseudohalides |
|------------------------|---------------------------|
| Cyanogen gas $(CN)_2$ | Cyanide ion CN^- |
| Thiocyanogen $(SCN)_2$ | Cyanamide ion CN_2^{2-} |
| | Azide ion N_3^- |
| | Thiocyanate ion SCN^- |
| | Cyanate ion OCN^- |
| | Fulminate ion ONC^- |

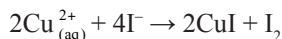
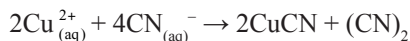
The cyanogens gas and CN^- ion are best-known pseudohalogen and pseudohalide. They behave like X_2 and X^- , e.g.,

- (a) $(CN)_2$ disproportionate in water like X_2 .



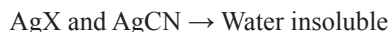


(b) CN^- behaves similar to I^- .

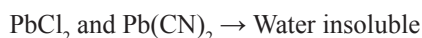


Both the above reactions are reduction of Cu^{2+} to Cu^+ by CN^- and I^- ions.

(c) The solubility of metal halides and metal cyanides are very similar,



(X = Cl, Br, I)



(d) Like halides pseudohalides (CN^- , SCN^- etc.) are good ligands CuCl_4^{2-} , ZnCl_4^{2-} , $\text{Cu}(\text{CN})_4^{2-}$, $\text{Zn}(\text{CN})_4^{2-}$.

(i) CN^- complexes with transition metals and Zn, Cd and Hg.

(ii) Most of the CN^- complexes are ionic $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Mn}(\text{CN})_6]^{4-}$ etc.

(iii) CN^- can stabilize low oxidation states also, e.g., $[\text{Ni}(\text{CN})_4]^{2-}$.

PRACTICE QUESTIONS

A. Explain the following in short.

- The F – F bond energy is lower than Cl – Cl although bond length in F_2 is smaller.
- The H – F bond is most polar among the H – X, but H – F is weakest acid.
- Electron affinity of chlorine is greater than fluorine.
- Cl_2 forms I_2 on reaction with KI but I_2 fails to form Cl_2 with KCl.
- I_2 is insoluble in water but dissolves in a solution of KI.
- F_2O_2 has very short O – O bond (1.217Å) compared to H_2O_2 (1.84Å).
- All the X_2 molecules are coloured (X = F, Cl, Br, I).
- F_2 is gas but I_2 is solid.
- AgF is soluble but AgCl is insoluble in water.
- When Cl_2 reacts with NaOH the products vary with temperature.

B. What happens when

- NH_3 is reacted with excess Cl_2 .
- NaBr is heated with conc. H_2SO_4 .
- NaI is treated with H_3PO_4 .

- Cl_2 gas is passed in hot conc. NaOH.
- I_2 is boiled with conc. HNO_3 .
- Cl_2 is passed over slaked lime $[\text{Ca}(\text{OH})_2]$.
- Iodine solution is treated with $\text{Na}_2\text{S}_2\text{O}_3$ (or write chemical reaction for decolourization of iodine solution by hypo).
- CuSO_4 solution is treated with excess KI.
- CuSO_4 solution is treated with KCN in the ratio ($\text{Cu}^{+2} : \text{CN}^- = 1 : 2$)
- SO_2 gas is passed in a solution of sodium iodate.
- Chlorine gas is bubbled through a solution of ferrous bromide.
- Sodium chloride is heated with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 .

C. Fill in the blanks

- Hypo _____ acid is not known at room temperature (HOX , X = F, Cl, Br, I).
- Hydrohalic acid, which dissolves glass, is _____.
- Chlorous acid is a _____ acid than hypo chlorous acid.
- Reaction of perchloric acid with P_4O_{10} gives _____.

- (e) Chlorine water with KI produces _____ coloured solution.
- (f) _____ acid gives hypo _____ ion (hydrobromic, hypobromous, perbromic, bromide, bromite, perbromate).
- (g) Silver fluoride is _____ in water.
- (h) When an aq. solution of NaF is electrolyzed, the gas liberated at anode is _____.
- (i) Iodine is practically insoluble in water but its solubility increases in an aq. solution of potassium iodide due to the formation of _____.
- (j) KI in CCl_4 produces _____ coloured solution with chlorine water.
- (k) Iodine reacts with hot conc. NaOH solution. The products are NaI and _____.

OBJECTIVE-TYPE QUESTIONS

- Which of the following has highest bond energy?
(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2
- The correct order of electron attachment enthalpy is
(a) $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (b) $\text{I} > \text{Br} > \text{Cl} > \text{F}$
(c) $\text{Cl} > \text{F} > \text{Br} > \text{I}$ (d) $\text{Cl} > \text{Br} > \text{F} > \text{I}$
- Chlorine gas is passed in a hot concentrated NaOH solution. The product is
(a) NaOCl (b) NaOClO
(c) NaOClO₂ (d) NaOClO₃
- The following acids have been arranged in the order of increasing acid strength. Identify the correct order.
(I) ClOH
(II) BrOH
(III) IOH
(a) $\text{I} < \text{II} < \text{III}$ (b) $\text{III} < \text{II} < \text{I}$
(c) $\text{II} < \text{I} < \text{III}$ (d) $\text{III} < \text{I} < \text{II}$
- Among the oxy acids of chlorine ClO_nH ($n = 1, 2, 3, 4$) HOCl is strongest oxidizing agent. It is because
(a) Oxidation number of Cl in it is lowest
(b) The Cl – O bond is weakest in it.
(c) Cl is joined with least number of O – atoms.
(d) The ion ClO^- is linear in shape.
- The catalyst used in the Deacon's process for the large-scale preparation of Cl_2 from HCl is
(a) Cu – Zn alloy (b) CuCl_2
(c) Cu_2S (d) CuO
- Bromine can be prepared in the laboratory by
(a) Heating KBr with HCl
(b) Heating KBr with MnO_2 and conc. H_2SO_4 .
(c) Hydrolyzing PBr_3 with water.
(d) Passing I_2 (vap) in a solution of KBr.
- Iodine is formed when KI is treated with a solution of
(a) FeSO_4 (b) NiSO_4
(c) CuSO_4 (d) ZnSO_4
- When aq. solution of NaI and NaIO_3 are mixed in acid medium, the product is
(a) I_2 (b) HOIO
(c) HOI (d) HOIO_3
- Chlorine acts as a bleaching agent only in the presence of
(a) Pure oxygen (b) Moisture
(c) Dry air (d) Sunlight
- Which of the following statements is correct for TI_3 ?
(a) It contains TI^{3+} and Br^- ions.
(b) It is a covalent compound
(c) It contains TI^+ , I^- and lattice I_2 molecules.
(d) It contains TI^+ , and I_3^- .
- When iodine is dissolved in CCl_4 , the colour that results is
(a) Bluish green (b) Violet
(c) Brown (d) Yellow
- When concentrated HNO_3 reacts with iodine, the product is
(a) HOI (b) HOIO
(c) HOIO_2 (d) HOIO_3

14. Hydrogen bond is strongest in
 (a) $F-H \cdots N$
 (b) $F-H \cdots O$
 (c) $F-H \cdots F$
 (d) All are equally strong
15. Iodine reacts with hypo to give
 (a) Na_2SO_3 (b) Na_2SO_4
 (c) Na_2SO_5 (d) $Na_2S_4O_6$
16. The correct order of oxidizing power is
 (a) $HOCl > HOClO > HOClO_2 > HOClO_3$
 (b) $HOClO_3 > HOClO_2 > HOClO > HOCl$
 (c) $HOClO_2 > HOClO_3 > HOCl > HOClO$
 (d) $HOCl > HOClO_2 > HOClO > HOClO_3$
17. The reaction $3ClO^-_{(aq)} \xrightarrow{HO^-} ClO^-_{3(aq)} + 2Cl^-_{(aq)}$, is an example of
 (a) Decomposition reaction
 (b) Reduction reaction
 (c) Disproportionation reaction
 (d) Oxidation reaction
18. Chlorine gas is passed on wet blue litmus. The colour is
 (a) Red
 (b) Yellow
 (c) Colourless
 (d) No colour change
19. Which of the following is not a pseudohalide?
 (a) SCN^- (b) OCN^-
 (c) CNO^- (d) $RCOO^-$
20. The correct $X-X$ bond dissociation energy is represented by
 (a) $F-F > Cl-Cl > Br-Br > I-I$
 (b) $I-I > Br-Br > Cl-Cl > F-F$
 (c) $Cl-Cl > Br-Br > F-F > I-I$
 (d) $Br-Br > Cl-Cl > F-F > I-I$
21. Euchlorine is mixture of
 (a) Cl_2 and ClO_2
 (b) Cl_2 and SO_2
 (c) Cl_2 and CO_2
 (d) Cl_2 and CO
22. Which of the following reactions is possible?
 (a) $2NaCl + I_2 \rightarrow 2NaI + Cl_2$
 (b) $2NaCl + Br_2 \rightarrow 2NaBr + Cl_2$
 (c) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$
 (d) $2NaBr + I_2 \rightarrow 2NaI + Br_2$
23. When $NaCl$ (or KCl) is heated with solid K_2CrO_7 and conc. H_2SO_4 , the product is
 (a) Chromous chlorine
 (b) Chromic Chloride
 (c) Chromyl chloride
 (d) Chromyl sulphate
24. The reaction, $2ClO_3^- + I_2 \rightarrow 2IO_3^- + Cl_2$
 (a) is not possible
 (b) is possible
 (c) depends upon the temperature
 (d) depends upon the state of products
25. Chlorine gas is passed in aqueous KI solution. The colour of solution is
 (a) Violet (b) Red
 (c) Light brown (d) Blue
26. The salt $K.ICl_2$ on heating gives
 (a) KCl, ICl (b) KI, Cl_2
 (c) KCl, I_2 (d) KI, KCl, Cl_2
 [Hint: Alkali metal halide is more stable when either the halogen or the metal is small].

ANSWERS

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (c) | 4. (b) | 5. (b) | 6. (b) | 7. (b) | 8. (c) | 9. (a) | 10. (b) |
| 11. (d) | 12. (b) | 13. (c) | 14. (c) | 15. (d) | 16. (a) | 17. (c) | 18. (c) | 19. (d) | 20. (c) |
| 21. (a) | 22. (c) | 23. (c) | 24. (b) | 25. (c) | 26. (a) | | | | |



19

Group – 18, The Noble Gases

Helium, Ne, Ar, Kr, Xe and Rn are noble gases and elements of group 18 (or zero group). They are minor constituents of the atmosphere. Sir William Ramse first isolated Ne, Ar, Kr and Xe. He also established He. It is found in stars, in radioactive minerals and some natural gasses. Its origin is entirely from the decay of thorium and uranium isotopes, which emit α -particles. The last member of the group Rn is radioactive (all isotopes). These gases are obtained by fractionation of liquid air.

Properties

Table 19.1

| Elements | Out electron configuration | Radii (\AA) | Ionization energy KJmol^{-1} | Volume % in atmosphere ($\times 10^{-14}$) |
|----------|----------------------------|------------------------|---------------------------------------|--|
| He | $1s^2$ | 1.20 | 2369 | 5.2 |
| Ne | $2s^2 2p^6$ | 1.60 | 2078 | 18.2 |
| Ar | $3s^2 3p^6$ | 1.91 | 1519 | 9340.0 |
| Kr | $4s^2 4p^6$ | 2.00 | 1349 | 11.4 |
| Xe | $5s^2 5p^6$ | 2.20 | 1169 | 0.08 |
| Rn | $6s^2 6p^6$ | — | 1036 | — |

Note

- (i) Ar is most abundant and Kr is least

Atomicity

All noble gases are monoatomic. It is due to closed-shell electron configuration. Monoatomic nature can be explained by

- (a) C_p/C_v ratio or
(a) Molecular orbitals model

The C_p/C_v ratio for monoatomic gases is 1.66. For all noble gas this ratio is almost equal to 1.66. Hence, all are monoatomic.

Molecular orbital model also explains their monoatomic nature.

He is $1s^2$. If it forms He_2 the MO diagram is

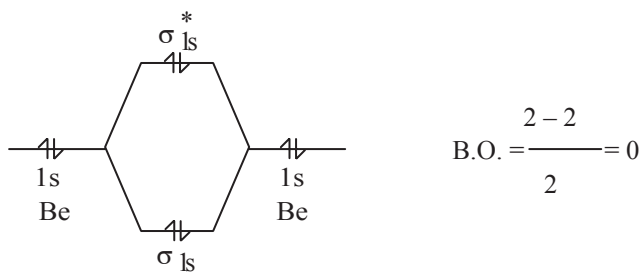


Figure 19.1

Thus, there is no bond between He and He. It is, therefore, monoatomic. For others also, as the valence shell is closed, octet bond order will become zero. It shows their monoatomic nature.

Radii

All noble gases are monoatomic. Their radii are non-bonded radii i.e., van der Waals' radii. Therefore, they have large atomic radii. The radii of halogens are covalent radii. Therefore, in each period, radii of noble gas atom is larger than its preceding halogen. It is opposite to the trend found up to group 17.

Table 19.2

| Halogen Gr – 17 | Radii (Å) | Noble gases Gr - 18 | Radii (Å) |
|-----------------|-----------|---------------------|-----------|
| F | 0.71 | Ne | 1.60 |
| Cl | 0.99 | Ar | 1.91 |
| Br | 1.14 | Kr | 2.00 |
| I | 1.33 | Xe | 2.20 |

Water Solubility

Noble gases are more soluble in water than that of N_2 or O_2 . The solubility of noble gases increases with increase in atomic number. The solubility is due to dipole induced dipole interaction. As polarizability of an atom (or ion) depends on its size, the larger the noble gas atom more polarizable it is. Therefore, solubility increases down the group.

Special properties of He

He has some peculiar properties. Such as:

- It has lowest bp (4K) of any known substance.
- It has no triple point that is, there is no combination of temperature and pressure at which solid, liquid and gas co-exist at equilibrium.
- It cannot be solidified at atmospheric pressure.
- Its zero point energy is very high.

Liquid He has two forms—He(I) at 4.2K and He(II) at around 2.2K. The change from He(I) to He(II) is followed with many remarkable changes:

- (i) He(II) is super conductor.
- (ii) Its thermal conductivity is enormously large (800 times more than Cu).
- (iii) Its viscosity is negligible. Liquids having such a low viscosity are known as super fluids. Because of this property, He(II) is also called fourth state of matter.

Uses of Noble Gases

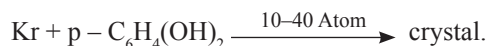
- (i) The main use of He is as the cryoscopic liquid.
- (ii) Neon is used for discharge lighting tubes (orange glow of 'neon' signs).
- (iii) Argon is mainly used to create inert atmosphere (in laboratory apparatus, in welding and in electric bulb, in G – M counter).
- (iv) Radon is used as a source of α -particle in the treatment of cancer.

Compounds of Noble Gases

1. Clathrate compounds
2. True chemical compounds

Clathrate

Clathrates (Latin – Clathratus meaning 'enclosed') are species which contain atoms or molecules trapped in the cavities of a host lattice. They contain neither ionic nor covalent bonds. The van der Waals' type force is responsible for their stability. Most of the clathrates have host which are H – bonded structure, Example, water – clathrate, quinol – clathrate etc.



The clathrate is shown below:

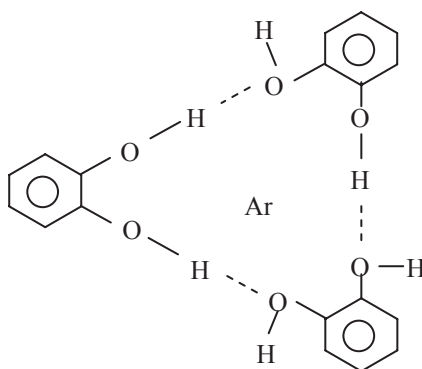


Figure 19.2

He and Ne do not form clathrate because they are small enough to be trapped.

Xe compounds

The first true chemical compound of Xe was prepared by Niel Bartlett (Canada – 1962). Dioxygen reacts with PtF₆ (a strong oxidizing agent) to form a red solid.



O₂ and Xe have almost equal first ionization energy (~12 eV). This led Bartlett to think that Pt F₆ should also react with Xe. He tried the reaction and got a yellowish solid.



The yellow solid has complex constitution $[\text{XeF}]^+ [\text{Pt}_2\text{F}_{11}]^-$, but simply may be represented as $\text{Xe}^+ [\text{PtF}_6]^-$. Later on, it was also found that F_2 reacts with Xe. It forms three types of compounds:

1. Fluorides,
2. Oxyfluorides
3. Oxides and Oxoanions

However, oxygen does not react directly with Xe. The oxygen derivatives are obtained from fluorides. Some compounds having Xe – Cl and Xe – N bonds are also reported.

Xe fluorides

Xenon reacts directly with fluorine (only). The products depend on respective amounts of Xe and F_2 and temperature also. The reactions are generally carried out in sealed tubes.

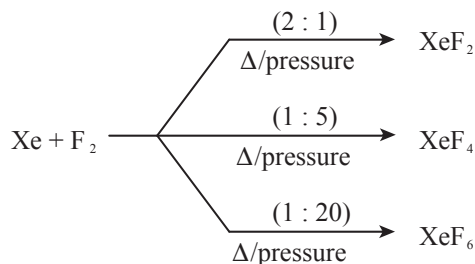
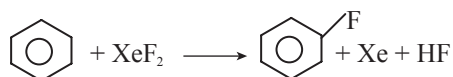


Figure 19.3

- These three fluorides are crystalline volatile substances which sublimes at room temperature but can be kept in nickel containers.
- The fluorides are strong oxidizing agents.



- They are good fluorating agents also.

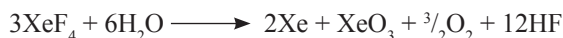


The fluorides differ in reaction with water.

- (a) XeF_2 is water soluble and undergoes slow oxidative hydrolysis.



- (b) XeF_4 reacts with water violently giving XeO_3 .



In this reaction, XeF_4 disproportionates as well as H_2O is partly oxidized.

(c) XeF_6 also reacts violently to give XeO_3



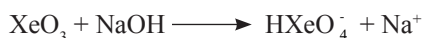
XeO_3 is a white deliquescent solid which is dangerously explosive. But with small amount of water XeF_6 forms XeOF_4 .



- XeF_6 is extremely reactive and reacts even with quartz (SiO_2) to form a colorless liquid XeOF_4 .



- XeO_3 reacts with NaOH solution ($\text{pH} > 10$) to form sodium xenate ion



- The xenate ion, HXeO_4^- , slowly disproportionate in basic medium to Xe and perxenate ion



The perxenate solutions are yellow and are powerful and rapid oxidants.

Some Xe compounds

Table 19.3

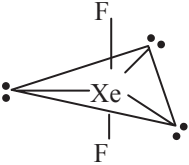
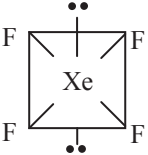
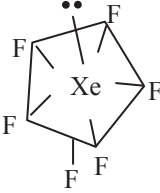
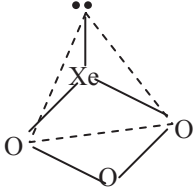
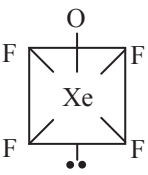
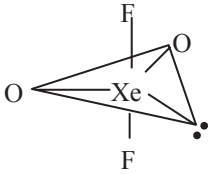
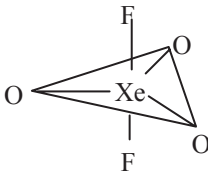
| Compound | Form | MP(°C) | Structure | Shape |
|--------------------------|--------------------|----------|----------------------|--------------------|
| XeF_2 | Colourless crystal | 129 | Trigonal bipyramid | Linear |
| XeF_4 | Do | 117 | Octahedral | Sq. planer |
| XeF_6 | Do | 49.6 | Pentagonal bipyramid | Distorted Oh. |
| XeO_3 | Do | Explodes | Tetrahedral | Trigonal pyramid |
| XeO_4 | Colourless gas | – 39.5 | Tetrahedral | Tetrahedral |
| XeOF_4 | Colourless liquid | – 46 | Octahedral | Square pyramid |
| XeO_2F_2 | – | – | Trigonal bipyramid | Distorted Td. |
| XeO_3F_2 | – | – | Do | Trigonal bipyramid |
| XeO_6^{4-} | Colourless salt | – | Octahedral | Octahedral |

Note:

- In tbp structure lp and O – atom occupy equatorial positions
- In octahedral structure, lp occupy axial position.

Structures

Table 19.4

| Molecule | Structure |
|--------------------------|---|
| XeF_2 |  |
| XeF_4 |  |
| XeF_6 |  |
| XeO_3 |  |
| XeOF_4 |  |
| XeO_2F_2 |  |
| XeO_3F_2 |  |

PRACTICE QUESTIONS

A. Explain the following in brief:

- Noble gases are monoatomic.
- Solubility of noble gases increases in water with increase in atomic number.
- In each period, atomic radius of noble gas is highest (or atomic radius of Ne is larger than F).
- Clathrates are not true chemical compounds.

- XeF_4 is square planar, from VSEPR model.
- He is found in certain minerals.

B. Complete the following equation:

- $\text{XeF}_4 + \text{H}_2\text{O} \longrightarrow$
- $\text{SiO}_2 + \text{XeF}_6 \longrightarrow$
- $\text{XeF}_4 + \text{SF}_4 \longrightarrow$
- $\text{HXeO}_4^- + \text{HO}^- \longrightarrow$
- $\text{Ba}_2\text{XeO}_6 + \text{H}_2\text{SO}_4 \longrightarrow$

OBJECTIVE-TYPE QUESTIONS

- Shape of XeOF_4 is
 - Trigonal bipyramid with lp at axial position.
 - Square pyramid with lp at axial position.
 - Distorted square pyramid with lp at axial position.
 - Square pyramid with lp at square plane.
- Which of the following liquids has the property of a superfluid?
 - Liquid NH_3
 - Liquid N_2
 - Liquid O_2
 - Liquid He(I)
- Which of the following noble gas is not found in atmosphere?

| | |
|--------|--------|
| (a) He | (b) Ar |
| (c) Xe | (d) Rn |
- The inert gas which is most abundant is

| | |
|--------|--------|
| (a) Ne | (b) Ar |
| (c) Kr | (d) Xe |
- The hybridization of Xe in XeO_2F_2 is

| | |
|---------------------------|-----------------------------|
| (a) sp^3 | (b) sd^3 |
| (c) sp^3d | (d) sp^3d^2 |
- In the structure of XeO_2F_2
 - lp and O – atoms are at equatorial positions
 - lp and F – atoms are at equatorial positions
 - O – atom and F – atoms are at equatorial positions
 - F atoms are at equatorial positions and lp is at the axial position
- Which of the following noble gas is used in G – M counter?

| | |
|--------|--------|
| (a) Ne | (b) Ar |
| (c) Kr | (d) Xe |
- Which of the following noble gases is not expected to form a clathrate?

| | |
|--------|--------|
| (a) Ne | (b) Ar |
| (c) Kr | (d) Xe |
- Which of the following statements is not correct for liquid He(II)?
 - Its thermal conductivity is very low.
 - It is a superconductor.
 - It has no triple point.
 - Its viscosity is negligible.
- XeF_6 reacts with excess water to give

| | |
|---------------------|-------------------------|
| (a) XeO_4 | (b) XeO_3 |
| (c) XeOF_4 | (d) XeO_6^{4-} |

ANSWERS

1. (c) 2. (d) 3. (d) 4. (b) 5. (c) 6. (a) 7. (b) 8. (a) 9. (a) 10. (b)

20

Analytical Chemistry (Salt Analysis)



Every salt contains a cation and an anion. The cation of a salt is called basic radical and the anion of a salt is called acid radical.

Table 20.1

| Salt | Cation or Basic radical | Anions or Acid radical |
|-----------------|-------------------------|------------------------|
| NaCl | Na^+ | Cl^- |
| BaSO_4 | Ba^{+2} | SO_4^{-2} |

The analysis is, therefore, performed in two steps:

- (i) Tests for acid radicals.
- (ii) Tests for basic radicals

In practice, tests for acid radicals are carried out first and after that basic radical are tested.

TEST FOR ACID RADICALS

It is carried out in two steps:

- (i) Preliminary tests
- (ii) Solution tests

Preliminary tests

Acid radicals are conjugate bases of acids.

Table 20.2

| Acid | Acid radical |
|-------------------------|--|
| H_2SO_4 | HSO_4^- or SO_4^{-2} |
| HCl | Cl^- |
| HNO_3 | NO_3^- |
| H_2S | S^{-2} |

The test reagent is acid, either dilute or concentrated (H_2SO_4 , HCl). Generally, H_2SO_4 is used.

Common acid radicals**Table 20.3**

| | | | |
|---------------------|--------------------|----------|--------------------|
| Carbonate | CO_3^{2-} | Chloride | Cl^- |
| Hydrogen carbonates | HCO_3^- | Bromide | Br^- |
| Sulphite | SO_3^{2-} | Iodide | I^- |
| Hydrogen sulphite | HSO_3^- | Sulphate | SO_4^{2-} |
| Nitrite | NO_2^- | Sulphide | S^{2-} |

Except, sulphate (SO_4^{2-}), the acid radicals are decomposed by acid (H_2SO_4). Some are decomposed by dil. H_2SO_4 and some by conc. H_2SO_4 , but the product is always a gas.

(a) Acid radicals decomposed by dil. H_2SO_4

Table 20.4

| Acid radicals | | Decomposition product of the acid radicals |
|--------------------|--------------------|--|
| Carbonates | CO_3^{2-} | CO_2 |
| Hydrogen carbonate | HCO_3^- | CO_2 |
| Sulphite | SO_3^{2-} | SO_2 |
| Hydrogen sulphite | HSO_3^- | SO_2 |
| Sulphide | S^{2-} | H_2S |
| Nitrite | NO_2^- | $\text{NO} \longrightarrow \text{NO}_2$ |

(b) Acid radicals decomposed by conc. H_2SO_4

Table 20.5

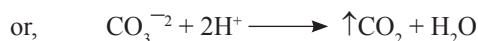
| Acid radicals | | Decomposition product of the acid radicals |
|---------------|-----------------|--|
| Nitrate | NO_3^- | NO_2 |
| Chloride | Cl^- | HCl |
| Bromide | Br^- | Br_2 |
| Iodide | I^- | I_2 |

(c) Sulphates (SO_4^{2-}) are not decomposed even by conc. H_2SO_4 .

Analytical chemistry of acid radicals, decomposed by dil. H_2SO_4 **Carbonates**

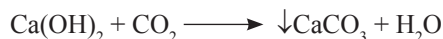
All carbonates (or hydrogen carbonates) are decomposed by dil. H_2SO_4 to CO_2 .



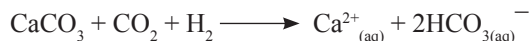


Carbon dioxide (CO_2) is colourless, odourless gas and evolves with effervescence. The test reagent for CO_2 is lime water [aq. sol. of $\text{Ca}(\text{OH})_2$] or baryta water [aq. sol. of $\text{Ba}(\text{OH})_2$].

CO_2 forms white turbidity with limewater. It is due to the formation of insoluble CaCO_3 .



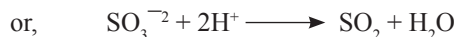
However, with excess CO_2 clear solution is produced due to the formation of soluble calcium hydrogen carbonate. It is formed due to acid medium with excess CO_2 .



Baryta water reacts exactly in the same way.

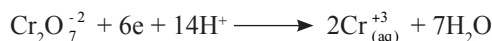
Sulphite (SO_3^{2-})

Sulphites (or hydrogen sulphites) are decomposed by dil. H_2SO_4 to SO_2 .



Sulphur dioxide (SO_2) is colourless pungent gas and evolves with effervescence. It can be tested as follows:

- (i) SO_2 turns acidic dichromate paper (orange) green. It is due to reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{+3} by SO_2 .

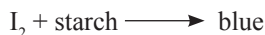
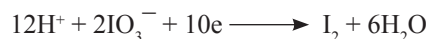
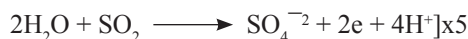


(Orange)

(Green)

- (ii) KIO_3 + starch solution reagent

SO_2 turns filter paper moistened with KIO_3 and starch solution blue. It is due to the formation of iodine (by a redox reaction), which is adsorbed by starch.



- (iii) Lime water reagent

SO_2 forms a white ppt of CaSO_3 with lime water.

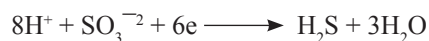


However, the ppt. dissolves when more SO_2 is passed, due to the formation of HSO_3^- ions,

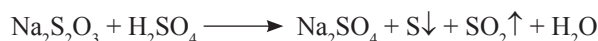


(iv) $\text{Zn} + \text{H}_2\text{SO}_4$ reagent

A sulphite is reduced to H_2S when treated with dil. H_2SO_4 and Zn. The evolved gas (H_2S) turns lead acetate paper black (Pbs is formed).



Thiosulphate ($\text{S}_2\text{O}_3^{-2}$) is also decomposed by dil. H_2SO_4 to SO_2 but with precipitation of S (white) distinction from (SO_3^{-2}).



Silver nitrate solution reagent can be used to distinguish SO_3^{-2} and $\text{S}_2\text{O}_3^{-2}$.

Table 20.6

| Reagent | SO_3^{-2} | S_2O_3 |
|--------------------------|--|--|
| AgNO_3 solution | White crystalline Ag_2SO_3 ppts, with more reagents. $\text{Ag}^+ + \text{SO}_3^{-2} \rightarrow \text{AgSO}_3^-$ $\text{Ag}^+ + \text{AgSO}_3^- \rightarrow \text{Ag}_2\text{SO}_3 \downarrow$ Aq. suspension of the ppt or solution of complex ion on heating gives grey metallic Ag. $2\text{AgSO}_3^- \xrightarrow{\Delta} 2\text{Ag} + \text{SO}_2 + \text{SO}_4^{-2}$ $2\text{AgSO}_3 + \text{H}_2\text{O} \xrightarrow{\Delta} 2\text{Ag} + \text{SO}_4^{-2} + 2\text{H}^+$ | White $\text{Ag}_2\text{S}_2\text{O}_3$ ppts $\text{Ag}^+ + \text{SO}_3^{-2} \rightarrow \text{AgS}_2\text{O}_3 \downarrow$ The ppt on warming decomposes to give dark Ag_2S $\text{AgS}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{Ag}_2\text{S} + 2\text{H}^+ + \text{SO}_4^{-2}$ |

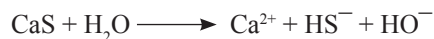
Sulphide (S^{-2})

Sulphides are common compound of metals. They vary widely in nature e.g., solubility, colour etc. Some general observations are:

- (i) Alkalimetal sulphides are water soluble. Their aqueous. solutions are basic due to hydrolysis of S^{-2} .



- (ii) Alkaline earth sulphides are sparingly soluble, but gradually change into soluble hydrogen sulphide in water.



- (iii) Sulphides of other metals (+2 or +3) are insoluble in water. Metal ions in +2 or +3 states are small and more polarizing and S^{-2} being large is more polarizable. Such interaction results into stable lattice and hence insolubility.

- (iv) Sulphides of Al^{+3} , Cr^{+3} , Mg^{+2} are known only in dry state. It is because they are completely hydrolyzed by water.



Therefore, sulphides of the above metal ions have foul smell in damp (i.e., in the presence of moisture) due to the formation of H_2S .

- (v) Transition metal sulphides are coloured. As, Sb, Sn, Pb, Cd, Hg sulphides are also coloured. Colour is due to charge transfer.

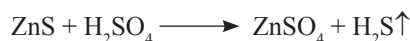
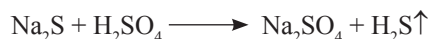
Table 20.7

| M^{n+} | Sulphide | Colour of sulphide |
|------------------|-------------------------|--------------------|
| Cu^{+2} | CuS | Black |
| Cd^{+2} | CdS | Yellow |
| Ni^{+2} | NiS | Black |
| As^{+3} | As_2S_3 | Yellow |
| Sb^{+3} | Sb_2S_3 | Orange – red |
| Pb^{+2} | PbS | Black |
| Sn^{+4} | SnS_2 | Yellow |

- (vi) The sulphides of Fe, Mn, Zn and alkali metals are decomposed by dil. HCl to form H_2S .
 (vii) The sulphides of Pb, Cd, Ni, Co, As, Sn(IV) are decomposed by conc. HCl.
 (viii) HgS dissolves only in aquaregia ($3\text{HCl} + \text{HNO}_3$).

Dilute H_2SO_4 reagent and S^{-2}

Alkali sulphides and a few others are decomposed by dil. H_2SO_4 to H_2S . It has suffocating odour (rotten egg).

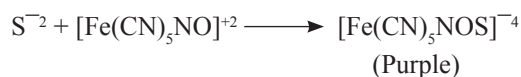


H_2S is detected by:

- (a) Pb – acetate paper or Cd – acetate paper.



- (b) Sodium nitroprusside reagent $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$. This reagent forms purple solution with S^{-2} .

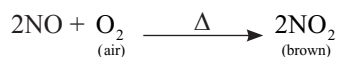


This test is highly sensitive.

The test fails with solution of H_2S or with the free gas. However, in the presence of NaOH or NH_4OH it becomes possible.

Nitrite (NO_2^-)

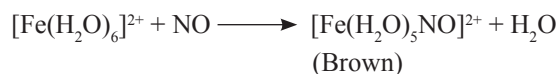
(i) Nitrites are decomposed by dil. H_2SO_4 to brown fumes (NO_2). It is produced as



(ii) Ring test (Fresh FeSO_4 + dil. H_2SO_4)

Nitrite solution forms brown ring with fresh FeSO_4 when acidified with dil

H_2SO_4 (or CH_3COOH).



The brown colour is due to charge transfer from NO to Fe^{+2} .

(iii) Nitrites are decomposed to N_2 on heating with solid NH_4Cl or urea.



The above reagents do not decompose nitrates. Therefore, the above reactions can be used to test NO_3^- in the presence of NO_2^- . The best reagent to decompose a nitrite is sulphamic acid (HOSO_2NH_2). It completely decomposes nitrite to N_2 without affecting NO_3^- .

**Summary of the above tests****Table 20.8**

| A. Radical | Product of reaction with dil. H_2SO_4 | Characteristics of the gas | Test reagent and product |
|---|---|---|--|
| Carbonate CO_3^{2-} or (HCO_3^-) | CO_2 | Evolves with effervescence, colourless, odourless | Limewater, forms white ppt of CaCO_3 , ppt |
| Sulphite SO_3^{2-} or (HSO_3^-) | SO_2 | Evolves with effervescence, colourless, pungent | (a) Acid dichromate, it turns green by SO_2 due to reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{+3} (b) Turns pot iodate starch paper blue due to formation of I_2 . |

(Continued)

| A. Radical | Product of reaction with dil. H_2SO_4 | Characteristics of the gas | Test reagent and product |
|------------------------------|---|---------------------------------------|---|
| Sulphide (S^{2-}) | H_2S | Suffocating odour | (a) Turns $\text{Pb}(\text{AcO})_2$ paper black, $\text{Cd}(\text{AcO})_2$ paper yellow. (b) Forms purple sol. with sodium nitroprusside solution. |
| NO_2^- (Nitrite) | Brown vap, NO_2 | Pungent brown vapour of NO_2 | Fresh $\text{FeSO}_4 + \text{dil. H}_2\text{SO}_4$. Nitrite solution form deep brown ring at the junction of aq. solution and acid. |

Acid radicals decomposed by conc. H_2SO_4

Table 20.9

| A.Radical | Product formed by conc. H_2SO_4 | Characteristics of the product |
|-----------------------------|---|---|
| Chloride (Cl^-) | HCl | → Pungent fumes of HCl . → Forms white clouds of NH_4Cl with glass rod moistened with NH_3 . |
| Bromide (Br_2) | Br_2 | → Reddish brown vap of Br_2 → Br_2 turns starch paper orange red. |
| Iodide (I^-) | I_2 | → Violet vapours of I_2 evolves. → I_2 turns starch paper blue. |
| Nitrate (NO_3^-) | NO_2 | → Brown fumes of NO_2 → Intensity of brown fumes increases when solid salt is heated with Cu turnings and conc. H_2SO_4 . It is used to distinguish between Br^- and NO_3^- . |

Analytical chemistry of Chlorides (Cl^-)

- (i) Chlorides when warmed with conc. H_2SO_4 form pungent fumes of HCl .



The fumes form white clouds of NH_4Cl with glass rod moistened with NH_3 .



(ii) Solution tests for Cl^- **(a) AgNO_3 solution reagent**

Chloride forms white curdy ppt. of AgCl with AgNO_3 solution. The ppt. is insoluble in dil. HNO_3 , but soluble in aq. NH_3 (or KCN or $\text{Na}_2\text{S}_2\text{O}_3$ solution).



Solubility of AgCl in aq. NH_3 is due to the formation of soluble complex $[\text{Ag}(\text{NH}_3)_2]^+$.

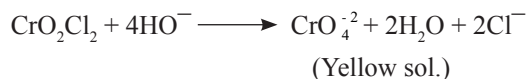
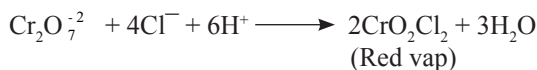
(b) Chromyl chloride (CrO_2Cl_2) test

It is most authentic test for chloride ion (Cl^-). Covalent chlorine fails this test.



The paste when gently warmed in a hard glass test tube gives deep red vapours of CrO_2Cl_2 . The red vapours on passing through NaOH solution, form yellow solution of sodium chromate (Na_2CrO_4), due to hydrolysis of CrO_2Cl_2 to CrO_4^{2-} .

The yellow solution gives yellow ppt. of PbCrO_4 with lead acetate solution.



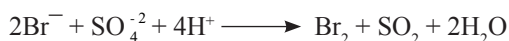
It is a very sensitive test. HgCl_2 usually fails this test.

Analytical chemistry of Bromide (Br^-)

- (i) When a bromide is warmed with conc. H_2SO_4 reddish brown vapours of Br_2 come out (due to oxidation of Br^- to Br_2 by conc. H_2SO_4).



or,

**(ii) AgNO_3 solution reagent**

A bromide gives light yellow curdy ppt. of AgBr with AgNO_3 solution. The ppt. is insoluble in dil. HNO_3 .



The ppt. is sparingly soluble in dil. NH_3 but readily dissolves in conc. NH_3 (or KCN or $\text{Na}_2\text{S}_2\text{O}_3$).

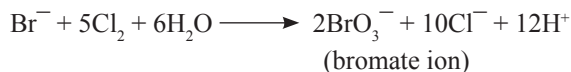


(iii) Chlorine water reagent

A bromide is oxidized to Br_2 by chlorine water, which dissolves in organic solvent (CS_2 , CHCl_3 , CCl_4 etc.) to give orange red solution which after sometime changes to reddish brown.

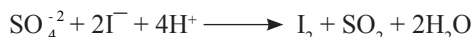
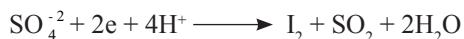


But with excess chlorine water a colourless solution of hypobromous or bromic acid is produced.



Analytical chemistry of Iodide (I^-)

- (i) When a salt having iodide is warmed with conc. H_2SO_4 , violet vapours of I_2 are evolved (due to oxidation of I^- to iodine I_2).



Or,



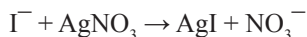
Liberated I_2 is identified by starch paper, which turns blue.



The colour is due to adsorption of I_2 on starch channels.

(ii) AgNO_3 solution reagent

An iodide forms yellow curdy ppt. of AgI with AgNO_3 solution. The ppt. is insoluble in dil. HNO_3 and NH_3 .

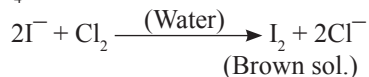


The yellow ppt. is soluble in KCN solution or $\text{Na}_2\text{S}_2\text{O}_3$ solution due to formation of complex ion.



(iii) Chlorine water reagent

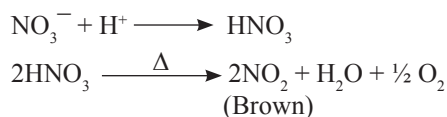
Chlorine water oxidizes an iodide to I_2 turning the solution brown. However, on shaking with CS_2 or CCl_4 , the organic layer turns violet due to dissolved I_2 .



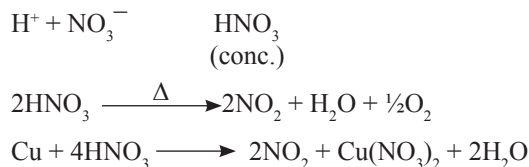
When excess chlorine water is added, I_2 is oxidized to colourless iodic acid (HIO_3).

**Analytical chemistry of Nitrate (NO_3^-)**

- (i) A nitrate on heating with conc. H_2SO_4 gives brown fumes of NO_2 .



- (ii) When a nitrate is heated with Copper turnings and conc. H_2SO_4 more intense brown fumes are produced. It is due to formation of additional NO_2 on reaction of Cu with conc. HNO_3 produced in situ.



This reaction distinguishes a NO_3^- from a Br^- . (In case of Br^- , there is no increase in the intensity of brown fumes on heating with Cu turnings).

(iii) Ring test for NO_3^-

Reagent for this test is fresh $FeSO_4$ solution and conc. H_2SO_4 . Nitrate solution (all nitrates are soluble in water) is treated with freshly prepared $FeSO_4$ solution. Then conc. H_2SO_4 is poured slowly down the side of the test tube. A brown ring is formed at the junction of aq. solution and conc. H_2SO_4 . The following reactions take place:



- (b) NO produced is absorbed by ferrous sulphate solution to form the deep brown compound, $[Fe(H_2O)_5NO]^{2+}$.



The deep brown colour is due to charge transfer from NO (it has one electron in π^* MO) to Fe^{2+} .

The formal oxidation number of iron in brown ring compound is +1.

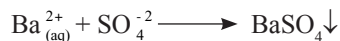
Analytical chemistry of Sulphate (SO_4^{2-})

- (i) Sulphates are not decomposed by acids.
- (ii) Tests for soluble and insoluble sulphates are performed in different ways.

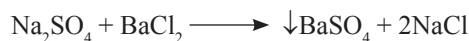
(a) Test for soluble sulphates

It is done with BaCl_2 solution reagent.

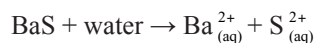
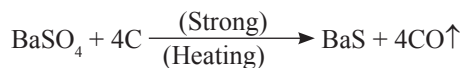
Sulphates form white ppt. of BaSO_4 , which is insoluble in dil. HCl or dil. HNO_3 .



Or,

**(b) Test for insoluble sulphate**

Insoluble sulphate is heated strongly with C (or Na). In this process, sulphate is reduced to sulphide. It is dissolved in water and is tested for sulphide by Pb – acetate or sodium nitroprusside.

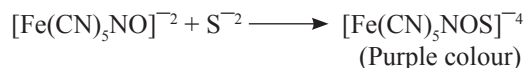
**Test with Pb – acetate**

Lead acetate solution forms black ppt. of PbS with S^{2-} .



Test with Na – nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$

Sodium nitroprusside solution forms purple colour with S^{2-} .

**TESTS FOR BASIC RADICALS**

Metal ion and NH_4^+ are basic radicals. The test consists the following steps:

- (i) Dry tests for basic radicals.
- (ii) Solution (or wet) tests for basic radicals.

Dry tests for basic radicals

Important steps in dry tests are:

- (i) Action of heat
- (ii) Heating on charcoal cavity
- (iii) Flame test
- (iv) Borax bead test
- (v) Microcosmic salt bead test.

Action of heat on salt

Heating of the salt in a dry test tube gives some very clear information.

Table 20.10

| Salt | Change observed | Inference |
|--------|--|---|
| Heated | (i) Sublimate is formed White Yellow | HgCl ₂ , HgBr ₂ , Hg ₂ Cl ₂ , NH ₄ Cl S, HgI ₂ |
| | (ii) Yellow when hot colourless when cold | Zn – salt (ZnO) |
| | (iii) Yellow hot and cold both | PbO (Pb – salt) |
| | (iv) Brown fumes | Nitrates (NO ₃ ⁻) of heavy metals (+2 or +3 oxidation states) |

Heating on charcoal cavity

The salt is heated on a charcoal cavity in an oxidizing flame with the help of a blowpipe.

Table 20.11

| Observation | Inference |
|--|---|
| Glows It is due to the formation of oxides like MgO, CaO, Al ₂ O ₃ , ZnO etc., which are refractory materials. | Alkaline earth metal salt, Al – salt, Zn – salt. |

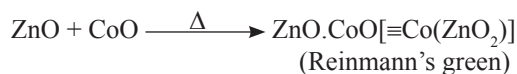
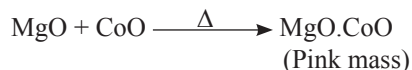
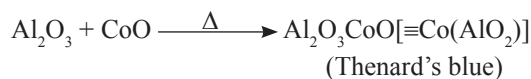
If the above happens, the salt is heated with 1–2 drops of Co(NO₃)₂ solution in O. F.?

| | |
|------------|-----------|
| Blue mass | Al – salt |
| Green mass | Zn – salt |
| Pink mass | Mg – salt |

Salts of Al, Mg and Zn on heating are converted into corresponding oxides, Al₂O₃, MgO and ZnO respectively. The Co(NO₃)₂ also breaks into CoO on heating.



Al₂O₃, MgO and ZnO combine with CoO giving mixed oxides having specific colour.



Flame test

A Pt. wire is dipped into conc. HCl and then into the salt. It is then placed into the base of the non-luminous Bunsen flame. The flame acquires specific colour. It shows presence of a specific metal.

The sodium golden yellow flame masks other colours. Therefore, to get rid of this trouble the flame is viewed through cobalt blue glass. The results are given:

Table 20.12

| Flame colour with naked eye | Flame colour through Co – glass | Metal |
|-----------------------------|---------------------------------|-------|
| Persistent golden yellow | Nil | Na |
| Violet (or Lilac) | Crimson | K |
| Brick red | Light green | Ca |
| Crimson | Purple | Sr |
| Yellowish green | Bluish green | Ba |
| Bluish flame | – | Cu |

Note:

In the presence of Cu, Pt – wire is slowly corroded.

Reason for use of conc. HCl

The chlorides of the metal are more volatile. So conc. HCl is used.

Reason for flame colour

The flame colour is due to emission of radiation in the visible region. When heated loosely bound electron is excited to higher energy levels. When the excited electron returns to the ground state, radiation in the visible region is emitted producing colour. The energy gap between the ground and the excited levels differ from one metal to the other. Thus each metal produces its unique colours.

Borax bead test

This test is effective for coloured salts, that is, salts containing transition metal ions (M^{n+}).

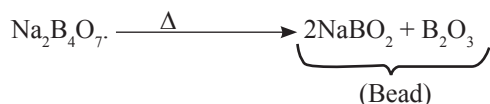
Borax is heated on a Pt–wire loop. First it swells and then on strong heating converts into an opaque bead, which contains $NaBO_2$ and B_2O_3 . The hot bead is touched with the salt. Then heated in RF and OF. Colour of the bead is observed in hot and cold conditions. The results are given below:

Table 20.13

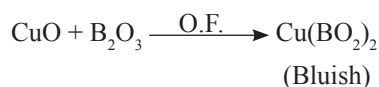
| Colour | | | | Metal |
|------------|------------|---------------|-------------|-------|
| R.F. | | O.F. | | |
| Cold | Hot | Cold | Hot | |
| Reddish | Colourless | Blue | Green | Cu |
| Green | Green | Yellow | Reddish | Fe |
| Green | Green | Green | Dark yellow | Cr |
| Colourless | Colourless | Violet | Violet | Mn |
| Blue | Blue | Blue | Blue | Co |
| Black | — | Reddish brown | — | |

Chemistry of Borax bead test

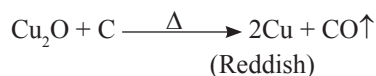
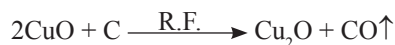
Borax is, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. On strong heating it converts into NaBO_2 and B_2O_3 i.e., the bead material.



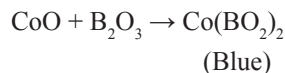
Tr – metal salt on heating decomposes to metal oxide. This reacts with bead material to produce metal metaborate.



In the reducing flame metal comes down to lower oxidation state. Therefore, colour is different.



In the case of Co salt, the oxide CoO , is not reduced by C. Therefore, shows the same colour.

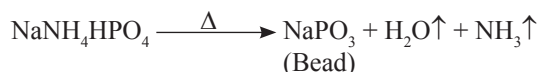


For Fe – salt:

Fe(III) metaborate, $\text{Fe}(\text{BO}_2)_3$ in OF, so the colour is yellowish (cold). But Fe(II) metaborate is present in R.F. Hence the colour is greenish.

Microcosmic salt bead test

It is used to test silicates. Sodium ammonium hydrogen phosphate tetrahydrate $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ is known as microcosmic salt. This salt on heating produces colourless transparent bead, which is sodium metaphosphate.



When a silicate is strongly heated in the bead, SiO_2 is liberated which moves in the bead as skeleton (silica skeleton).



Fusion mixture

A mixture of Na_2CO_3 and K_2CO_3 in the ratio 1: 3 (i.e., $\text{Na}_2\text{CO}_3: 3\text{K}_2\text{CO}_3$) is called fusion mixture. It is used for melting salt on charcoal cavity.

Solution test for basic radicals

There are many cations, included in salt analysis. It is impossible to test them one by one. To make the test process practically easy and suitable, the cations are first separated into groups (of analytical table). This separation is based on in solubility of compounds. It is given below:

Table 20.14

| Group | Cations | Medium of ppt. | Reagent for ppt. | ppt. |
|------------------|---|--|--|---|
| I | $\text{Ag}^+, \text{Pb}^{+2}, \text{Hg}_2^{2+}$ | dil. HCl | dil. HCl | Chlorides (AgCl , PbCl_2 , HgCl_2) |
| II | (II _A ⁻) $\text{Hg}^{2+}, \text{Pb}^{+2}, \text{Cu}^{2+}$, $\text{Cd}^{+2}, \text{Bi}^{+3}$ (II _B ⁻) $\text{As}^{+3\text{or}+5}$, $\text{Sb}^{+3\text{or}+5}, \text{Sn}^{+2\text{or}+4}$ | dil. HCl | dil. HCl + H_2S gas | Sulphides |
| III _A | $\text{Fe}^{3+}, \text{Cr}^{+3}, \text{Al}^{+3}$ | Alkaline (NH_4OH) | NH_4Cl + NH_4OH | Hydroxides ($\text{M}(\text{OH})_3$) |
| III _B | $\text{Mn}^{+2}, \text{Co}^{+2}, \text{Ni}^{+2}, \text{Zn}^{+2}$ | Alkaline (NH_4OH) | NH_4Cl + NH_4OH + H_2S gas | Sulphides MS |
| IV | $\text{Ca}^{+2}, \text{Sr}^{+2}, \text{Ba}^{+2}$ | Alkaline (NH_4OH) | NH_4Cl + NH_4OH + $(\text{NH}_4)_2\text{CO}_3$ | Carbonates MCO_3 |
| V | $\text{NH}_4^+, \text{Na}^+, \text{K}^+, \text{Mg}^{+2}$ No group reagent. The solution left after the separation of group IV is analysed for these cations. | | | |

Note

- (i) Group ppt. is analysed for individual metal ions.
- (ii) The concentration of HCl, 0.3M, is essential for precipitation of group II metals. With higher HCl concentration Pb, Cd and Sn(II) are incompletely precipitated. With very low HCl concentration Gr III_B sulphides (MnS, CoS, NiS and ZnS) may be precipitated. (Common ion effect of H⁺ from HCl).
- (iii) For precipitation of Gr III_A hydroxides, solution after precipitation of Gr II is boiled first with a few drops of conc. HNO₃. It is to oxidize Fe²⁺ to Fe³⁺. The Fe²⁺ hydroxide is partially soluble. NH₄Cl is added in NH₄OH to check HO⁻ ions conc. So that Gr III_B and Mg hydroxides will not ppt. (common ion effect of NH₄⁺ ions)
- (iv) During the precipitation of Gr III_B, too much H₂S should not be passed. It converts NiS partially into colloidal solution.

Precautions for precipitations of Gr IV

- (a) The solution for precipitation of group IV contains high concentration of NH₄⁺ ions. It may lead to incomplete precipitation of Gr IV metal ions due to the reaction.



(Hydrogen carbonates are water soluble).

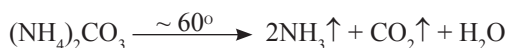
The high concentration of NH₄⁺ is destroyed by heating with a few drops of conc. HNO₃ at lower temperature.



- (b) The (NH₄)₂CO₃ reagent contains NH₄HCO₃, which forms soluble hydrogen carbonate with Gr IV metal ions, M(HCO₃)₂. Therefore, for complete precipitation high concentration of NH₄OH is maintained which destroys NH₄HCO₃ and increases the concentration of CO₃²⁻ ions.



- (c) For precipitating Gr IV metal ions, the solution should not be warmer than ~ 50°C as above 60°C (NH₄)₂CO₃ decomposes.



- (d) The solution in no case be boiled because of the reaction.



which will shift equilibrium towards right i.e., incomplete precipitation.

Test for NH₄⁺ ion

It is tested in the original salt because NH₄⁺ ions are added during separation of groups, III_A, III_B and IV.

- (i) All NH₄⁺ salts evolve NH₃ gas with alkali (NaOH)



NH₃ is tested:

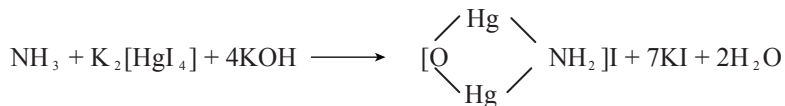
- (a) By its specific smell.
- (b) NH₃ turns red litmus blue or turmeric paper brown.
- (c) NH₃ forms white fumes of NH₄Cl with glass rod moistened with conc. HCl.

- (d) NH_3 turns filter paper moistened with $\text{MnCl}_2 + \text{H}_2\text{O}_2$, brown. It is due to formation of hydrated Mn(IV) oxide.



- (ii) Nessler's reagent test

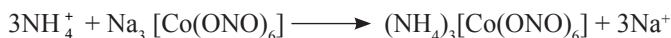
Alkaline solution of $\text{K}_2[\text{HgI}_4]$ (i.e., $\text{K}_2[\text{HgI}_4] + \text{KOH}$) is known as Nessler's reagent. This reagent produces brown ppt. or colour with NH_3 or NH_4^+ .



This test is very sensitive ($0.3 \mu\text{g NH}_3$ in 0.002 ml) and can detect traces of NH_3 in drinking water.

- (iii) Sodium cobaltinitrite solution reagent

This reagent forms yellow ppt. with NH_4^+ ion (similar to K^+ , as both have almost equal radii).

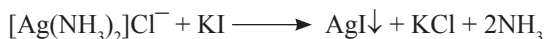
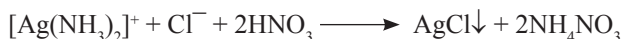


Test for Gr I metal ions, Ag^+ , Pb^{+2} , Hg_2^{+2}

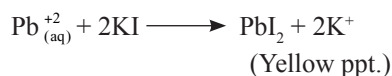
Table 20.15

| Gr I ppt. | Solvent for ppt. | Reagent for M^{n+} | Product (ppt. or colour) |
|--------------------------|--|---------------------------------------|---|
| AgCl | NH_3 solution | (i) dil. HNO_3 | White ppt. AgCl |
| | | (ii) KI solution | Yellow ppt. AgI |
| PbCl_2 | Hot water | (i) K_2CrO_4 solution | Yellow ppt, PbCrO_4 |
| | | (ii) KI solution | Yellow ppt. PbI_2 |
| Hg_2Cl_2 | Aquaregia (conc. $\text{HNO}_3 + 3\text{HCl}$) | (i) SnCl_2 solution | White ppt, Hg_2Cl_2 |
| | | (ii) Cu - foil | ultimately grey, Hg Grey Hg deposit on foil. |

Reactions involved :

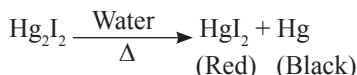
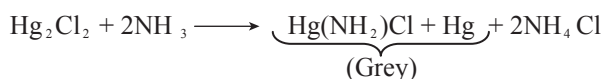
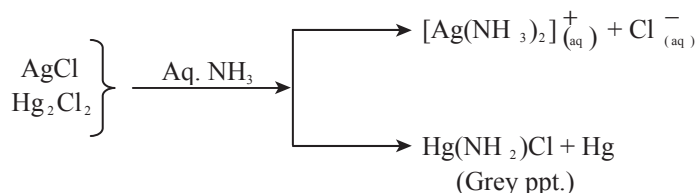
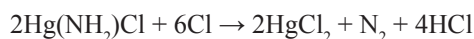


- (ii) PbCl_2 ppt.



(iii) Hg_2Cl_2 ppt(b) KI reagent + Hg_2^{+2} The Hg_2^{+2} ion has some specific reaction with iodide ions.(i) When KI solution is added slowly in a cold solution of Hg_2^{+2} , green Hg_2I_2 precipitate.

(ii) With excess reagent disproportionation reaction takes place giving tetraiodomercurate (II) and finely divided Hg.

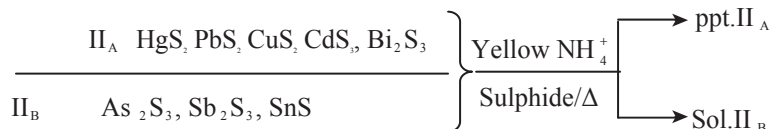
(iii) When Hg_2I_2 is boiled with water red HgI_2 and finely divided black Hg are formed.**Note:**Aq. NH_3 can be used to separate AgCl from Hg_2Cl_2 . It is because aq. NH_3 converts AgCl into soluble complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ and precipitates mercury as $[\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}]$.The grey ppt. also dissolves in aquaregia producing HgCl_2 . it is tested as above

From
aquaregia

Tests for GrII

The Gr II of analytical table constitutes Gr II_A and Gr II_B. They are separated with the help of yellow ammonium sulphide. It is a polysulphide but formulated as (NH₄)₂S₂ for writing reaction.

The GrII ppt. is heated with yellow ammonium sulphide at around 50 – 60°C for a few minutes (~5 mins). The GrII_A sulphides are insoluble in yellow ammonium sulphide whereas GrII_B sulphides dissolve in it forming thiosalts.

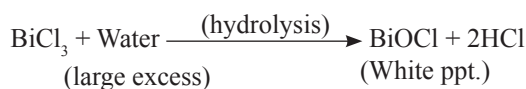
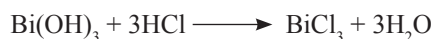
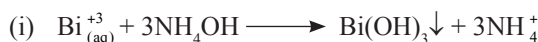
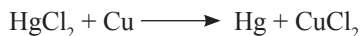


Or,

**Test for GrII_A metal ions****Table 20.16**

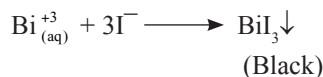
| GrII _A ppt | Solvent for ppt. | Reagent for M ⁿ⁺ | Product (ppt/colour) |
|--------------------------------|----------------------|---|---|
| HgS | Aquaregia | (i) SnCl ₂ | First white ppt., Hg ₂ Cl ₂ changing ultimately to gray (Hg) |
| | | (ii) Cu foil | Gray Hg deposits on foil |
| PbS | 50% HNO ₃ | (i) H ₂ SO ₄ | White ppt. of PbSO ₄ . It is soluble in AcONH ₄ . |
| | | (ii) K ₂ CrO ₄ sol. | Yellow ppt. PbCrO ₄ |
| Bi ₂ S ₃ | 50% HNO ₃ | NH ₄ OH | White ppt. Bi(OH) ₃ . It dissolves in dil. HCl sol. when added in large volume of water gives white ppt. of BiOCl. |
| CuS | 50% HNO ₃ | K ₄ [Fe(CN) ₆] | Brown ppt., Cu ₂ [Fe(CN) ₆] |
| CdS | 50% HNO ₃ | H ₂ S | Solution is neutralized by NH ₄ OH. Then forms an yellow ppt. of CdS. |

Reactions

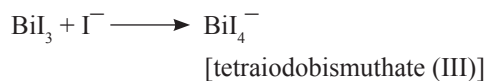


The $\text{Bi}^{+3}_{(\text{aq})}$ has some specific reactions with iodide (I^-) ions.

(a) When KI sol. is added dropwise, black ppt. of BiI_3 is formed.

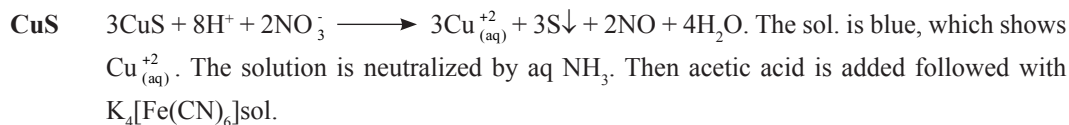


(b) The black ppt. dissolves in excess KI and forms orange coloured BiI_4^- .



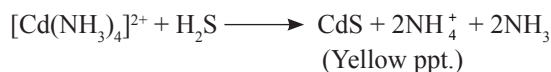
(c) When diluted, the BiI_4^- ion gives back black BiI_3 .

(d) When the black ppt. of BiI_3 is heated with water, orange coloured bismuthyl iodide (BiOI) is formed.





The solution is colourless. The solution is neutralized by aq. NH_3 and H_2S is passed immediately. A yellow ppt. is formed.



(1) Test of Cu^{2+} and Cd^{2+} in a mixture (i.e., in the presence of each other)

Both Cu^{2+} and Cd^{2+} ppt. with H_2S in dil. HCl medium as CuS and CdS. They can be separated by

- (i) dil. H_2SO_4
- (ii) KCN solution.

(i) Dilute H_2SO_4 (Molar solution)

CuS is insoluble in boiling dil. H_2SO_4 where as CdS is soluble.



When the filtrate is diluted and H_2S gas is passed, yellow CdS ppts,

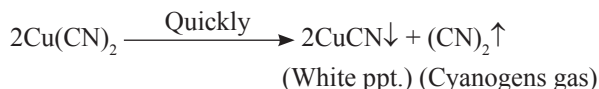
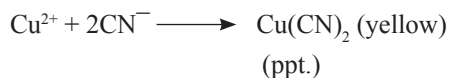


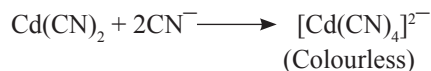
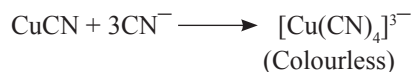
The ppt. CuS is dissolved in HNO_3 . The solution is neutralized by aq. NH_3 . Then made acidic with CH_3COOH followed with addition of $\text{K}_4[\text{Fe}(\text{CN})_6]$ reagent. A brown ppt. indicates Cu^{2+} .



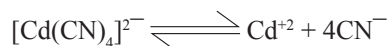
(ii) KCN solution

When excess KCN is added to a solution containing Cu^{2+} and Cd^{2+} , tetracyanocuprate(I). $\text{Cu}(\text{CN})_4^{3-}$ and tetracyanocadmiate (II) are produced. The reactions are



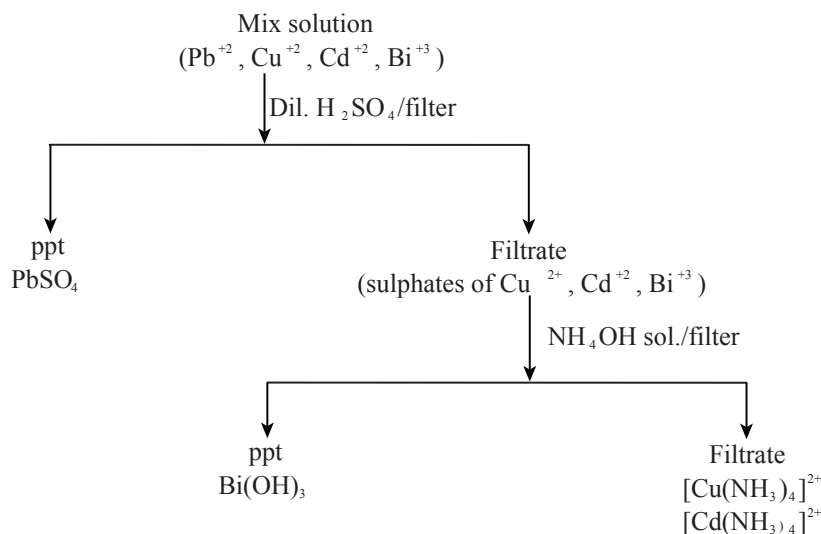


The Cd^{+2} complex is not too stable and ionizes to produce enough Cd^{+2} ions.

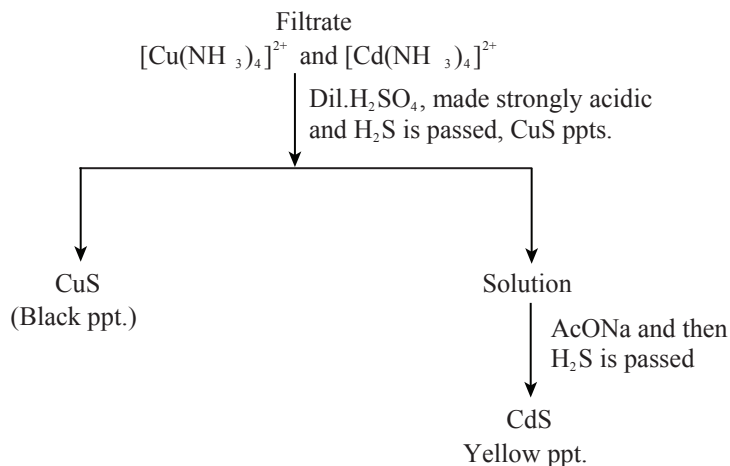


Therefore, when H_2S gas is passed in the solution whole of the Cd^{+2} ppt. as yellow CdS and is separated from Cu^{2+} . Copper is then tested from the filtrate after filtering out CdS .

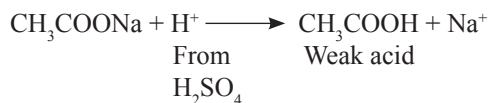
(2) Analysis of a mixture containing Pb^{+2} , Cu^{+2} , Cd^{+2} , Bi^{+3}



Then the individual M^{+n} ions are tested as described above or below.



On treating the solution with AcONa, the acidity is reduced due to the reaction.



So, Cd⁺² ppts with S⁻²



Tests for GrII_B metal ions (As⁺³, Sb⁺³, Sn⁺²)

Group II_B sulphides are present in yellow ammonium sulphide as soluble thiosalts. This solution on acidification with dil. HCl ppts sulphides of As⁺⁵, Sb⁺⁵ and Sn⁺⁴.

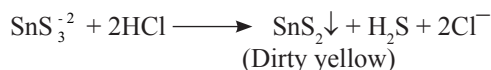
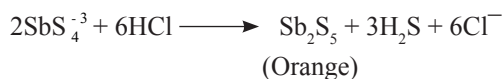
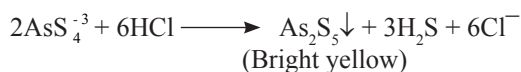
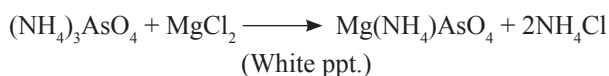


Table 20.17

| GrII _B ppt. | Solvent | Reagent for M ⁿ⁺ | Product (ppt or colour) |
|--------------------------------|--|--|--|
| As ₂ S ₅ | H ₂ O ₂ /NH ₃ | Magnesia mixture (MgCl ₂ +NH ₄ Cl+liq.NH ₃) | (i) White ppt. Mg(NH ₄) AsO ₄ (ii) White ppt. + AgNO ₃ sol.+CH ₃ COOH → Reddish ppt. Ag ₃ AsO ₄ |
| Sb ₂ S ₅ | Conc. HCl | NH ₃ sol. then oxalic acid + H ₂ S | Orange ppt. Sb ₂ S ₃ |
| SnS ₂ | Conc. HCl | Sol. diluted +Fe +HgCl ₂ solution reagent | White ppt. Hg ₂ Cl ₂ , ultimately changing into gray (Hg) |

Reactions

As₂S₅ It is oxidized by H₂O₂ in alkaline solution to AsO₄⁻³.

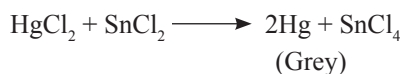
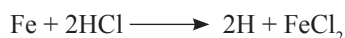


**Sb₂S₅**

The solution is neutralized by NH_4OH , and some oxalic acid is added and heated. Then H_2S gas is passed. Orange coloured Sb_2S_3 ppt is formed.

**SnS₂**

Solution is diluted with water and clean iron wire is added and warmed. This solution is treated with HgCl_2 reagent. A white ppt. of Hg_2Cl_2 is first formed which ultimately changes into gray due to formation of impure Hg.

**Test for group III_A metal ions (Fe^{3+} , Al^{+3} , Cr^{+3})**

The group ppt. is hydroxide, $\text{M}(\text{OH})_3$. Among the hydroxides $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are amphoteric but not the $\text{Fe}(\text{OH})_3$. This difference is exploited in their separation and tests.

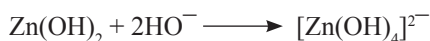
Table 20.18

| GrIII _A ppt. | Solvent for the ppt. | Reagent for M ⁿ⁺ | Product (ppt or colour) |
|--|--|---|---|
| $\text{Al}(\text{OH})_3$ (colourless) | $\text{NaOH} + \text{H}_2\text{O}_2$ Or aq. Na_2O_2 Colourless solution $\text{Al}(\text{OH})_4^-$ | $\text{NH}_4\text{Cl}/\Delta$ | White getlatnous ppt. $\text{Al}(\text{OH}_3)$ |
| $\text{Cr}(\text{OH})_3$ (Green) | $\text{NaOH} + \text{H}_2\text{O}_2$ Yellow solution containing CrO_4^{-2} | (i) $\text{AcOH}/\text{Pb}(\text{AcO})_2$ (ii) dil. HNO_3 + amyl alcohol + a few drops H_2O_2 | Yellow ppt. PbCrO_4 Blue oranic layer, CrO_5 in amyl alcohol |
| $\text{Fe}(\text{OH})_3$ (Brown) | Dil. HCl | (i) Solid NH_4SCN (ii) $\text{K}_4[\text{Fe}(\text{CN})_6]$ sol. | $[\text{FeSCN}]^{2+}$ Blood red colour $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ Blue sol. |

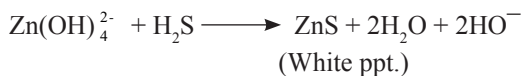
| GrIII _B ppt | Solvent for ppt. | Reagent for M ⁿ⁺ | Product (ppt. or colour) |
|------------------------|------------------|--|--|
| CoS (black) | Aquaregia | NH ₄ SCN + amyl alcohol + conc. HCl | Deep blue colour, due to H ₂ [Co(SCN) ₄]. It is stable in amyl alcohol. |
| NiS (black) | Aquaregia | Dimethyl glyoxime + NH ₄ OH | Red ppt. of Ni(Dmg) ₂ |

Reaction**MnS**

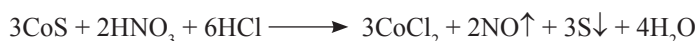
The nitric acid solution on treatment with PbO₂ (or NaBiO₃) form purple sol. of permanganic acid (HMnO₄).

**ZnS**

Even without acidification with acetic acid, H₂S may precipitate ZnS.

**CoS**

It dissolves in aquaregia.

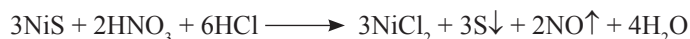


Solution is treated with a few drops of conc. HCl about 1ml amyl alcohol and solid NH_4SCN are added. After shaking, the alcoholic layer turns blue.



NiS

It also dissolves in aquaregia.



Solution is treated with dimethyl glyoxime reagent followed by excess NH_4OH . A red ppt is formed, $\text{Ni}(\text{Dmg})_2$.



The red ppt. is a hydrogen bonded chelate complex. It has square planar structure and N – atoms are coordinated to Ni^{2+} .

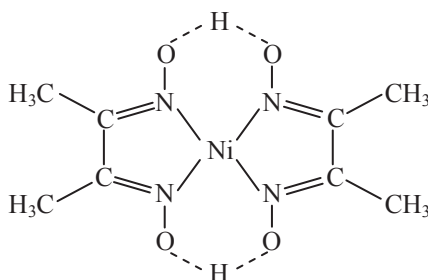


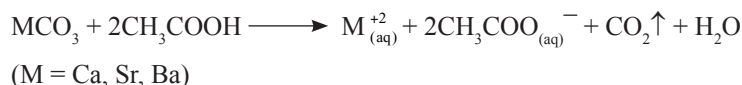
Figure 20.1

The H – bonding is strong enough to make both O – H bonds equal (shown as perforated line).

Tests of group IV metal ions (Ca^{+2} , Sr^{+2} , Ba^{+2})

Table 20.20

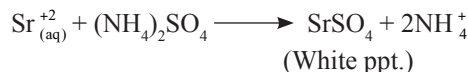
| Gr IV ppt. | Solvent for ppt. | Reagent for M^{n+} | Product (colour/ppt) |
|-----------------|------------------|---|---|
| BaCO_3 | Acetic acid | K_2CrO_4 sol. | Yellow ppt. of BaCrO_4 , further confirmed by flame test, grass green flame. |
| SrCO_3 | Acetic acid | $(\text{NH}_4)_2\text{SO}_4$ saturated sol. | White ppt. of SrSO_4 , produces crimson flame |
| CaCO_3 | Acetic acid | $(\text{NH}_4)_2\text{C}_2\text{O}_4$ | White ppt. of CaC_2O_4 produces brick red flame |

Reactions

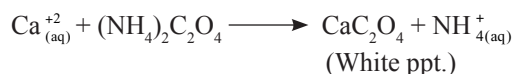
(i) Solution is treated with K_2CrO_4 sol. an yellow ppt. proves presence of Ba^{+2} .



(ii) Solution is concentrated and treated with $(\text{NH}_4)_2\text{SO}_4$ saturated solution. A white ppt. proves Sr^{+2} .



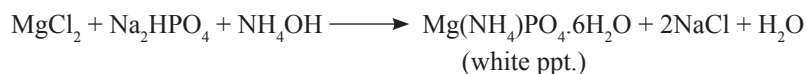
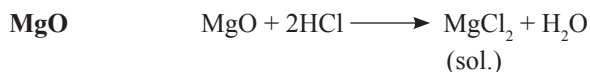
(iii) Solution is concentrated and treated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and warmed. A white ppt. shows the presence of Ca^{+2} .

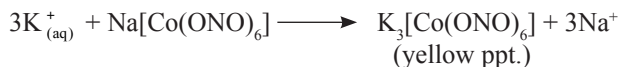
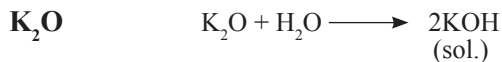
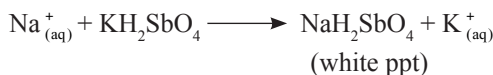
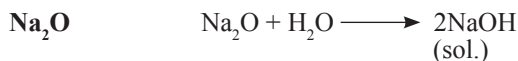
**Tests for group V cations (NH_4^{+} , Mg^{+2} , Na^{+} , K^{+})**

There is no specific reagent for this group. The filtrate after separation of group IV is analysed for the group cations. As NH_4^{+} -compounds are added during group separation, it is tested in original salt supplied. The filtrate is concentrated to dryness. The dry mass may contain oxides of Mg, Na and K.

Table 20.21

| Oxide | Solvent | Reagent for M^{n+} | Product (ppt. or colour) |
|-----------------------|----------|---|--|
| MgO | dil. HCl | NH_4Cl + NH_4OH + Na_2HPO_4 | White ppt. $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ |
| K_2O | Water | Sodium cobaltinitrite sol., $\text{Na}_3[\text{Co}(\text{ONO})_6]$ | Yellow ppt of $\text{K}_3[\text{Co}(\text{ONO})_6]$ confirmed by flame test, violet (or lilac) flame |
| Na_2O | Water | Pot pyroantimonate sol., KH_2SbO_4 | White ppt., NaH_2SbO_4 confirmed by flame test, persistent golden yellow flame |

Reactions



PRACTICE QUESTIONS

- An inorganic salt aq. solution and CCl_4 when treated with chlorine water produces violet organic layer, the salt may be
 - a nitrate
 - a bromide
 - an iodide
 - an iodate
- A salt solution when treated with $-\text{K}_4[\text{Fe}(\text{CN})_6]$ produces brown ppt. The salt may contain the metal ion
 - Fe^{2+}
 - Cu^{2+}
 - Mn^{2+}
 - Ni^{2+}
- Which of the following hydroxides forms yellow solution on reaction with NaOH and H_2O_2 ?
 - $\text{Sn}(\text{OH})_2$
 - $\text{Zn}(\text{OH})_2$
 - $\text{Cr}(\text{OH})_3$
 - $\text{Al}(\text{OH})_3$
- When a metal chloride, solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 are heated together, deep red vapour evolves which is formulated as
 - CrOCl_2
 - CrO_2Cl_2
 - CrO_2Cl
 - Cr_2OCl_2
- Blue colour or ppt is produced when $\text{K}_3[\text{Fe}(\text{CN})_6]$ reacts with
 - $\text{Fe}(\text{III})$ ions
 - $\text{Fe}(\text{II})$ ion
 - $\text{Cu}(\text{II})$ ions
 - $\text{Zn}(\text{II})$ ions
- A colourless solid is soluble in hot water. When H_2S is passed in hot acidic solution of the solid, a black ppt. is formed. The solid is
 - Cu^{2+} – salt
 - Hg^{2+} – salt
 - Pb^{2+} – salt
 - Na^+ – salt
- A white solid is first heated with dil. H_2SO_4 and then with conc. H_2SO_4 . No change was seen in either case. The solid is a
 - thiosulphate
 - sulphide
 - sulphite
 - sulphate
- Which of the following ions cannot be precipitated by H_2S in the presence of aq. NH_3 ?
 - Mn^{2+}
 - Zn^{2+}
 - Co^{+2}
 - Cd^{+2}
- Mark the correct statement, when H_2S gas is passed in aq. solution of sodium nitroprusside solution
 - no violet colour is produced
 - the complex ion $[\text{Fe}(\text{CN})_5\text{NOS}]^{-4}$ is formed
 - the complex ion $[\text{Fe}(\text{CN})_5\text{NOS}]^{-2}$ is formed
 - the complex ion $[\text{Fe}(\text{CN})_4\text{NOS}]^{-4}$ is formed
- A salt solution is acidified with HCl , ammonium thiocyanate is added and then some conc. HCl is also added. There develops a deep blue colour. The metal ion in the salt and blue compound respectively are
 - Fe^{2+} , $\text{Fe}(\text{SCN})_2$
 - Co^{+2} , $\text{H}_2\text{Co}(\text{SCN})_4$
 - Co^{+3} , $\text{Co}(\text{SCN})_3$
 - Ni^{2+} , $[\text{Ni}(\text{CNS})^+]$
- A solution contains, Fe^{3+} , CO^{+3} , Cr^{+3} , Mn^{+2} , NH_4Cl and NH_4OH is added to the solution. Mark the correct statement.
 - Fe^{3+} and CO^{+3} hydroxides will ppt.
 - CO^{+3} and Cr^{+3} hydroxides will ppt.
 - Fe^{3+} and Cr^{+3} hydroxides will ppt
 - Cr^{+3} and Mn^{+2} hydroxides will ppt.

12. An inorganic salt liberates a pungent gas with dil. HCl, which turns dichromate paper green. The salt is a
- (a) Carbonate (b) Nitrate
(c) Sulphite (d) Sulphate
13. Which of the following statements is not correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?
- (a) A deep red vapour is evolved.
(b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4 .
(c) Chlorine gas is evolved.
(d) Chromyl chloride is formed.
14. A salt solution is acidified with HCl, ammonium thiocyanate is added and then some conc. HCl is also added. There develops a deep blue colour. The metal ion in the salt and blue compound respectively are
- (a) Fe^{2+} , $Fe(SCN)_2$
(b) Co^{+2} , $H_2Co(SCN)_4$
(c) Co^{+3} , $Co(SCN)_3$
(d) Ni^{2+} , $[Ni(CNS)]^+$
15. Flame colour produced by potassium salts is
- (a) Crimson (b) Yellow
(c) Violet (d) red

21

Problems on Inorganic Reactions



1. An inorganic salt (X) behaves in the following way:
 - (a) Sublimes on heating and the aqueous solution of X is slightly acidic.
 - (b) Solution of X gives blood red solution with solid NH_4SCN containing B.
 - (c) X when heated strongly with solid $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 gives off deep red vapour of a compound C.
 - (d) The deep red vapours form yellow solution of compound D with NaOH solution.

Identify X, B, C and D and give balance equation for each step.

2. White inorganic compound (X) is used as disinfectant and gives the following reactions:
 - (i) Forms greenish yellow gas with CO_2 .
 - (ii) A light brown coloured solution when KI and CH_3COOH is added to its suspension in water.Identify X and write balance chemical equations for the steps (i) and (ii).

3. A strong base [A] which is not stable in water on reaction with carbon at high temperature gives a diatomic gas [B] and a water soluble compound [C]. The compound [C] on reaction with CuSO_4 gives another gas [D]. The stoichiometric mixture of [D] and oxygen burns to produce one of the hottest flames. The compound [A] produces golden yellow flame.

Identify A, B, C, D and write chemical equations for each change.

4. When 10 g of a compound A was analysed, contained 5.0 g C, 1.25 g H and 3.75 g Al. The compound A reacts in the following way:
 - (i) 'A' with excess water gives a gas B and forms a white ppt. C.
 - (ii) C dissolves in dil NaOH and HCl.
 - (iii) 10 cm^3 of B requires 20 cm^3 of oxygen for complete combination producing only CO_2 and H_2O .

Identify A, B, C and write balance chemical equation for the changes taking place in the steps (i), (ii) and (iii).

5. A colourless crystalline solid [A] gives two gases B and C on strong heating along with a metallic residue D. The gas B dissolves in water in the presence of oxygen to form a compound E. The residue D is soluble in E regenerating A. The solid A gives white ppt. with KCN, which is soluble in excess of KCN. Identify A to E giving chemical equations.
6. When a mineral A is fused with a strong alkali in the presence of air, a green mass B is obtained. The green mass on extraction with water followed by acidification with dil. H_2SO_4 , converts into a red purple solution containing C and A is regenerated. Identify A, B and C. Write the chemical equations also.

7. When a mineral A is fused with Na_2CO_3 in air and the fused mass is extracted with water two substances B and C are obtained. The compound C is brown, water insoluble whereas B is soluble in water forming yellow solution. The compound C is filtered out and the yellow filtrate containing B on acidification turns orange corresponding to another compound D. The solution on crystallization gives orange crystals of D. The compound D forms a blue solution with H_2O_2 in acid medium, corresponding to E which is not stable in aq. medium. Identify A to E and write the chemical equation.
8. An unknown mixture contains one or two of the following:
 AgNO_3 , BaCO_3 , CaCl_2 , $(\text{Al})_2(\text{SO}_4)_3$ and NaOH . The mixture behaves in the following way:
 (a) Completely soluble in water and the solution gives pink colour with phenolphthalein.
 (b) On adding dil. HCl to the above solution, a white ppt. is obtained which dissolves with further addition of the acid.
 What components is/are present in the mixture. Write involved chemical equations.
9. A metal chloride (X) may be any one of the following HgCl_2 , PbCl_2 , CuCl_2 and SnCl_2 . The X behaves in the following way:
 (i) An aq sol. of X forms black ppt with H_2S gas.
 (ii) The black ppt. is insoluble in yellow ammonium sulphide
 (iii) When an aq. solution of KI is added in stoichiometric amount to a solution of X, yellowish precipitates is formed.
 (iv) When an aq. solution of NaOH is added in stoichiometric amount to a solution of X, yellowish precipitates is formed.
 Identify X and write balance chemical equation for each step.
10. Compound A is light green crystalline solid. It gives the following tests:
 (i) Dissolves in dil. H_2SO_4 without evolution of any gas
 (ii) When a drop of KMnO_4 is added to the above solution of A, the pink colour disappears.
 (iii) 'A' on strong heating gives a brown solid B and two gases C and D which are pungent in smell.
 (iv) The gas mixture. (C + D) is passed into dichromate solution which turns green.
 (v) The green solution from step (iv) gives a white ppt. E with $\text{Ba}(\text{NO}_3)_2$ solution.
 Identify A to E and write the chemical equations.
11. A crystalline compound forms white ppt. with AgNO_3 solution which is soluble in aq. NH_3 and responds following reaction also:
 (i) Forms black ppt. A with KI solution when added dropwise.
 (ii) The ppt. A dissolves in excess KI solution to produce an orange compound B.
 (iii) When diluted with water, the orange compound B gives black precipitate A.
 (iv) When the ppt. A is heated with water an orange compound C is formed.
 Identify X, A, B and C and write chemical reactions.
12. When a white crystalline compound X is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 , a reddish brown gas A is evolved. On passing A through caustic soda solution, a yellow coloured solution of B is obtained. Neutralizing the solution of B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X. Write the equations of reactions involved.
13. (a) A white solid is either Na_2O or Na_2O_2 . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
 (b) A, B and C are three complexes of chromium (III) with the empirical formula $\text{H}_{12}\text{O}_6\text{Cr}$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated

H_2SO_4 , whereas complexes B and C lose 6.75% and 13.5% of their original weight, respectively, on treatment with concentrated H_2SO_4 . Identify A, B and C.

14. A white substance A reacts with dilute H_2SO_4 to produce a colourless gas B and a colourless solution C. The reaction between B and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution produces a green solution and a slightly coloured precipitated D. The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. An anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify A, B, C, D and E. Write the equation of the reactions involved.
15. (i) An inorganic iodide 'A' on heating with KOH gives a gas B and the solution of a compound C.
(ii) The gas B on strong heating with air gives a compound D and water.
(iii) A copper sulphate solution finally gives metallic Cu on passing the gas B.
(iv) CuSO_4 solution gives a white ppt. E on reaction with C.
Identify A to E and write chemical equations for steps (i) to (iv).
16. An inorganic compound A when heated decomposes completely into two gases B and C. The gas B is neutral and decomposes on heating to two gases D and E. The compound A on warming with NaOH gives a pungent gas F which turns $\text{Hg}_2(\text{NO}_3)_2$ paper black. After some time the evolution of the gas F ceases. However, the gas F is formed by warming the residual solution with Al powder. Identify A to F and write balanced chemical equation for each change.
17. A colourless inorganic salt decomposes completely at about 250°C to give only two products B and C leaving no residue. The oxide C is a liquid at room temperature and neutral to moist litmus paper while the gas B is a neutral oxide. White phosphorous burns in excess of B to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above processes.
18. (a) A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved.
(b) Write balanced equations for the following:
(i) Manufacture of triple superphosphate from fluorapatite.
(ii) Oxidation of cuprous oxide to cupric hydroxide by alkaline KMnO_4 .
(iii) Reaction of alkaline perbromate with zinc giving tetrahydroxozincate anion.
19. A soluble compound of a poisonous element M, when heated with $\text{Zn}/\text{H}_2\text{SO}_4$ gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N.
20. A scarlet compound A is treated with conc. HNO_3 to give a chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralized with NaOH . Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with conc. HNO_3 in the presence of $\text{Mn}(\text{NO}_3)_2$ produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence.
21. An orange red solid A on heating gives a green solid B, a colourless gas C and an oxide D which is liquid at room temperature. The dry gas C when passed over hot Mg gave a white solid E. The solid E when treated with the liquid D gives a gas F which forms weak basic solution with D. Identify A to F and write the chemical reactions.

ANSWERS

1. $\text{X} = \text{FeCl}_3$, $\text{B} = \text{Fe}(\text{SCN})_2^{2+}$, $\text{C} = (\text{CN})_2$, $\text{D} = \text{Na}_2\text{CrO}_4$
2. $\text{X} = \text{Ca}(\text{OCl})\text{Cl}$

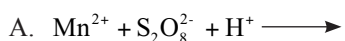
3. $A = \text{NaNH}_2$, $B = \text{H}_2$, $C = \text{NaCN}$, $D = (\text{CN})_2$
4. $A = \text{Al}_2(\text{CH}_3)_6$, $B = \text{CH}_4$, $C = \text{Al}(\text{OH})_3$
5. $A = \text{AgNO}_3$, $B = \text{NO}_2$, $C = \text{O}_2$, $D = \text{Ag}$, $E = \text{HNO}_3$
6. $A = \text{MnO}_2$, $B = \text{K}_2\text{MnO}_4$, $C = \text{KMnO}_4$
7. $A = \text{Fe}(\text{CrO}_2)_2$, $B = \text{Na}_2\text{CrO}_4$, $C = \text{Fe}_2\text{O}_3$, $D = \text{Na}_2\text{Cr}_2\text{O}_7$, $E = \text{CrO}_5$
8. NaOH and $\text{Al}_2(\text{SO}_4)_3$
9. HgCl_2
10. $A = \text{FeSO}_4$, $B = \text{Fe}_2\text{O}_3$, $C = \text{SO}_2$, $D = \text{SO}_3$, $E = \text{BaSO}_4$
11. $X = \text{BiCl}_3$, $A = \text{BiI}_3$, $B = \text{BiI}_4^-$, $C = \text{BiOI}$
12. $X = \text{NH}_4\text{Cl}$, $A = \text{CrO}_2\text{Cl}_2$, $B = \text{Na}_2\text{CrO}_4$, $C = \text{PbCrO}_4$, $D = \text{H}_2\text{NHgOHI}$
13. White solid is Na_2O_2
Red litmus will turn yellow ($\text{Na}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{NaOH}$)
14. $A = \text{ZnS}$, $B = \text{H}_2\text{S}$, $C = \text{ZnSO}_4$, $D = \text{S}$, $E = \text{SO}_2$
15. $A = \text{PH}_4\text{I}$, $B = \text{PH}_3$, $C = \text{KI}$, $D = \text{P}_4\text{O}_{10}$
16. $A = \text{NH}_4\text{NO}_3$, $B = \text{N}_2\text{O}$, $C = \text{H}_2\text{O}$, $D = \text{O}_2$, $E = \text{N}_2$, $F = \text{NH}_3$
17. $A = \text{NH}_4\text{NO}_3$, $B = \text{N}_2\text{O}$, $C = \text{H}_2\text{O}$
18. $A = \text{Br}_2$, $B = \text{NaBr}$, $C = \text{NaBrO}_3$
19. $M = \text{As}$, $N = \text{AsH}_3$
20. $A = \text{Pb}_3\text{O}_4$, $B = \text{PbO}_2$, $C = \text{PbI}_2$, $D = \text{HMnO}_4$
21. $A = \text{NH}_4\text{Cr}_2\text{O}_7$, $B = \text{Cr}_2\text{O}_3$, $C = \text{N}_2$, $D = \text{H}_2\text{O}$, $E = \text{Mg}_3\text{N}_2$, $F = \text{NH}_3$

MATCH THE COLUMN QUESTIONS

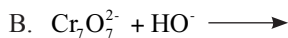
1. Match the complexes in Column I with their properties listed in Column II:

| Column I | Column II |
|---|--------------------------------|
| A. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ | 1. Paramagnetic |
| B. $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ | 2. Optical isomers |
| C. $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ | 3. Metal in +3 oxidation state |
| D. $\text{Ni}(\text{CO})_4$ | 4. Diamagnetic |

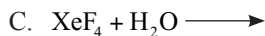
2. Match the reactions (or statements) in Column I with nature of the reactions, type of the products in column II:

Column I**Column II**

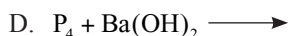
1. Redox reaction



2. Disproportionation



3. Tetrahedral anion



4. Yellow solution

3. Match the statements in Column I with that in the Column II:

Column I**Column II**

A. Argentite

1. Hydrometallurgy

B. Copper

2. Metal reduction

C. Tin

3. Carbon reduction

D. Silicon

4. Self reduction

4. Match the alloy in the Column I with its constituents in the Column II:

Column I**Column II**

A. Monel metal

1. Copper

B. German silver

2. Nickel

C. Brass

3. Zinc

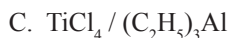
D. Bell metal

4. Manganese

5. Match the compounds or process in Column I with Chemical facts given in Column II:

Column I**Column II**

1. Aromatisation of alkane

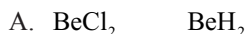
2. Conversion of $\text{CH}_2 = \text{CH}_2$ to $\text{CH}_3 - \text{CHO}$ 

3. Hydrogenation of alkene

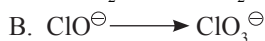
D. Wacker Process

4. Linear polymerization of ethene

6. Match the structural feature in Column II with the reaction products given in Column I:

Column I**Column II**

1. No change in the hybrid nature of the central atom



2. Change in oxidation number

- C. $\text{PCl}_3 \longrightarrow \text{PCl}_5$ 3. Irregular structure
 D. $\text{SiF}_4 \longrightarrow \text{SiF}_6^{2-}$ 4. Multicentre bonding

7. Match Column I with Column II:

| Column I | Column II |
|--|---|
| A. $\text{NO}_2 \xrightarrow{\text{Water}} \text{NO} + \text{HNO}_3$ | 1. Ratio oxidizing to reducing agent 5/2 |
| B. $\text{Mn}^{2+} \xrightarrow[\text{H}^+]{\text{BiO}_3} \text{MnO}_4^- + \text{Bi}^{3+}$ | 2. Ratio of reducing to oxidizing agent 3/2 |
| C. $\text{S}^{2-} + \text{NO}_3^- \longrightarrow \text{S} + \text{N}_2\text{O}$ | 3. Disproportionation reaction |
| D. $\text{Fe}^{2+} + \text{NO}_2^- \longrightarrow \text{Fe}^{3+} + \text{NO}$ | 4. Paramagnetic species in the product |

8. Match Column I with Column II and select correct answer:

| Column I | Column II |
|-------------------------------------|--|
| A. Demineralized water | 1. $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$ |
| B. Enriched water | 2. D_2O |
| C. Heavy water | 3. H_2O^{18} |
| D. Temporary and permanent hardness | 4. No foreign ion in water |

9. Match Column I with Column II correctly:

| Column I | Column II |
|---------------------------|---|
| A. Superphosphate of lime | 1. $\text{NaNH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$ |
| B. Thomas slag | 2. $3\text{Ca}(\text{H}_2\text{PO}_4)_2$ |
| C. Microcosmic salt | 3. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} \cdot 0.2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| D. Triple super phosphate | 4. No foreign ion in water |

10. Match the statement made in Column I with Chemical species or statement in Column II:

| Column I | Column II |
|--|---------------------------|
| A. Similar M—F bonds | 1. Charge transfer colour |
| B. Hydrolysis | 2. BF_4^- |
| C. $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ | 3. BeF_4^{2-} |
| D. Dissimilar M—F bonds | 4. SF_4 |

11. Match the compound and reactions in Column I with statements in Column II:

Column I

- A. NO_2 dissolves in water
 B. XeF_4 dissolves in water
 C. $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$
 D. $[\text{Co}(\text{H}_2\text{O})_6\text{Cl}_3]$

Column II

1. Diamagnetic
 2. One of the products is explosive
 3. Disproportionation
 4. Paramagnetic

12. Match the species in Column I with statements in Column II:

Column I

- A. $(\text{SiH}_3)_3\text{N}$ and R_3N
 B. $[\text{TiCl}_5]^{2-}$ and $[\text{PCl}_5]$
 C. I_5^\ominus
 D. N_3^\ominus and NCN^{2-}

Column II

1. Similar structures
 2. Do not follow VSEPR
 3. Dissimilar structure
 4. Pseudohalide

13. Match the species in Column I with statement in Column II:

Column I

- A. AgBr
 B. $\text{S}_2\text{O}_3^{2-}$
 C. NaCl
 D. $\text{S}_2\text{O}_4^{2-}$

Column II

1. S—S bond
 2. Schottky defect
 3. Reducing agent
 4. Frenkel defect

ANSWERS

- | | | | |
|---------------------|------------------|------------------|---------------|
| 1. (A) – 3 and 4 | (B) – 1 and 3 | (C) – 2, 3 and 4 | (D) – 4 |
| 2. (A) – 1 and 3 | (B) – 3 and 4 | (C) – 1 and 2 | (D) – 2 and 3 |
| 3. (A) – 1 and 2 | (B) – 3 and 4 | (C) – 3 | (D) – 2 |
| 4. (A) – 1, 2 and 4 | (B) – 1, 2 and 3 | (C) – 1 and 3 | (D) – 1 and 3 |
| 5. (A) – 3 | (B) – 1 | (C) – 4 | (D) – 2 |
| 6. (A) – 4 | (B) – 1 and 2 | (C) – 3 and 2 | (D) – 2 |
| 7. (A) – 3 and 4 | (B) – 1 | (C) – 2 and 4 | (D) – 4 |
| 8. (A) – 4 | (B) – 3 | (C) – 2 | (D) – 1 |
| 9. (A) – 3 | (B) – 4 | (C) – 1 | (D) – 2 |
| 10. (A) – 2 and 3 | (B) – 2 and 4 | (C) – 1 | (D) – 4 |
| 11. (A) – 3 and 4 | (B) – 3 and 2 | (C) – 4 | (D) – 1 |
| 12. (A) – 3 | (B) – 3 | (C) – 2 | (D) – 1 and 4 |
| 13. (A) – 2 and 4 | (B) – 1 and 3 | (C) – 2 | (D) – 1 |

Additional Practice Questions

CHAPTER 1 : PERIODIC TABLE AND PERIODICITY OF PROPERTIES

1. The correct order of radii is represented by
 - (a) $K^+ > Cl^-$ (b) $S^{6+} > S^{4+}$
 - (c) $^{35}Cl^- > ^{37}Cl^-$ (d) $Cr^{3+} > Mn^{6+}$
2. The number of unpaired electrons in which of the following is maximum
 - (a) Zn^{2+} (b) Ni^{2+}
 - (c) Fe^{2+} (d) Co^{2+}
3. In the periodic table oxidizing power of elements
 - (a) Decreases from left to right in a period
 - (b) Increases from left to right in a period
 - (c) Does not change from left to right in a period
 - (d) Increases and then decreases in a period from left to right
4. For which of the following positive oxidation number is not possible
 - (a) Oxygen (b) Fluorine
 - (c) Nitrogen (d) Chlorine
5. Which one exists as discrete polyatomic molecule
 - (a) White – P (b) Diamond
 - (c) Graphite (d) Black – P
6. Effective nuclear charge (Z^*)
 - (a) Increases in a period from left to right
 - (b) Decreases in a period from left to right
 - (c) Decreases in a group from top to bottom
 - (d) Increases in a group from top to bottom
7. Which of the following can adopt only one non-zero oxidation state
 - (a) Sn (b) Bi
 - (c) F (d) S
8. The melting points of halogens decrease as:
 - (a) $F > Cl > Br > I$
 - (b) $I > Br > Cl > F$
 - (c) $I > F > Cl > Br$
 - (d) $Br > I > Cl > F$
9. Mark the correct statement for group 2 metals
 - (a) Reducing power decreases from top to bottom
 - (b) Oxidizing power increases from top to bottom
 - (c) Reducing power increases from top to bottom
 - (d) Reducing power does not change from top to bottom
10. The electrical conducting power of fused $MgCl_2$, Al_2Cl_6 , $SiCl_4$ decreases as:
 - (a) $SiCl_4 > MgCl_2 > Al_2Cl_6$
 - (b) $MgCl_2 > Al_2Cl_6 > SiCl_4$
 - (c) $Al_2Cl_6 > SiCl_4 > MgCl_2$
 - (d) $SiCl_4 > Al_2Cl_6 > MgCl_2$
11. The correct decreasing order of acidity is represent by
 - (a) $K_2O > CaO > MgO$
 - (b) $CO_2 > N_2O_5 > SO_3$
 - (c) $CaO > K_2O > MgO$
 - (d) $Cl_2O_7 > N_2O_5 > SO_3$
12. Atomic volume of elements in the periodic table
 - (a) Increases regularly with increase in atomic number
 - (b) Decreases regularly with increase in atomic number
 - (c) Changes discontinuously with increase in atomic number
 - (d) Is small when atomic radius is large
13. Identify the correct order of acidity of CO_2 , NO_2 , SnO_2 and KO_2
 - (a) $KO_2 > SnO_2 > CO_2 > NO_2$
 - (b) $NO_2 > CO_2 > SnO_2 > KO_2$
 - (c) $SnO_2 > KO_2 > NO_2 > CO_2$
 - (d) $CO_2 > NO_2 > KO_2 > SnO_2$
14. Which of the following has highest density
 - (a) Pt (b) Hg
 - (c) Ir (d) W
15. The set that represents isoelectronic species is
 - (a) K^+ , Ca^{2+} , Sr^{2+}
 - (b) Sc^{3+} , K^+ , Cl^-
 - (c) N^{3-} , F^- , S^{2-}
 - (d) Ca^{2+} , N^{3-} , O^{2-}

16. Which of the following represents correct order of first ionization enthalpy
 (a) $B < S < P < F$
 (b) $S < P < F < B$
 (c) $P < S < B < F$
 (d) $P < B < S < F$
17. The increasing order of radii for La^{+3} , Ce^{3+} , Pm^{3+} , Yb^{3+} is
 (a) $\text{La}^{+3} < \text{Ce}^{3+} < \text{Pm}^{3+} < \text{Yb}^{3+}$
 (b) $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{+3}$
 (c) $\text{Pm}^{3+} < \text{Yb}^{3+} < \text{La}^{+3} < \text{Ce}^{3+}$
 (d) $\text{Yb}^{3+} < \text{La}^{+3} < \text{Ce}^{3+} < \text{Pm}^{3+}$
18. Among SO_2 , P_4O_6 , SiO_2 and Al_2O_3 , the correct order of acidity is
 (a) $\text{SO}_2 > \text{P}_4\text{O}_6 > \text{SiO}_2 > \text{Al}_2\text{O}_3$
 (b) $\text{P}_4\text{O}_6 > \text{SO}_2 > \text{SiO}_2 > \text{Al}_2\text{O}_3$
 (c) $\text{SiO}_2 > \text{SO}_2 > \text{P}_4\text{O}_6 > \text{Al}_2\text{O}_3$
 (d) $\text{SO}_2 > \text{SiO}_2 > \text{P}_4\text{O}_6 > \text{Al}_2\text{O}_3$
19. Which of the following is correct order with respect to property shown against it
 (a) $F > \text{Cl} > \text{Br} > \text{I}$
 Electron affinity
- (b) $S > \text{Se} > \text{O}$
 Electron affinity
- (c) $B < C < N < \text{O}$
 First ionization energy
- (d) $\text{F}^- < \text{Mg}^{2+} < \text{Na}^+$
 Ionic radii
20. The order of radii, which is correct is
 (a) $\text{F}^- > \text{O}^{2-} > \text{H}^-$
 (b) $\text{O}^{2-} > \text{F}^- > \text{H}^-$
 (c) $\text{H}^- > \text{O}^{2-} > \text{F}^-$
 (d) $\text{H}^- > \text{F}^- > \text{O}^{2-}$
21. The ground state electron structures of Pd(46) is
 (a) Kr $4d^8 5s^2$
 (b) Kr $4d^9 5s^1$
 (c) Kr $4d^{10}$
 (d) Kr $4d^2 5s^2 5p^6$
22. Which is expected to have very similar ionic size
 (a) Zn^{2+} , Hf^{2+}
 (b) Ti^{2+} , Zr^{2+}
 (c) Zr^{4+} , Hf^{4+}
 (d) Ni^{2+} , Hf^{2+}

ANSWER

SINGLE ANSWER

1. (d) 2. (c) 3. (b) 4. (b) 5. (a) 6. (a) 7. (c) 8. (b) 9. (c) 10. (b)
 11. (d) 12. (c) 13. (b) 14. (c) 15. (b) 16. (a) 17. (b) 18. (a) 19. (b) 20. (c)
 21. (c) 22. (c)

CHAPTER 2 : CHEMICAL BONDING AND MOLECULAR STRUCTURE

1. The correct order of bond angle (ONO) is represented by
 - (a) $\text{NO}_2^+ > \text{NO}_2 > \text{NO}_2^-$
 - (b) $\text{NO}_2^- > \text{NO}_2 > \text{NO}_2^+$
 - (c) $\text{NO}_2^- > \text{NO}_2^+ > \text{NO}_2$
 - (d) $\text{NO}_2 > \text{NO}_2^+ > \text{NO}_2^-$
2. Which of the following is a superoxide
 - (a) BaO_2
 - (b) SnO_2
 - (c) RbO_2
 - (d) PbO_2
3. The species that has bond order different from that of N_2 is
 - (a) CO
 - (b) CN^-
 - (c) NO^+
 - (d) NO^-
4. The correct order of increasing bond angles is represented by
 - (a) $\text{ClO}_2 > \text{ClO}_2^- > \text{Cl}_2\text{O}$
 - (b) $\text{Cl}_2\text{O} > \text{ClO}_2 > \text{ClO}_2^-$
 - (c) $\text{ClO}_2 > \text{Cl}_2\text{O} > \text{ClO}_2^-$
 - (d) $\text{ClO}_2^- > \text{ClO}_2 > \text{Cl}_2\text{O}$
5. Which of the following is paramagnetic
 - (a) CN^-
 - (b) CO
 - (c) B_2
 - (d) NO^+
6. The compounds that has sp^2 -hybridised central atom is
 - (a) CO_2
 - (b) NO_2
 - (c) SO_2
 - (d) KO_2
7. Which has trigonal pyramidal geometry
 - (a) XeO_3
 - (b) SO_3
 - (c) CO_3^{2-}
 - (d) NO_3^-
8. The molecule which is linear is
 - (a) SO_2
 - (b) SiO_2
 - (c) NO_2
 - (d) CO_2
9. The species which has sp^2 hybridised central atom is
 - (a) HClO_3
 - (b) H_2CO_3
 - (c) H_2PO_3^-
 - (d) H_2PO_2^-
10. Among CO_3^{2-} , NO_3^- , ClO_3^- and SO_3 , which are isoelectronic and isostructural
 - (a) CO_3^{2-} , SO_3
 - (b) ClO_3^- , NO_3^-
 - (c) CO_3^{2-} , ClO_3^-
 - (d) CO_3^{2-} , NO_3^-
11. The species which is expected to have maximum (s-p) mixing in its molecular orbital
 - (a) F_2
 - (b) O_2
 - (c) N_2
 - (d) B_2
12. The hybridization of nitrogen atomic orbitals in NH_2^- , NO_2^+ and NO_3^- are
 - (a) sp^2 , sp , sp^3
 - (b) sp^3 , sp , sp^2
 - (c) sp , sp^3 , sp^2
 - (d) sp , sp^2 , sp^3
13. The molecular shape of BF_3 , ClF_3 and NF_3 are
 - (a) The same with equal number of lone pair electrons at the central atom
 - (b) The same with 0, 1, 2 lone pair of electrons at the central atom
 - (c) Different with 0, 2 and 1 lone pair of electrons at the central atom
 - (d) Different with 0, 1 and 2 lone pair of electrons at the central atom
14. Which is expected least stable
 - (a) Be^-
 - (b) C^-
 - (c) Li^-
 - (d) B^-
15. Which of the following has maximum number of non-bonded electrons at the central atom
 - (a) XeOF_2
 - (b) IF_2^-
 - (c) SOF_4
 - (d) SF_4
16. Most favourable condition for an ionic bond is
 - (a) Large cation small anion
 - (b) Small cation large anion
 - (c) Small cation small anion
 - (d) Large cation large anion
17. The compound in which carbon uses the sp^3 hybrid orbitals is
 - (a) $(\text{H}_2\text{N})_2\text{CO}$
 - (b) $(\text{HO})_2\text{CO}$
 - (c) $(\text{CH}_3)_3\text{COH}$
 - (d) HCOOH
18. The H – bond is strongest in
 - (a) $\text{F} - \text{H} \cdots \text{O}$
 - (b) $\text{F} - \text{H} \cdots \text{F}$
 - (c) $\text{O} - \text{H} \cdots \text{F}$
 - (d) $\text{F} - \text{H} \cdots \text{S}$
19. The maximum number of H-bonds NH_3 can form in water medium is
 - (a) 3
 - (b) 4
 - (c) 2
 - (d) 5

ONE OR MORE THAN ONE OPTION CORRECT

20. The species which have equal bond order are
 (a) CN^- (b) NO
 (c) CO (d) NO^+
21. CO_2 is isostructural with
 (a) N_2O (b) HgCl_2
 (c) SnCl_2 (d) AgCl_2^-
22. Dipolemoment is shown by
 (a) $\text{Ag}(\text{CN})_2^-$
 (b) $\text{cis} [\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 (c) $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$
 (d) $\text{trans} [\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
23. The linear structure is possessed by
 (a) N_3^- (b) NCS^-
 (c) CS_2 (d) NO_2^+
24. The species which have sp^3 hybridised central atom
 (a) ClO_3^- (b) H_2PO_3^-
 (c) HSO_3^- (d) CO_3^{2-}
25. Mark the correct statements for the following changes
 (i) $\text{O}_2 \longrightarrow \text{O}_2^+ + \text{e}$
 (ii) $\text{N}_2 \longrightarrow \text{N}_2^+ + \text{e}$
 (a) Magnetic nature and bond order changes in (i)
 (b) Magnetic nature and bond order changes in (ii)
 (c) Bond order increases and paramagnetism decreases in (i)
 (d) Bond order and bond energy decrease in (ii)
26. The species which can have dipolemoment are
 (a) $\text{cis} - 3 - \text{hexane}$
 (b) $\text{trans} - 2 - \text{pentene}$
 (c) $\text{cis} - 1, 2 - \text{dichloroethene}$
 (d) $2, 2 - \text{dimethyl propane}$
27. Which of the following are isostructural
 (a) CH_3^- (b) ClO_3^-
 (c) CH_3^+ (d) Br_3^-
28. Dipolemoment is shown by
 (a) $1, 4 - \text{dichlorobenzene}$
 (b) $1, 4 - \text{dihydroxybenzene}$
 (c) $\text{trans} 1, 2 - \text{dichloroethene}$
 (d) $\text{cis} - 1, 2 - \text{dichloroethene}$
29. Which of the following is(are) correct
 (a) The first ionization energy of H_2 is greater than H
 (b) The first ionization energy of O_2 is less than O
 (c) The first ionization energy of NO is less than CO
 (d) The first ionization energy of NO is greater than CO
30. The species which have equal bond orders are
 (a) B_2 (b) C_2
 (c) B_2^- (d) BN
31. Which of the following probable structures for CCl_4 are expected to have zero dipolemoment
 (a) Tetrahedral
 (b) Square pyramid
 (c) Square planar
 (d) Irregular tetrahedral

SINGLE DIGIT INTEGER (0 TO 9) ANSWER TYPE QUESTIONS

32. The number of coordination water molecules in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is
33. The coordination number of Cu in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is
34. The number of σ bonds in magnesium propynide is
35. The number of unpaired electrons in $\text{Ni}(\text{CO})_4$ is
36. The number of compounds which give similar gaseous product on heating along is $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NH_4NO_3 , NH_4NO_2
37. The total number of $-\text{OH}$ groups in cyclotrimetaphosphoric acid is
38. The number of complexes which can give geometrical isomers is

- $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$,
 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Ni}(\text{HDMg})_2]$,
 $[\text{Pd}(\text{NH}_3)\text{PyClBr}]$, $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
39. The number of equivalent oxygen atoms in pyrosilicate is
40. The number of H – atoms directly linked to P in hypophosphorous acid is
41. The total number of compounds which can form coloured solution is
 $\text{Co}(\text{NO}_3)_2$, CrCl_3 , TiCl_4 , CdS , $\text{Zn}(\text{NO}_3)_2$,
 $\text{Sc}(\text{NO}_3)_3$, FeSO_4
42. The number of unpaired electrons in $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$
43. The number of water molecules in a pure crystal of sodium chloride is
44. The number of complexes which are paramagnetic is
 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}[\text{Co}(\text{CO})_4]$,
 $[\text{CoF}_6]^{3-}$, $[\text{Cr}(\text{OX})_3]^{3-}$,
 $[\text{TiCl}_4]^-$, $[\text{MnCl}_4]^{2-}$
45. The total number of Si – Si bond in cyclic trimethasilicate is
46. The total number of isomers for $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is
47. The number of O – atoms being shared in a sheet silicate is
48. The total number of compounds which have linear geometry is
 XeF_2 , SnCl_2 , HgCl_2 , N_2O , SO_2 , CO_2

ANSWER**SINGLE ANSWER**

1. (a) 2. (c) 3. (d) 4. (c) 5. (c) 6. (c) 7. (a) 8. (d) 9. (b) 10. (d)
 11. (d) 12. (b) 13. (c) 14. (a) 15. (b) 16. (a) 17. (c) 18. (b) 19. (b)

ONE OR MORE THAN ONE OPTION CORRECT

20. (a, c, d) 21. (a, b, d) 22. (b, c) 23. (a, b, c, d) 24. (a, b, c)
 25. (b, c, d) 26. (a, b, c) 27. (a, b) 28. (b, d) 29. (a, b, c)
 30. (b, d) 31. (a, c)

CHAPTER 3 : ACIDS AND BASES

1. The correct acidity order is represented by
 - (a) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$
 - (b) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
 - (c) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3$
 - (d) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4$
2. Mark the correct statement
 - (a) H_3PO_2 is reducing and triprotic
 - (b) H_3PO_2 is reducing and monoprotic
 - (c) H_3PO_2 is reducing and diprotic
 - (d) H_3PO_2 is oxidizing and diprotic
3. The pH of 0.1M solution of NaCl , Na_2S , NH_4Cl and H_2S increases in the order
 - (a) $\text{H}_2\text{S} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{Na}_2\text{S}$
 - (b) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{H}_2\text{S} < \text{Na}_2\text{S}$
 - (c) $\text{NH}_4\text{Cl} < \text{H}_2\text{S} < \text{Na}_2\text{S} < \text{NaCl}$
 - (d) $\text{Na}_2\text{S} < \text{H}_2\text{S} < \text{NH}_4\text{Cl} < \text{NaCl}$
4. Methylamine 0.1M is mixed with 0.04M HCl and diluted to one litre. The resulting solution is
 - (a) a basic buffers
 - (b) an acidic buffer
 - (c) not a buffer
 - (d) a buffer of low pH
5. Which of the following can increase concentration of H^+ in water
 - (a) CO
 - (b) Al_2O_3
 - (c) NO
 - (d) SO_2
6. The acid which is triprotic is:
 - (a) H_3BO_3
 - (b) H_3PO_4
 - (c) H_3PO_3
 - (d) H_3PO_2
7. The mixture which forms an acidic buffer is
 - (a) $\text{NaOH} + \text{NaCl}$
 - (b) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
 - (c) $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$
 - (d) $\text{CH}_3\text{COOH} + \text{NaCl}$
8. Aqueous solution of a salt made by strong acid and weak base is
 - (a) acidic
 - (b) basic
 - (c) buffer solution
 - (d) neutral
9. Borax (0.05M) in water forms a solution which is
 - (a) acidic
 - (b) basic
 - (c) a buffer
 - (d) neutral
10. Aqueous solution of $\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$ (0.01M each) forms
 - (a) an acidic solution only
 - (b) a basic solution only
 - (c) an acidic buffer solution
 - (d) a basic buffer solution
11. Which of the following acid can form a normal salt only
 - (a) H_3PO_3
 - (b) H_3PO_2
 - (c) H_2CO_3
 - (d) H_2CrO_4
12. The hydroxide which is amphoteric is
 - (a) $\text{Ca}(\text{OH})_2$
 - (b) $\text{Cu}(\text{OH})_2$
 - (c) $\text{Sn}(\text{OH})_2$
 - (d) $\text{Fe}(\text{OH})_2$
13. The formula of telluric acid is
 - (a) H_6TeO_6
 - (b) H_2TeO_4
 - (c) H_4TeO_5
 - (d) H_5TeO_6
14. Which of the following is a hard base in the Lewis sense
 - (a) CN^-
 - (b) HO^-
 - (c) SCN^-
 - (d) S^{2-}
15. For an amphoteric hydroxide like $\text{M}(\text{OH})_3$ mark the correct statement
 - (a) $\text{M}-\text{O}$ bond is more reactive than $\text{O}-\text{H}$ bond
 - (b) $\text{M}-\text{O}$ bond is less reactive than $\text{O}-\text{H}$ bond
 - (c) $\text{M}-\text{O}$ bond and $\text{O}-\text{H}$ bond are almost equally reactive
 - (d) $\text{M}-\text{O}$ bond or $\text{O}-\text{H}$ bond is not responsible for amphoterism
16. The strongest acid among the following in water, is
 - (a) $\text{SO}_2(\text{OH})_2$
 - (b) $\text{ClO}_2(\text{OH})$
 - (c) $\text{ClO}_3(\text{OH})$
 - (d) $\text{PO}(\text{OH})_3$

17. Which of the following solutions will have a pH close to 1.0
- (a) 100 ml M NaOH + 100 ml M HCl
 - (b) 25 ml M NaOH + 75 ml M HCl
 - (c) 45 ml M NaOH + 55 ml M HCl
 - (d) 90 ml M NaOH + 10 ml M HCl
18. One litre of a solution contains 1M CH_3COOH and 1M CH_3COONa . When 0.2M HCl is added to the solution its pH is close to
- (a) 5.4
 - (b) 5.0
 - (c) 4.6
 - (d) 3.8

ONE OR MORE THAN ONE OPTION CORRECT

19. Which of the following pair of compounds in equal concentration can form a buffer solution
- (a) $\text{CH}_3\text{COONa} + \text{HCl}$
 - (b) potassium hydrogen lthalate + water
 - (c) $\text{HCl} + \text{HCOOH}$
 - (d) $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$
20. Which of the following statement(s) is(are) correct
- (a) The pH of 10^{-2} M HCl and CH_3COOH each is equal
 - (b) The pH of 10^{-8} M HCl is 8
 - (c) The only conjugate base of H_3PO_2 is H_2PO_2^-
 - (d) The autoprotolysis constant of water increases with rise in temperature
21. Mark the correct statement(s)
- (a) Aqueous solution of FeCl_3 is neutral
 - (b) Aqueous solution of FeCl_3 is acidic
 - (c) Aqueous solution of Na_2S is basic
 - (d) H_3PO_2 is a triprotic acid

SINGLE DIGIT INTEGER (0 TO 9) TYPE QUESTION

22. Total number of bases NH_3 can produce is
23. The total number of monoprotic acid among the following is
- H_3PO_2 , H_3PO_3 , H_3BO_3 ,
 H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_2\text{S}_2\text{O}_4$
24. The number of species that can not form a basic solution in water is
- CN^- , HO^- , NO_2^- , S^{2-} ,
 ACO^- , NO_3^- , SCN^-

FILL IN THE BLANKS

25. In the reaction $2\text{PCl}_5 \longrightarrow \text{PCl}_4^+ \cdot \text{PCl}_6^-$, the Lewis base is _____.
26. The conjugate acid of H_2PO_2^- is _____.
27. A metal that can exist in acid as a positive ion but in base as a negative ion is called _____.
28. In the reaction $\text{I}_2 + \text{I}^- \longrightarrow \text{I}_3^-$, the Lewis acid is _____.
29. The conjugate base of amide is _____.
30. The aqueous solution of Li_3N is _____.
31. KO_2 is water forms the gas _____.

ANSWER

SINGLE ANSWER

1. (a) 2. (b) 3. (a) 4. (a) 5. (d) 6. (b) 7. (c) 8. (a) 9. (c) 10. (c)
11. (b) 12. (c) 13. (a) 14. (b) 15. (c) 16. (c) 17. (b) 18. (c)

ONE OR MORE THAN ONE OPTION CORRECT

19. (a, b) 20. (c, d) 21. (b, c)

SINGLE DIGIT INTEGER (0 TO 9) ANSWER TYPE QUESTIONS

22. (3) 23. (2) 24. (2)

FILL IN THE BLANKS

25. (PCl₅) 26. (H₃PO₄) 27. (Amphoteric) 28. (I₂) 29. (Imide)
30. (Basic) 31. (O₂)

CHAPTER 4 : CHEMICAL REACTIONS

OBJECTIVE QUESTION (ONLY ONE CORRECT)

- The standard reduction potential of three metals x, y, z are -3.03 , $+0.52$ and -1.18V respectively. The order of their reducing power is
 (a) $x > y > z$ (b) $x > z > y$
 (c) $z > y > x$ (d) $z > x > y$
- Standard electron potential of some half-cells are given below

$$\text{MnO}_4^- \xrightarrow{\text{H}^+} \text{Mn}^{2+}_{(\text{aq})} \quad E^0 = +1.51\text{V}$$

$$\text{Fe}^{3+}_{(\text{aq})} / \text{Fe}^{2+}_{(\text{aq})} \quad E^0 = +0.771\text{V}$$

$$\text{Cr}_2\text{O}_7^{2-} \xrightarrow{\text{H}^+} \text{Cr}^{3+}_{(\text{aq})} \quad E^0 = +1.38\text{V}$$

$$\text{Cl}_{2(\text{g})} / \text{Cl}^-_{(\text{aq})} \quad E^0 = +1.40\text{V}$$
 Mark the incorrect statement for the quantitative estimation of $\text{Fe}^{2+}_{(\text{aq})}$
 (a) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous HCl
 (b) MnO_4^- can be used in aqueous H_2SO_4
 (c) MnO_4^- can be used in aqueous HCl
 (d) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous H_2SO_4
- The oxidation potential of the species x, y and z are -1.82V , -2.65V and -1.52V respectively. The order of their oxidizing power is
 (a) $y > x > z$ (b) $x > y > z$
 (c) $z > x > y$ (d) $y > z > x$
- Cu does not react with dil. H_2SO_4 , because
 (a) Cu is a transition metal
 (b) Cu is a coinage metal
 (c) Cu has E^0 positive
 (d) Cu has E^0 negative
- A redox process can proceed when
 (a) the combination of the two half-cells is negative
 (b) the combination of the two half-cells is zero
 (c) the combination of the two half-cells is positive
 (d) the combination of the two half-cells has no effect on redox reaction
- Which of the following statements is correct
 (a) SO_2 is stronger reducing agent in water than in a base
 (b) SO_2 is stronger reducing agent in a base than in a water
 (c) SO_2 is stronger reducing agent in an acid than in a base
 (d) SO_2 is equally reducing in water and in a base
- The reduction of N in aqueous NO_3^- by Zn and NaOH involves
 (a) 2 electrons
 (b) 4 electrons
 (c) 6 electrons
 (d) 8 electrons
- The reaction $\text{ClO}^- \xrightarrow{\text{HO}^-} \text{ClO}_3^- + \text{Cl}^-$ is an example of
 (a) Reduction reaction
 (b) Decomposition reaction
 (c) Oxidation reaction
 (d) Disproportionation reaction
- For decolourisation of 1mol of KMnO_4 , the molecules of H_2O_2 needed is
 (a) $3/2$ (b) $5/2$
 (c) $1/2$ (d) $7/2$
- In the balanced chemical reaction $a\text{I}^- + \text{IO}_3^- + \text{H}^+ \longrightarrow \text{H}_2\text{O} + b\text{I}_2$; a & b respectively are
 (a) 3 & 5 (b) 5 and 3
 (c) 6 & 3 (d) 4 & 3
- The product of oxidation of I^- by MnO_4^- in alkaline medium is
 (a) IO_2^- (b) I_2
 (c) IO_3^- (d) IO_4^-

OBJECTIVE QUESTION (MORE THAN ONE CORRECT)

12. The reaction $\text{Pb}_3\text{O}_4 + \text{HCl} \longrightarrow \text{PbCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$ is an example of
 (a) acid-base reaction
 (b) disproportionation reaction
 (c) redox reaction
 (d) not a redox reaction
13. The reduction of NO_3^- ion in water to NO has $E^0 = 0.97\text{V}$. Value of E^0 for some metal ions are given below
 $\text{Ag}_{(\text{aq})}^+ + \text{e} \longrightarrow \text{Ag} \quad E^0 = +0.8\text{V}$
 $\text{Au}_{(\text{aq})}^{3+} + 3\text{e} \longrightarrow \text{Au} \quad E^0 = +1.4\text{V}$
 $\text{Fe}_{(\text{aq})}^{3+} + 3\text{e} \longrightarrow \text{Fe} \quad E^0 = -0.04$
 $\text{Cu}_{(\text{aq})}^{2+} + 2\text{e} \longrightarrow \text{Cu} \quad E^0 = +0.34\text{V}$
 The pair(s) of metal(s) that is(are) oxidized by NO_3^- in aqueous solution is(are)
 (a) Cu and Au (b) Ag and Fe
 (c) Fe and Cu (d) Ag and Au
14. The standard electrode potentials of some half-cells are given below
 $\text{Cl}_2 + 2\text{e} \longrightarrow 2\text{Cl}^- \quad E^0 = 1.36\text{V}$
 $\text{Mn}^{3+} + \text{e} \longrightarrow \text{Mn}^{2+} \quad E^0 = 1.50\text{V}$
 $\text{I}_2 + 2\text{e} \longrightarrow 2\text{I}^- \quad E^0 = 0.50\text{V}$
 $\text{Fe}^{3+} + \text{e} \longrightarrow \text{Fe}^{2+} \quad E^0 = 0.77\text{V}$
 Identify the correct statement(s)
 (a) Fe^{2+} is not oxidized by iodine
 (b) Iodine is oxidized by chlorine
 (c) Fe^{2+} is oxidized by chlorine
 (d) Mn^{2+} is oxidized by chlorine
15. Which of the following reaction(s) is(are) disproportionation
 (a) $\text{KO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{O}_2 + \text{KOH} + \text{O}_2$
 (b) $\text{P}_4 + \text{HO}^- + \text{H}_2\text{O} \longrightarrow \text{PH}_3 + \text{H}_3\text{PO}_2^-$
 (c) $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
 (d) $\text{Cl}_2 + \text{HO}^- \longrightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$
16. Which of the following have different oxidation number of oxygen
 (a) CrO_5 (b) $\text{H}_2\text{S}_2\text{O}_3$
 (c) H_2SO_5 (d) $\text{H}_2\text{S}_2\text{O}_4$
17. In the reaction $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$, the chemical species which suffer change in oxidation number is(are)
 (a) NH_4^{++} only
 (b) NH_4^+ and NO_2^- both
 (c) NO_2^- only
 (d) N_2 only
18. Reduction of manganese in aqueous MnO_4^- ion involves
 (a) 5 electrons in acid medium
 (b) 3 electrons in neutral medium
 (c) 5 electrons in neutral medium
 (d) 3 electrons in dil. alkali
19. In the reaction $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$
 (a) $\text{S}_2\text{O}_3^{2-}$ is oxidized (b) I_2 is oxidized
 (c) I_2 is reduced (d) $\text{S}_2\text{O}_3^{2-}$ is reduced

ANSWER

SINGLE ANSWER

1. (a) 2. (c) 3. (b) 4. (c) 5. (b) 6. (c) 7. (c) 8. (c) 9. (c) 10. (b)
 11. (c)

ONE OR MORE THAN ONE CORRECT OPTION QUESTIONS

12. (b) 13. (c) 14. (c) 15. (c) 16. (c) 17. (b) 18. (d) 19. (d)

CHAPTER 5: TRANSITION METALS, LANTHANIDES AND ACTINIDES

OBJECTIVE QUESTIONS

- The ground state electron configuration of Cr (24) is:
 (a) $3d^4 4s^2$ (b) $4s^2 4p^4$
 (c) $3d^5 4s^1$ (d) $3d^6$
- The pair of ions which has equal number of unpaired electrons:
 (a) Fe^{2+} , Co^{2+} (b) Mn^{2+} , Fe^{2+}
 (c) Cu^{2+} , Co^{2+} (d) Co^{3+} , Fe^{2+}
- For M^{3+}/M^{2+} system, the E° values for some metal is
 Cr^{3+}/Cr^{2+} $E^\circ = -0.40V$
 Fe^{3+}/Fe^{2+} $E^\circ = +0.80V$
 Mn^{3+}/Mn^{2+} $E^\circ = +1.50V$
 The decreasing order of stability of Mn^{2+} is:
 (a) $Mn^{2+} > Fe^{2+} > Cr^{2+}$
 (b) $Cr^{2+} > Mn^{2+} > Fe^{2+}$
 (c) $Mn^{2+} > Cr^{2+} > Fe^{2+}$
 (d) $Fe^{2+} > Mn^{2+} > Cr^{2+}$
- The paramagnetic moment of $\sqrt{8}$ BM is associated with which of the following ion:
 (a) Fe^{2+} (b) V^{2+}
 (c) Ni^{2+} (d) Cr^{2+}
- Which of the following has maximum number of unpaired electrons?
 (a) Ti^{3+} (b) Fe^{3+}
 (c) V^{3+} (d) Mg^{2+}
- The oxide of chromium which is amphoteric is
 (a) CrO_3 (b) CrO
 (c) CrO_5 (d) Cr_2O_3
- The number of moles of $KMnO_4$ required to react with one mole of SO_3^{2-} in acidic solution is
 (a) $\frac{5}{2}$ (b) $\frac{3}{5}$
 (c) $\frac{2}{5}$ (d) 1.0
- Which of the following transition metals shows maximum number of oxidation states?
 (a) V (b) Cr
 (c) Mn (d) Fe
- The thermal conductivity of Al, Cu and Ag decreases in the order
 (a) $Al > Cu > Ag$ (b) $Ag > Cu > Al$
 (c) $Cu > Ag > Al$ (d) $Al > Ag > Cu$
- Which of the following has highest second ionisation energy?
 (a) V (b) Cr
 (c) Mn (d) Fe
- Which will form colourless aqueous solution?
 (a) $VOSO_4$ (b) Na_3VO_4
 (c) VCl_3 (d) $TiCl_3$
- The basic nature of transition metal oxides MO follow the order
 (a) $CrO > TiO > FeO$
 (b) $VO > FeO > TiO$
 (c) $VO > CrO > FeO$
 (d) $TiO > FeO > VO$
- When MnO_2 is fused with KOH in the presence of oxygen, a coloured compound is formed. The product and its colour is
 (a) $KMnO_4$, purple
 (b) K_2MnO_4 , brown
 (c) K_2MnO_4 , purple green
 (d) Mn_2O_4 , black
- Ammonium dichromate is used in fire works. The green colour seen in air is due to:
 (a) $Cr(O)O_2$ (b) $Cr(O)O_4$
 (c) Cr_2O_3 (d) CrO_3
- Which of the following will give colourless aqueous solution?
 (a) Fe^{2+} (b) Cu^{2+}
 (c) Ni^{2+} (d) Sc^{3+}
- The first ionization energy of Cu, Ag and Au decrease as:
 (a) $Au > Cu > Ag$
 (b) $Cu > Ag > Au$
 (c) $Au > Ag > Cu$
 (d) $Cu > Au > Ag$

17. The ground state electron configuration of Pd(46) is:
 (a) $4d^8 5s^2$ (b) $4d^9 5s^1$
 (c) $4d^{10}$ (d) $4d^5 5s^2 5p^3$
18. Which of these will form coloured aqueous solution?
 (a) Ti^{4+} (b) Sc^{3+}
 (c) La^{3+} (d) Cr^{3+}
19. The first ionization energy of Ni, Pd and Pt:
 (a) $Pt > Ni > Pd$ (b) $Pt > Pd > Ni$
 (c) $Ni > Pd > Pt$ (d) $Ni > Pt > Pd$
20. The ground state electron configuration of Gd(64) is:
 (a) $4f^7 5d^1 6s^2$ (b) $4f^3 5d^5 6s^2$
 (c) $4f^9 5d^5 6s^1$ (d) $4f^8 6s^2$
21. The correct order of ionic radii is represented by:
 (a) $Ce^{3+} < Pr^{3+} < Pm^{3+} < Gd^{3+}$
 (b) $Gd^{3+} < Pm^{3+} < Pr^{3+} < Ce^{3+}$
 (c) $Pr^{3+} < Pm^{3+} < Ce^{3+} < Gd^{3+}$
 (d) $Pm^{3+} < Gd^{3+} < Ce^{3+} < Pr^{3+}$
22. The chemically equivalent Cr–O bonds in $Cr_2O_7^{2-}$ is:
 (a) 7 (b) 6
 (c) 4 (d) 5
23. The term Lanthanide contraction is due to:
 (a) strong screening effect of 4f electrons
 (b) strong screening effect of 5d electrons
 (c) very poor screening effect of 4f electrons
 (d) strong screening effect of 4f and 5d electrons
24. The common oxidation state of Ce(58) is:
 (a) +2 and +4 (b) +4 only
 (c) +3 and +4 (d) +3 only
25. The vanadium (V) oxide is:
 (a) strong reducing agent
 (b) strong oxidizing agent
 (c) strong dehydrating agent
 (d) a bleaching agent
26. The electrical conductance of Cu, Ag and Au decreases as:
 (a) $Cu > Ag > Au$ (b) $Au > Ag > Cu$
 (c) $Ag > Cu > Au$ (d) $Ag > Au > Cu$
27. The +1 oxidation state of gold is not stable in water and disproportionate as:

$$Au^+_{(aq)} \rightleftharpoons Au^{3+}_{(aq)} + Au_{(s)}$$
 In the presence of which of the following equilibrium is expected to lie well towards left?
 (a) NO_3^- (b) SO_4^{2-}
 (c) F^- (d) I^-
28. The metal which is leached by CN^- ions in aqueous solution is
 (a) Cu (b) Ag
 (c) Al (d) Fe
29. When ferrous chromite ($Fe(CrO_2)_2$) is fused with Na_2CO_3 in air (or $NaNO_3$) a coloured product is formed. The colour and the product respectively are
 (a) Yellow and Na_2CrO_4
 (b) Orange and $Na_2Cr_2O_7$
 (c) Orange and Na_2CrO_4
 (d) Yellow and $Na_2Cr_2O_7$
30. Which of the following mixture is used for cleaning greasy glassware?
 (a) $KMnO_4 + H_2SO_4$
 (b) $K_2Cr_2O_7 + \text{conc } H_2SO_4$
 (c) $K_2CrO_4 + HCl$
 (d) $KMnO_4 + HCl$
31. Which of the following is not a transition metal ion?
 (a) Ti^{4+} (b) V^{4+}
 (c) Mn^{4+} (d) Cr^{4+}
32. When a transition metal forms interstitial compound, it becomes
 (a) more ductile
 (b) more brittle
 (c) more soft
 (d) less brittle
33. For which of the lanthanides +2 oxidation state is expected most stable?
 (a) Ce (b) Ga
 (c) Eu (d) Pm
34. Li_2O doped NiO is:
 (a) an insulator
 (b) a semiconductor
 (c) a piezoelectric crystal
 (d) a superconductor

- | | | | | | | | | | |
|---------|------------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (a) | 4. (c) | 5. (b) | 6. (d) | 7. (c) | 8. (c) | 9. (b) | 10. (b) |
| 11. (b) | 12. (c) | 13. (c) | 14. (c) | 15. (d) | 16. (a) | 17. (c) | 18. (d) | 19. (b) | 20. (a) |
| 21. (b) | 22. (b) | 23. (c) | 24. (c) | 25. (b) | 26. (c) | 27. (d) | 28. (b) | 29. (a) | 30. (b) |
| 31. (a) | 32. (b) | 33. (c) | 34. (b) | 35. (b) | 36. (d) | 37. (b) | 38. (c) | 39. (b) | 40. (b) |
| 41. (c) | 42. (b, d) | | | | | | | | |

- The oxidation number of cobalt in $\text{K}(\text{Co}(\text{CO})_4)$ is:
 - +2
 - +1
 - 1
 - +3
- The complex which is expected most stable is:
 - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 - $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
 - $[\text{Cr}(\text{accac})_3]$
 - $[\text{Cr}(\text{CN})_6]^{3-}$
- The complex ion which has no electrons in the d orbitals of the complexed metal:
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{MnCl}_4]^{2-}$
 - $[\text{MnO}_4]^-$
 - $[\text{Mn}(\text{SCN})_6]^{4-}$
- The complex which is paramagnetic is:
 - $\text{K}_3[\text{CoF}_6]$
 - $\text{K}[\text{Co}(\text{CO})_4]$
 - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
 - $\text{K}_3[\text{Co}(\text{OX})_3]$
- Among the following carbonyls, the C—O bond distance is largest in:
 - $[\text{V}(\text{CO})_6]^-$
 - $[\text{Cr}(\text{CO})_6]$
 - $[\text{Mn}(\text{CO})_6]^+$
 - $[\text{Mo}(\text{CO})_6]$
- Which of the following is not expected to absorb visible wave length of electromagnetic radiation in aqueous solution?
 - SeCl_3
 - TiCl_3
 - VCl_3
 - CrCl_3
- The carbonyl complex in which M—C bond order is maximum in:
 - $[\text{Ni}(\text{CO})_4]$
 - $[\text{Co}(\text{CO})_4]^-$
 - $[\text{Fe}(\text{CO})_4]^{2-}$
 - $[\text{Mn}(\text{CO})_4]^{3-}$
- The number of unpaired electrons in the d-orbitals of iron in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is:
 - 3
 - 1
 - 4
 - 2
- The total number of geometrical isomers possible for $[\text{Pt}(\text{NH}_3)(\text{NH}_2 - \text{OH})\text{ClBr}]$ is:
 - 2
 - 3
 - 4
 - 6
- The complex which is diamagnetic and tetrahedral is
 - $[\text{NiCl}_4]^{2-}$
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$
 - $[\text{Ni}(\text{CO})_4]$
- The complex which contains metal in +2 oxidation state is
 - $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{+2}$
 - $[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$
 - $[\text{Fe}(\text{acac})_2\text{Cl}]$
 - $[\text{Fe}(\text{CO})]^{-2}$
- The number of unpaired electrons in $\text{Fe}(\text{CO})_5$ is
 - 2
 - 4
 - zero
 - 3
- Which of the following has square planar geometry?
 - $[\text{Ni}(\text{CO})_4]$
 - $[\text{NiCl}_4]^{2-}$
 - $[\text{Ni}(\text{PPh}_3)_3\text{Cl}]^-$
 - $[\text{Ni}(\text{HDmg})_2]$
- Which of the following is dimethyl glyoximate?
 - $$\begin{array}{c} \text{CH}_3 - \text{C} = \text{N} - \text{OH} \\ | \\ \text{CH}_3 - \text{C} = \text{N} - \text{OH} \end{array}$$
 - $$\begin{array}{c} \text{CH}_3 - \text{C} = \text{N} - \text{O}^\ominus \\ | \\ \text{HO} - \text{C} = \text{N} - \text{CH}_3 \end{array}$$
 - $$\begin{array}{c} \text{HO} - \text{C} = \text{N} - \text{CH}_3 \\ | \\ \text{HO} - \text{C} = \text{N} - \text{CH}_3 \end{array}$$
 - $$\begin{array}{c} \text{CH}_3 - \text{C} = \text{N} - \text{OCH}_3 \\ | \\ \text{HO} - \text{C} = \text{N} - \text{OH} \end{array}$$
- The ionization isomer of $[\text{Co}(\text{NH}_3)_4\text{ClNO}_4]\text{Cl}$ is
 - $[\text{Co}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{Cl}$
 - $[\text{Co}(\text{NH}_3)_3\text{Cl}_2\text{NO}_2]\cdot\text{NH}_3$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$
 - $[\text{Co}(\text{NH}_3)_4\text{NO}_2]\text{Cl}_2$
- The complex that has spin-only magnetic moment of 2.83BM is
 - $[\text{Ni}(\text{HDmg})_2]$
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{NiBr}_2(\text{PET}_3)_2]$
 - $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$
- The complex that cannot form isomer is
 - $[\text{Ni}(\text{en})_3]\text{Cl}_2$
 - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 - $\text{K}_3[\text{Cr}(\text{OX})_3]$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$

18. The spin-only paramagnetic moment of $\text{Cr}(\text{CO})_6$ in BM is
 (a) 3.86 (b) 0.0
 (c) 2.86 (d) 1.73
19. The oxidation number of Cu in $\text{Cu}(\text{acac})_2$ is
 (a) +1 (b) 0
 (c) +2 (d) +4
20. The IUPAC name of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ is
 (a) hexacyano cobalt (III) hexamine cobalt (III)
 (b) hexaammine cobalt (III) hexacyano cobalt (III)
 (c) hexaammine cobalt (III) hexacyanano cobaltate (III)
 (d) hexaammine cobalt (III) hexacyanano cobaltate (0)
21. The complex which is coloured is
 (a) $[\text{CuCl}_2]^-$
 (b) $[\text{Cu}(\text{CN})_4]^{3-}$
 (c) $[\text{CuCl}_4]^{2-}$
 (d) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$
22. Both $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{Ni}(\text{CO})_4$ are diamagnetic. The hybridization of nickel in these complexes respectively are
 (a) dsp^2 , sp^3 (b) sp^3 , sp^3
 (c) sp^3 , dsp^2 (d) dsp^2 , dsp^2
23. Which of the d-orbitals are used by Co^{3+} for the formation of $[\text{Co}(\text{OX})_3]^{3-}$?
 (a) $3d_{z^2}$, $3d_{yz}$ (b) $3d_{x^2-y^2}$, $3d_{z^2}$
 (c) $3d_{x^2-y^2}$, $3d_{xy}$ (d) $4d_{x^2-y^2}$, $4d_{z^2}$
24. In strong acidic solution, vanadium forms many complexes. One of them is $[\text{VO}_2(\text{EDTA})]^{3-}$.
- The oxidation number of V in the complex ion is:
 (a) +3 (b) +2
 (c) +5 (d) +2
25. For the complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$, which of the following statements is not correct?
 (a) it is square planar
 (b) it is diamagnetic
 (c) it is an organometallic
 (d) all Pt-Cl bonds are equal
26. The paramagnetic moment of 3.87 BN corresponds with which of the following?
 (a) $[\text{Cu}(\text{acac})_2]$ (b) $[\text{Ni}(\text{HDmg})_2]$
 (c) $\text{Hg}[\text{Co}(\text{SCN})_4]$ (d) $[\text{Co}(\text{en})_3]\text{Cl}_3$
27. The d-orbital used by iron in the complex $[\text{Fe}(\text{CO})_5]$ is:
 (a) d_{yz} (b) $d_{x^2-y^2}$
 (c) d_{xz} (d) d_{z^2}
28. The $d_{\text{C-O}}$ in free CO is 1.128 Å. The expected value of $d_{\text{C-O}}$ in $\text{Fe}(\text{CO})_5$ is:
 (a) 1.128 Å (b) 1.52 Å
 (c) 1.118 Å (d) 1.150 Å
29. Which of the following is coloured due to charge transfer?
 (a) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (b) $\text{K}_3[\text{Fe}(\text{OX})_3]$
 (c) $\text{K}_3[\text{Cr}(\text{OX})_3]$ (d) $\text{Co}(\text{en})_3\text{Cl}_3$
30. The Wilson's disease, a genetic disease is caused due to:
 (a) excess Cu in the body
 (b) excess Fe in the body
 (c) excess Zn in the body
 (d) excess Mn in the body

MULTIPLE CHOICE (ONE OR MORE THAN ONE CORRECT)

31. The complexes which can form geometrical isomer(s) is (are):
 (a) $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$
 (b) $[\text{Pt}(\text{NH}_3)_4(\text{en})]\text{Cl}_4$
 (c) $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$
 (d) $[\text{Pt}(\text{en})_2(\text{NH}_3)_2]\text{Cl}_4$
32. The complexes which have tetrahedral geometry is (are):
 (a) $[\text{PtCl}_4]^{2-}$ (b) $[\text{NiCl}_4]^{2-}$
 (c) $[\text{Pd}(\text{CN})_4]^{2-}$ (d) $[\text{CuCl}_4]^{2-}$
33. The complexes which are expected to be coloured due to charge transfer is (are):
 (a) $[\text{MnO}_4]^-$
 (b) $[\text{Fe}(\text{CN})_6]^{3-}$
 (c) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$
 (d) $[\text{CrF}_6]^{3-}$

34. The compound(s) which exhibit(s) stereo-isomerism is (are):
 (a) $[\text{Ni}(\text{en})_3]\text{Cl}_2$
 (b) $[\text{Co}(\text{NH}_3)_4\text{ClNO}_2]\text{Cl}$
 (c) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (d) $[\text{Rh}(\text{NH}_3)_3\text{Cl}_3]$
35. The complex(es) which can form structural and stereoisomer is(are):
 (a) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{NO}_2$
 (b) $[\text{Co}(\text{en})_3]\text{Cl}_3$
 (c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (d) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
36. The complex ion(s) which have no d-electrons is(are):
 (a) $[\text{Sc}(\text{NH}_3)_6]^{3+}$
 (b) $[\text{CrO}_4]^{2-}$
 (c) $[\text{Co}(\text{NO}_2)_6]^{3-}$
 (d) $[\text{VO}_2(\text{OX})_2]^{3-}$
37. The aqueous solution of the following salt(s) is(are) coloured in the case(s) of:
 (a) $\text{Sc}(\text{NO}_3)_2$
 (b) $\text{Co}(\text{NO}_3)_2$
 (c) $\text{Zn}(\text{NO}_3)_2$
 (d) CrCl_3
38. The kind of isomer(s) formed by octahedral $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ is(are):
 (a) Geometrical
 (b) Optical
 (c) Ionisation
 (d) Linkage

SINGLE DIGIT INTERGER (0 TO 9) ANSWER TYPE QUESTIONS

39. The number of compounds which will form colorless aqueous solution is
 (a) $\text{Cu}(\text{NO}_3)_2$, AgNO_3 ,
 (b) $\text{Sc}(\text{NO}_3)_2$, CrCl_3 ,
 (c) $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$,
 (d) $\text{La}(\text{NO}_3)_3$, $\text{V}(\text{NO}_3)_3$.
40. The total number of complexes which are paramagnetic is
 (a) $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$,
 (b) $[\text{Cr}(\text{CO})_6]$, $[\text{Co}(\text{OX})_3]^{3-}$,
 (c) $[\text{PtCl}_4]^{2-}$, $[\text{NiCl}_4]^{2-}$,
 (d) $[\text{CoCl}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$
41. The total number of complexes which can absorb visible wavelength of electromagnetic radiation is
 (a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Sc}(\text{H}_2\text{O})_6]\text{Cl}_3$,
 (b) $[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$, $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_3$,
 (c) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$,
 (d) $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cu}(\text{NH}_3)_4]\text{Cl}$,
 $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
42. The total number of complexes which can form optical isomers only is
 (a) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$,
 (b) $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, $\text{K}_3[\text{Fe}(\text{OX})_3]$
 (c) $[\text{Ni}(\text{en})_3]\text{SO}_4$, $\text{K}_2[\text{NiCl}_4]$,
 (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
43. The total number of complexes which are diamagnetic is
 (a) $\text{Fe}(\text{CO})_5$, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$,
 (b) $\text{K}_2(\text{HgI}_4)$, $\text{K}_3[\text{Co}(\text{OX})_3]$,
 (c) $\text{K}_3[\text{CoF}_6]$, $\text{K}_3[\text{Cr}(\text{OX})_3]$
 (d) None of these
44. The total number of complexes which have a magnetic moment of 2.86 BN is:
 (a) $\text{Hg}[\text{Co}(\text{SCN})_4]$, $\text{K}_4[\text{Ni}(\text{CN})_4]$,
 (b) $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$, $\text{K}_3[\text{V}(\text{OX})_3]$,
 (c) $\text{K}_3[\text{Cr}(\text{CN})_6]$, $[\text{Ni}(\text{CO})_4]$,
 (d) $\text{K}[\text{Co}(\text{CO})_4]$
45. The total number of complexes which have no electrons in the e_g set of orbitals
 (a) $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Cr}(\text{CO})_6]$,
 (b) $[\text{Cr}(\text{en})_3]\text{Cl}_3$, $[\text{Co}(\text{en})_3]\text{Cl}_3$,
 (c) $[\text{V}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_3[\text{Mn}(\text{CN})_6]$,
 (d) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
46. The total number of salts which will be coloured in aqueous solution is
 (a) LiNO_3 , $\text{Co}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$,
 (b) CrCl_3 , SnCl_4 , TiCl_4 ,
 (c) VCl_3 , $\text{Cu}(\text{NO}_3)_2$
 (d) None of these

COMPREHENSION TYPE

47. NiCl_2 solution is treated separately with excess KCN and conc. HCl leading to the formation of A and B respectively. Work out the following:

[A] Mark the correct one with respect to magnetic nature of A and B:

- (a) Both are paramagnetic
- (b) Both are diamagnetic
- (c) A is diamagnetic and B is paramagnetic
- (d) B is paramagnetic for 3 electrons

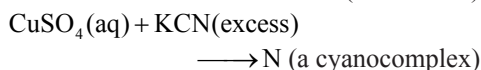
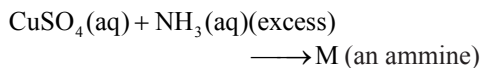
[B] The IUPAC name of A is:

- (a) Potassium tetracyano nickel (II)
- (b) Potassium tetracyano nickelate (II)
- (c) Tetra cyano nickel (II)
- (d) Tetra cyano potassium nickelate (II)

[C] The hybridization of Ni in A and B are:

- (a) sp^3 , dsp^2
- (b) dsp^2 , dsp^2
- (c) dsp^2 , sp^3
- (d) sp^3 , sp^3

48. Consider the reactions:



[A] The IUPAC name of N is:

- (a) tetracyano copper (II)
- (b) tetracyano cuprate (II)
- (c) tetracyano cuprate (I)
- (d) tetracyano copper (I)

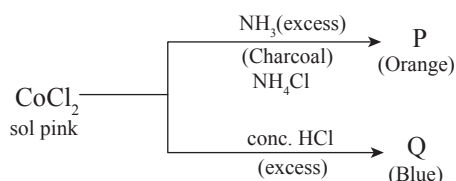
[B] Mark the correct one:

- (a) M and N both are coloured
- (b) M is coloured and N is colourless
- (c) M is colourless and N is coloured
- (d) M and N both are diamagnetic

[C] The hybridization of Cu in M and N are:

- (a) sp^3 , sp^3
- (b) dsp^2 , dsp^2
- (c) sp^2d , sp^3
- (d) sp^2d , sp^2d

49. CoCl_2 in water reacts as



The complex is:

[A] P is

- (a) $[\text{Co}(\text{NH}_3)_6]^{2+}$
- (b) $[\text{Co}(\text{NH}_3)_4]^{3+}$
- (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (d) $[\text{Co}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$

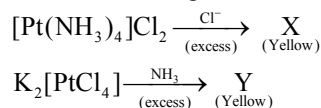
[B] The complex Q is:

- (a) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$
- (b) $[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]^+$
- (c) $[\text{Co}(\text{H}_2\text{O})\text{Cl}_3]$
- (d) $[\text{CoCl}_4]^{2-}$

[C] Identify structure and magnetic nature of P and Q.

- (a) P and Q both are octahedral and paramagnetic
- (b) P and Q both are tetrahedral and paramagnetic
- (c) P is octahedral and paramagnetic and Q is tetrahedral and diamagnetic
- (d) Q is tetrahedral and paramagnetic and P is octahedral and diamagnetic.

50. Platinum in +2 oxidation state mainly forms four coordinated complexes



[A] The IUPAC name of X is:

- (a) Tetrachloroplatinate (II)
- (b) cis-diammine dichloro platinum (II)
- (c) trans-diammine dichloro platinum (II)
- (d) Ammine trichloro platinate (II)

[B] The IUPAC name of Y is:

- (a) cis-diammine dichloro platinum (II)
- (b) trans-diammine dichloro platinum (II)
- (c) Ammine trichloro platinum (II)
- (d) Ammine trichloro platinate (II)

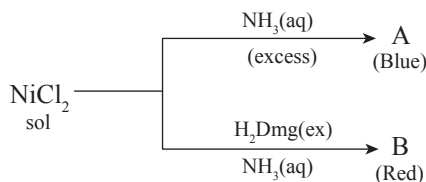
[C] Predict magnetic nature of X and Y:

- (a) both are paramagnetic
- (b) both are diamagnetic
- (c) X is diamagnetic and Y is paramagnetic with one unpaired electron
- (d) Y is paramagnetic with two unpaired electrons and X is diamagnetic

[D] The hybridization of platinum in X and Y are:

- (a) sp^3 , sp^3 (b) dsp^2 , sp^3
 (c) dsp^2 , dsp^2 (d) sd^3 , sd^3

51. Ni forms octahedral, square planar and tetrahedral complexes in +2 oxidation state. Consider the following:



[A] The complex A is:

- (a) $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$
 (b) $[\text{Ni}(\text{NH}_3)_2]\text{Cl}_2$
 (c) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
 (d) $[\text{Ni}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Cl}_2$

[B] The IUPAC name of A is:

- (a) Hexammine nickel (II) chloride
 (b) Hexammine nickel (III) chloride
 (c) Tetrammine nickel (II) chloride
 (d) Tetrammine diaqua nickel (II) chloride

[C] The complex B is:

- (a) tris-dimethylglyoximate nickalate (II)
 (b) bis-dimethylglyoximate nickalate (II)
 (c) bis-dimethylglyoximate nickal (II)
 (d) dimethyl glyoximate nickel (II)

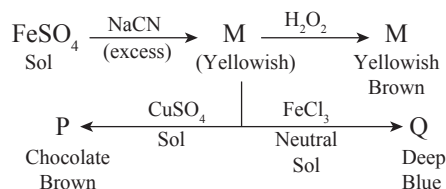
[D] The magnetic nature of A and B are:

- (a) A is diamagnetic and B is paramagnetic
 (b) A is paramagnetic and B is diamagnetic
 (c) A is paramagnetic for one electrons
 (d) B is paramagnetic for two electrons

[E] The hybridization of Ni in A and B respectively are:

- (a) sp^3d^2 , dsp^2 (b) d^2sp^3 , dsp^2
 (c) sp^3d^2 , sp^3 (d) d^2sp^3 , sp^3

52. Iron in +2 and +3 oxidation states forms many tetrahedral and octahedral complex



[A] The compounds M and N respectively are:

- (a) $\text{Fe}(\text{CN})_2$, $\text{Fe}(\text{CN})_3$
 (b) $\text{Fe}(\text{CN})_3$, $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_2[\text{Fe}(\text{CN})_4]$

[B] The magnetic nature of M and N are:

- (a) M and N both are paramagnetic
 (b) M and N both are diamagnetic
 (c) M is diamagnetic, N is paramagnetic
 (d) N is paramagnetic for two electrons

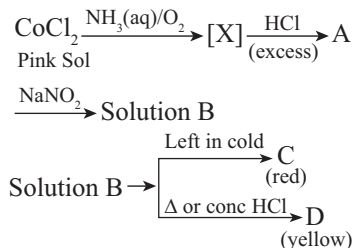
[C] The compound O and P are:

- (a) $\text{Fe}_2[\text{Fe}(\text{CN})_6]$, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$
 (b) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$
 (c) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, $\text{Cu}_4[\text{Fe}(\text{CN})_6]$
 (d) $\text{Fe}_2[\text{Fe}(\text{CN})_4]_3$, $\text{Cu}[\text{Fe}(\text{CN})_4]$

[D] The hybridization of iron in M and N respectively are:

- (a) d^2sp^3 , d^2sp^3
 (b) sp^3d^2 , d^2sp^3
 (c) sp^3d^2 , sp^3d^2
 (d) sp^3d^2 , sp^3

53. Cobalt forms variety of complexes. Consider the following:



[A] The compound A is:

- (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$
 (b) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
 (c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (d) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

[B] The compound C is:

- (a) $[\text{Co}(\text{NO}_2)_6]^{3-}$
- (b) $[\text{Co}(\text{ONO})_6]^{3-}$
- (c) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$
- (d) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$

[C] The compound D is:

- (a) $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$
- (b) $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{+2}$
- (c) $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{+2}$
- (d) $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$

ANSWERS

SINGLE ANSWER

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (c) | 4. (a) | 5. (a) | 6. (a) | 7. (d) | 8. (a) | 9. (b) | 10. (d) |
| 11. (b) | 12. (c) | 13. (d) | 14. (b) | 15. (c) | 16. (d) | 17. (d) | 18. (b) | 19. (c) | 20. (c) |
| 21. (c) | 22. (a) | 23. (b) | 24. (c) | 25. (d) | 26. (c) | 27. (d) | 28. (d) | 29. (a) | 30. (a) |

MULTIPLE ANSWER

- | | | | | |
|---------------|------------|------------|---------------|---------|
| 31. (c, d) | 32. (b, d) | 33. (a, c) | 34. (a, b, d) | 35. (a) |
| 36. (a, b, d) | 37. (b, d) | 38. (a, c) | | |

SINGLE DIGIT INTEGER (0 TO 9) ANSWER TYPE QUESTION

- | | | | | |
|---------|---------|---------|---------|---------|
| 39. (5) | 40. (3) | 41. (5) | 42. (2) | 43. (4) |
| 44. (3) | 45. (5) | | | |

COMPREHENSIVE TYPE

- 47. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{b}); \text{C} \rightarrow (\text{c})$
- 48. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{b}); \text{C} \rightarrow (\text{c})$
- 49. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{d}); \text{C} \rightarrow (\text{d})$
- 50. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{a}); \text{C} \rightarrow (\text{b}); \text{D} \rightarrow (\text{c})$
- 51. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{a}); \text{C} \rightarrow (\text{c}); \text{D} \rightarrow (\text{b}); \text{E} \rightarrow (\text{a})$
- 52. $\text{A} \rightarrow (\text{c}); \text{B} \rightarrow (\text{c}); \text{C} \rightarrow (\text{b}); \text{D} \rightarrow (\text{a})$
- 53. $\text{A} \rightarrow (\text{d}); \text{B} \rightarrow (\text{c}); \text{C} \rightarrow (\text{b})$

CHAPTER 7: ABUNDANCE AND METALLURGY

OBJECTIVE QUESTIONS

- The slag in the isolation of copper from chalcopyrite is:
 - CaSiO_3
 - $\text{FeO} + \text{CuSiO}_3$
 - FeSiO_3
 - $\text{Cu}_2\text{S} + \text{FeO}$
- Which of the following metal is obtained by electrolytic reduction?
 - Fe
 - Pb
 - Sn
 - Al
- Iron is not extracted from which of the following?
 - FeS_2
 - Fe_2O_3
 - FeCO_3
 - $\text{FeO}(\text{OH})$
- Zinc is extracted from zinc blende by:
 - reduction with carbon
 - roasting followed by self-reduction
 - roasting followed by carbon reduction
 - roasting followed by electrolytic reduction
- Which of the following has lowest percentage of carbon?
 - Pig iron
 - cast iron
 - steel
 - wrought iron
- Which of the following is involved in the extraction of Ag from argentite?
 - $[\text{Ag}(\text{NH}_3)_2]^+$
 - $[\text{Ag}(\text{SCN})_4]^{3-}$
 - $[\text{Ag}(\text{CN})_2]^-$
 - $[\text{AgCl}_2]^-$
- The element which is present maximum as the impurity in Pig-iron is
 - Si
 - P
 - C
 - Mn
- Slag in the extraction of iron from haematite is:
 - CaSiO_3
 - CuSiO_3
 - MnSiO_3
 - $\text{Mn}_3(\text{PO}_4)_2$
- The metal which is obtained ultra pure by Mond's process is:
 - Mn
 - Fe
 - Co
 - Ni
- The reducing agent in the middle portion of blast furnace in the extraction of iron is:
 - $\text{C} + \text{CO}$
 - CO
 - C
 - $\text{C} + \text{CO}_2$
- Roasting is an essential step for sulphide ores for extraction of metal because:
 - CO_2 is less stable than CS_2
 - Metal sulphides are more stable than metal oxides
 - Metal sulphides are less stable than metal oxides
 - CS_2 is liquid and CO_2 is a gas
- Lead from low grade ore is extracted by:
 - C-reduction
 - self-reduction
 - electrolytic reduction
 - metal-reduction
- When bauxite contains Fe_2O_3 as major matrix, pure alumina is obtained by:
 - Serpek's process
 - Dow – process
 - Baeyer's – process
 - Wacker – process
- The metal which can be refined by liquation and electrolytic methods both is:
 - Fe
 - Pb
 - Sn
 - Ag
- Which of the following ore does not contain iron?
 - Limonite
 - Magnesite
 - Magnetite
 - Siderite
- Silicon for use as semiconductor is defined by?
 - Van Arkel method
 - Heating under vacuum
 - Hoop's method
 - Zone refining

17. Which of the following sulphide ore is concentrated by leaching and not by froth floatation process:

(a) Chalcopyrite (b) Sphalerite
(c) Argentite (d) Galena

18. Cassiterite is an ore of:

(a) Ti (b) Sn
(c) Ni (d) Sb

19. Conversion of Pig-iron into steel involves:

(a) addition of carbon to pig-iron
(b) addition of Si to pig-iron
(c) removal of C from pig-iron
(d) reduction of MnO in pig-iron

20. Which of the following can be magnetized permanently:

(a) Pig-iron
(b) Wrought-iron
(c) Steel
(d) Cast iron

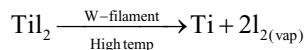
21. In the reaction $\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \xrightarrow{\Delta} \text{Cu} + \text{SO}_2$, the reducing agent is

(a) O^{-2} (b) Cu^{+}
(c) S (d) S^{-2}

22. In which of the following mineral Al is not present:

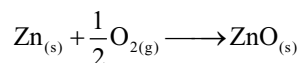
(a) Fluorspar (b) Feldspar
(c) Mica (d) Cryolite

23. The method of purification given below corresponds with which of the following processes

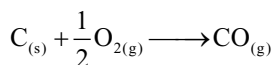


(a) Kroll process
(b) Degusa process
(c) Van Arkel process
(d) Cupellation

24. Consider the following reaction at 25°C .



$$\Delta G^\circ = -627\text{KJ}$$

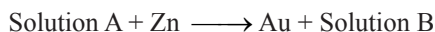
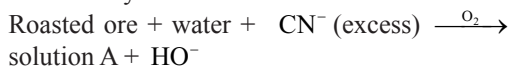


$$\Delta G^\circ = -230\text{KJ}$$

Choose the correct statement at 1000°C .

(a) C will reduce ZnO to Zn
(b) C will not reduce ZnO to Zn
(c) Zn will reduce CO to C
(d) Zn will oxidize $\text{CO}_2 + \text{CO}$

25. The extraction of gold involves leaching of ore followed by extraction of metal



The chemical species in solution A and solution B respectively are:

(a) $[\text{Au}(\text{CN})_4]^-$, $[\text{Zn}(\text{CN})_4]^{2-}$
(b) $[\text{Au}(\text{CN})_2]^-$, $[\text{Zn}(\text{CN})_4]^{2-}$
(c) $[\text{Au}(\text{CN})_4]^{2-}$, $[\text{Zn}(\text{CN})_6]^{4-}$
(d) $[\text{Au}(\text{CN})_2]^-$, $[\text{Zn}(\text{CN})_2]$

26. The chief methods of extraction of Sn and Pb respectively are:

(a) self-reduction and carbon-reduction
(b) C-reduction and self-reduction
(c) C-reduction and electrolytic-reduction
(d) Cyanide process and C-reduction

27. Heating a mixture of Cu_2S and Cu_2O gives:

(a) $\text{Cu} + \text{SO}_2$ (b) $\text{Cu} + \text{SO}_3$
(c) $\text{CuO} + \text{SO}_2$ (d) CuSO_4

28. The leaching agent in the production of pure Al_2O_3 from bauxite by Hall's process is:

(a) NaOH solution
(b) NaCN solution
(c) $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$
(d) $\text{Ba}(\text{OH})_2$ solution

29. For removal of iron from roasted ore of Cu the flux used is:

(a) CO_2 (b) SiO_2
(c) SO_2 (d) NO_2

MORE THAN ONE CORRECT

30. Among the following metal(s), the one which cannot be obtained by electrolysis of aqueous solution of their salt is (are):
 (a) Mg (b) Cu
 (c) Al (d) Au
31. Which of the following alloy(s) contain(s) Ni?
 (a) Bell metal (b) Monel metal
 (c) Gun metal (d) German silver
32. The metal(s) which is (are) obtained by C-reduction and self-reduction both:
 (a) Pb (b) Zn
 (c) Sn (d) Cu
33. Which of the following ore(s) is (are) concentrated by froth floatation process?
 (a) Magnetite (b) Malachite
 (c) Sphalerite (d) Chalcopyrite
34. The function of cryolite in the electrolysis of alumina is to:
 (a) remove SiO_2 from alumina
 (b) decrease the melting point of alumina
 (c) reduce the oxidation of graphite anode
 (d) to convert a poor electrolyte into a good electrolyte
35. The main reaction(s) in the middle zone of blast furnace in the metallurgy of iron is (are):
 (a) $\text{CaCO}_3 \rightarrow \text{CaO} \xrightarrow{\text{SiO}_2} \text{CaSiO}_3$
 (b) $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
 (c) $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$
 (d) $\text{CO}_2 + \text{C} \longrightarrow 2\text{CO}$
36. Calcium silicate (CaSiO_3) is (are) slag in the metallurgy of which of the following metal(s):
 (a) Fe (b) Cu
 (c) Pb (d) Zn
37. The extraction of pure metal from the ore cassiterite involves:
 (a) C-reduction metallurgy
 (b) self-reduction metallurgy
 (c) removal of iron impurity
 (d) removal of Cu impurity
38. Native gold forms a soluble complex in aqueous medium in the presence of which of the following?
 (a) S^{2-} (b) CN^-
 (c) O_2 (d) CO
39. Which of the following alloy(s) contain Cu?
 (a) Duralumine (b) Solder
 (c) Magnesium (d) Bronze
40. Electrolysis of brine (Saturated solution of NaCl) produces:
 (a) H_2 (b) NaOH
 (c) O_2 (d) Cl_2
41. The important role of fluorspar (CaF_2) that is added in small quantity in the electrolytic reduction of Al_2O_3 (to Al) dissolved in fused cryolite (Na_3AlF_6) is:
 (a) to check the rate of oxidation of graphite anode
 (b) as a catalyst
 (c) to lower the fusion temperature of Al_2O_3
 (d) to make the melt more conducting
42. The anode mud in the electrolytic refining of Cu contains:
 (a) Au (b) Sn
 (c) Zn (d) Ag
43. The metallurgy of iron involves reactions in the blast furnace, which of the following statement(s) is (are) correct?
 (a) FeO is reduced to Fe below 1070K
 (b) Fe_2O_3 is reduced to Fe below 1070K
 (c) FeO is reduced to Fe above 1070K
 (d) CaSiO_3 is formed above 1070K
44. Coke is added during roasting of haematite. Its purpose is (are) to
 (a) Make the ore porous
 (b) Check the reduction of Fe_2O_3 to Fe_3O_4
 (c) Reduce Fe_2O_3 to FeO
 (d) Reduce FeO to Fe
45. The roasting of copper pyrite (or Chalcopyrite) produces:
 (a) ($\text{FeS} + \text{Cu}_2\text{S}$) only
 (b) ($\text{Cu}_2\text{O} + \text{FeO}$) only
 (c) ($\text{Cu}_2\text{S} + \text{Cu}_2\text{O}$)
 (d) ($\text{FeO} + \text{FeS}$)

46. Lead from low grade ore is obtained by carbon reduction method. Roasted ore is heated with C and lime. Recovered lead is further purified by electrolytic method:
- (i) Slag in this metallurgy is:
- (a) CaSiO_3
(b) FeSiO_3
(c) MnSiO_3
(d) CaCO_3
- (ii) The anode in the purification of Pb is:
- (a) Pt – wire
(b) graphite rod
(c) Impure – Pb
(d) Pure – Zn
47. Two ores A and B of a metal behave in the following way:
- (i) Mark the correct statement for A:
- (a) A is an oxide ore
(b) A is a sulphide ore
(c) A is not a sulphide ore
(d) A is a chloride ore
- (ii) Which of the following is true for B:
- (a) B is a sulphide ore
(b) B is not a sulphide ore
(c) B is a carbonate ore
(d) B is a nitrite ore
48. P and Q are two ores of M which forms many alloys. The ores P and Q undergo the following reactions:
- P $\xrightarrow{\text{Calcine}}$ White solid + Gas $\xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7}$ X
- |
C/ Δ → Metal + CO
- Q $\xrightarrow{\text{Roast}}$ White solid + Gas $\xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7}$ Green sol.
- |
C/ Δ → Metal + CO
- (i) The chemical class of the ore P is:
- (a) Sulphide
(b) Oxide
(c) Carbonate
(d) Nitrate
- (ii) The ore B is a:
- (a) Carbene
(b) Sulphide
(c) Chloride
(d) Oxide
49. Copper is an important metal known from prehistoric time. It is found in many ores like cuprite (Cu_2O), Copper glance (Cu_2S), Chalcopyrite (CuFeS_2), Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) etc. The extraction of Cu may be carried out by C – reduction and self – reduction both:
- (i) Cu is extracted from malachite by:
- (a) Self – reduction
(b) Calcination followed by C – reduction
(c) Calcination followed by Self – reduction
(d) Roasting followed by C– reduction
- (ii) Slag in the metallurgy of Cu from Chalcopyrite is:
- (a) FeSiO_3
(b) CaSiO_3
(c) $\text{Fe}_2(\text{SiO}_3)_3$
(d) MnSiO_3
- (iii) In the self-reduction meta-llurgy of Cu the reducing agent is:
- (a) SO_2
(b) S
(c) O^{2-}
(d) S^{2-}

MATRIX MATCH

50. Match the changes shown in Column I with the type(s) of reaction(s) given in Column II.

| Column – I | Column – II |
|---|------------------------|
| (a) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$ | (p) Calcinations |
| (b) $\text{ZnS} \rightarrow \text{Zn}$ | (q) Roasting |
| (c) $\text{PbS} \rightarrow \text{Pb}$ | (r) Self-reduciton |
| (d) $\text{CaCO}_3 \rightarrow \text{CaO}$ | (s) Carbon – reduction |
| | (t) Galena |

51. Match the process of extraction listed in Column I with metals in Column II.

| Column – I | Column – II |
|--|-------------|
| (a) Carbon-reduciton | (p) Fe |
| (b) Self-reduction | (q) Ag |
| (c) Decomposition of iodide | (r) Ti |
| (d) Complex formation and displacement of M by metal | (s) Cu |
| | (t) B |

52. Match the ores given in Column I with process(es) mentioned in Column II.

| Column – I | Column – II |
|------------------|----------------------|
| (a) Cassiterite | (p) Metal reduction |
| (b) Chalcopyrite | (q) C – reduction |
| (c) Argentite | (r) Hydrometallurgy |
| (d) Silica | (s) Self – reduction |
| | (t) Zone – refining |

53. Match the metal(s) in Column I with alloy(s) in Column II.

| Column – I | Column – II |
|---------------|----------------|
| (a) Lead | (p) Solder |
| (b) Copper | (q) Duralumin |
| (c) Magnesium | (r) Bell-metal |
| (d) Zinc | (s) Bronze |
| | (t) Gun metal |

54. Match the metal(s) in Column I with ore(s) given in Column II.

| Column – I | Column – II |
|------------|----------------|
| (a) Mg | (p) Sphalerite |
| (b) Al | (q) Carnalite |
| (c) Zn | (r) Cryolite |
| (d) Cu | (s) Malachite |
| | (t) Calamine |

ANSWER

SINGLE ANSWER

1. (c) 2. (d) 3. (a) 4. (c) 5. (d) 6. (c) 7. (c) 8. (a) 9. (d) 10. (b)
 11. (b) 12. (a) 13. (c) 14. (c) 15. (b) 16. (d) 17. (c) 18. (b) 19. (c) 20. (c)
 21. (d) 22. (a) 23. (c) 24. (a) 25. (b) 26. (b) 27. (a) 28. (c) 29. (b)

MULTIPLE ANSWER

30. (a, c) 31. (b, d) 32. (a, d) 33. (c, d) 34. (b, d) 35. (a, d) 36. (a, c) 37. (a, c, d)
 38. (b, c) 39. (a, d) 40. (a, b, d) 41. (c, d) 42. (a, d) 43. (c, d) 44. (a) 45. (c, d)

COMPREHENSIVE TYPE QUESTIONS

46. (i) \rightarrow (a); (ii) \rightarrow (b) 47. (i) \rightarrow (c); (ii) a
48. (i) \rightarrow (c); (ii) \rightarrow (b) 49. (i) \rightarrow (b); (ii) \rightarrow (a); (iii) \rightarrow (d)

MATRIX MATCH QUESTIONS

50. (a) \rightarrow (q, r); (b) \rightarrow (q, s); (c) \rightarrow (q, r, t); (d) \rightarrow (p)
51. (a) \rightarrow (p, s); (b) \rightarrow (s); (c) \rightarrow (r, t); (d) \rightarrow (q)
52. (a) \rightarrow (q); (b) \rightarrow (s); (c) \rightarrow (p, r); (d) \rightarrow (q, t)
53. (a) \rightarrow (p); (b) \rightarrow (q, r, s, t); (c) \rightarrow (q); (d) \rightarrow (r)
54. (a) \rightarrow (q); (b) \rightarrow (r); (c) \rightarrow (p, t); (d) \rightarrow (s)

CHAPTER 9: HYDROGEN AND ITS CHEMISTRY

ONLY ONE OPTION IS CORRECT

1. The coloured oxide which gives H_2O_2 on reaction with dil. acid is:
 - (a) KO_2
 - (b) PbO_2
 - (c) TiO_2
 - (d) MnO_2
2. The oxidation states of most electronegative element in the product when KO_2 reacts with water is:
 - (a) 0, -1, -2
 - (b) 0, -2
 - (c) 0, -1
 - (d) -1, -2
3. The heavy water is:
 - (a) H_2O
 - (b) $^2\text{H}_2\text{O}$
 - (c) $^3\text{H}_2\text{O}$
 - (d) H_2O_3
4. The volume strength of 1.2N H_2O_2 solution is:
 - (a) 6.7
 - (b) 5.2
 - (c) 7.6
 - (d) 4.8
5. The molarity of 30 volume H_2O_2 solution is:
 - (a) 3.6
 - (b) 4.6
 - (c) 2.7
 - (d) 6.2
6. The structure of H_2O_2 is:
 - (a) Linear
 - (b) Non-planar
 - (c) Planar
 - (d) Trigonal pyramidal
7. Electrolysis of 50% H_2SO_4 produces which of the following?
 - (a) $\text{H}_2\text{S}_2\text{O}_3$
 - (b) $\text{H}_2\text{S}_2\text{O}_4$
 - (c) $\text{H}_2\text{S}_2\text{O}_5$
 - (d) $\text{H}_2\text{S}_2\text{O}_8$
8. Hydrolysis of one mole of peroxydisulphuric produces which of the following?
 - (a) H_2O_2 and $\text{H}_2\text{S}_2\text{O}_3$
 - (b) $2\text{H}_2\text{O}_2$ and H_2SO_4
 - (c) H_2O_2 and $2\text{H}_2\text{SO}_4$
 - (d) H_2O_2 and $2\text{H}_2\text{SO}_3$
9. The correct order of decreasing electrical conductance is:
 - (a) $\text{CaH}_2 > \text{BeH}_2 > \text{TiH}_2$
 - (b) $\text{TiH}_2 > \text{CaH}_2 > \text{BeH}_2$
 - (c) $\text{CaH}_2 > \text{TiH}_2 > \text{BeH}_2$
 - (d) $\text{BeH}_2 > \text{TiH}_2 > \text{CaH}_2$
10. Which is expected to have lowest conductivity?
 - (a) Hard water
 - (b) Heavy water
 - (c) Demineralized water
 - (d) H_2^{18}O
11. The reducing power of H_2O , NaH and MgH_2 increases in the order:
 - (a) $\text{H}_2\text{O} > \text{NaH} > \text{CaH}_2$
 - (b) $\text{CaH}_2 > \text{NaH} > \text{H}_2\text{O}$
 - (c) $\text{NaH} > \text{H}_2\text{O} > \text{CaH}_2$
 - (d) $\text{NaH} > \text{MgH}_2 > \text{H}_2\text{O}$
12. Which is neither a Lewis acid nor a Lewis base?
 - (a) C_2H_4
 - (b) C_3H_4
 - (c) C_4H_4
 - (d) C_2H_6
13. Hot NaH and CO_2 react to form:
 - (a) C and NaOH
 - (b) CO and NaOH
 - (c) HCOONa only
 - (d) Na and HCOOH
14. The density of water at 4°C is maximum because:
 - (a) more of hydrogen-bonds are formed
 - (b) thermal expansion is minimum
 - (c) thermal expansion dominate over H – bond
 - (d) thermal expansion and H– bond balance each other
15. The $\text{g}^\ell\text{L}^{-1}$ of 20 volume H_2O_2 solution is:
 - (a) 60.7
 - (b) 50.7
 - (c) 65.7
 - (d) 55.7
16. Nascent hydrogen is:
 - (a) Hydrogen molecule with extra energy
 - (b) Hydrogen atom formed in a solution
 - (c) Hydrogen ions in excited state
 - (d) Aquated proton only as H_3O^+

17. The normality of 10 volume H_2O_2 solution is:
(a) 1.8 (b) 1.4 (c) 1.5 (d) 2.1
18. If 0.81 g $\text{Ca}(\text{HCO}_3)_2$ is dissolved in one lakh g of water, its hardness is:
(a) 1° (b) 2° (c) 0.5° (d) 0.4°
19. Polyphosphates are used to remove hardness of water because they:
(a) precipitate cationic species
(b) precipitate anionic species
(c) form soluble complex with anionic species
(d) form soluble complex with cationic species
20. If 0.002 mol of MgSO_4 is dissolved in a water, its hardness in ppm is:
(a) 2000 (b) 1200 (c) 200 (d) 120
21. The dihedral angle in H_2O_2 in solid phase is close to:
22. The volume strength of 30% H_2O_2 solution is:
(a) 98.9V (b) 9.88V (c) 88.9V (d) 89.8V
23. The reagent that may be used to determine hardness of water by the method of titration is:
(a) Sodium dichromate
(b) Sodium thiosulphate
(c) Disodium salt of H_4EDTA
(d) Oxalic acid
24. The statement incorrect about H_2O_2 is:
(a) a pale blue liquid
(b) oxidized by O_3
(c) oxidizing and reducing agent
(d) both OH groups lie in the same plane

ONE OR MORE THAN ONE OPTION CORRECT

25. Which is (are) correct for H_2O_2 :
(a) H_2O_2 is denser than H_2O
(b) H_2O_2 is weaker acid than H_2O
(c) H_2O_2 is stronger acid than H_2O
(d) H_2O_2 is a linear molecule
26. The complete hydrolysis of peroxodisulphuric acid produces:
(a) one mole H_2SO_4
(b) two mole H_2SO_5
(c) one mole H_2O_2
(d) two mole H_2SO_4
27. When hard water is treated with zeolite, which is hydrated sodium aluminium silicate, the sodium ions are exchanged with:
(a) Mg^{2+}
(b) SO_4^{2-}
(c) Ca^{2+}
(d) Cl^-
28. Ozone is a strong oxidizing agent but it reacts with moist Ag_2O to give Ag. Other species formed during the reaction is (are):
(a) H_2O_2
(b) O_2
(c) AgOH
(d) AgO
29. Which of the following species on reaction with H_2O_2 will give MnO_2 ?
(a) Alkaline KMnO_4
(b) Acidic MnSO_4
(c) Acidic KMnO_4
(d) Alkaline MnSO_4

MATRIX MATCH

30. Match the Chemical substances given in Column I with Chemical process(es) given in Column II.

Column – I

(a) Calgan

(b) Syngas

Column – II

(p) Synthesis of methanol

(q) Moderator in nuclear reactors

(c) H_2O_2

(d) Heavy water

(r) Oxidizing agent

(s) Softening of water

(t) Reducing agent

ANSWER**SINGLE ANSWER**

1. (a) 2. (a) 3. (b) 4. (a) 5. (c) 6. (b) 7. (d) 8. (c) 9. (b) 10. (c)
 11. (d) 12. (d) 13. (c) 14. (d) 15. (a) 16. (b) 17. (a) 18. (c) 19. (d) 20. (c)
 21. (d) 22. (a) 23. (c) 24. (d)

MULTIPLE ANSWER

25. (a, c) 26. (c, d) 27. (a, c) 28. (a, b) 29. (a, d)

MATRIX MATCH

30. (a) \rightarrow (s); (b) \rightarrow (p, t); (c) \rightarrow (r, t); (d) \rightarrow (q)

CHAPTER 10: GROUP 1 (I_A) THE ALKALI METALS

ONLY ONE OPTION IS CORRECT

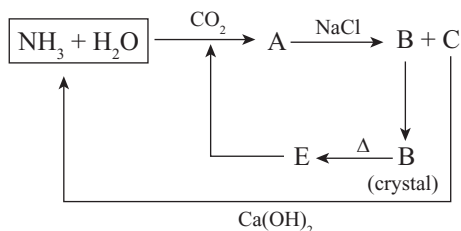
- The pair of metals which possess chemical similarity is:
 - Li, Ca
 - Li, Mg
 - Li, Al
 - Li, Ti
- Which of the following has an unpaired electron?
 - BaO₂ and PbO₂
 - AlO₂⁻ only
 - KO₂ and AlO₂⁻
 - KO₂ only
- Brine (saturated aqueous solution of NaCl) on electrolysis will not give:
 - O₂
 - NaOH
 - Cl₂
 - H₂
- The metal ions in water are hydrated and represented as
 [I] Na⁺_{(H₂O)_x} [II] Li⁺_{(H₂O)_x} [III] K⁺_{(H₂O)_x}
 The size of the above hydrated ions decreases in the order:
 - I > II > III
 - III > II > I
 - II > I > III
 - I > III > II
- Taking into account different parameters, which one is expected to have highest melting point?
 - KCl
 - NaCl
 - LiCl
 - RbCl
- The paramagnetic species is:
 - SiO₂
 - TiO₂
 - RbO₂
 - BaO₂
- A solution of Na in liquid NH₃ is strong reducing due to the presence of:
 - solvated Na⁺
 - solvated electrons
 - sodium amide
 - sodium imide
- The metallic lustre in Na is due to:
 - its body centred cubic lattice
 - excitation of free electrons
 - oscillation of loosely held electrons
 - adsorption of electrons
- Sodium sulphate solution when electrolysed using Pt-electrodes (inert) produces which of the following at anode and cathode respectively:
 - O₂ and Na
 - O₂ and H₂
 - H₂ and O₂
 - H₂ and SO₂
- Which of the following mixture will give a coloured solution in tetrahydrofuran?
 - Me₂CH – OH + Na
 - Me₂C – OH + Na
 - Ph₂CO + Na
 - Me₂CCH₂ – OH + Na
- The metal ion essential for the metabolism of glucose inside the cell is:
 - Na⁺
 - K⁺
 - Mg²⁺
 - Cu⁺
- In animal cells, the concentration of which of the following metal ion is highest?
 - K⁺
 - Na⁺
 - Cs⁺
 - Rb⁺
- In body fluids, the concentration of which of the following is largest?
 - K⁺
 - Cs⁺
 - Rb⁺
 - Na⁺
- The metal which is used in photocells is
 - Ba
 - Cs
 - Li
 - Ti

ONE OR MORE THAN ONE OPTION CORRECT

15. Which of the following is(are) used as coolant in fast breeder nuclear reactors:
- Liquid lithium
 - Liquid caesium
 - Liquid sodium
 - Na – K alloy
16. Sodium metal is used in which of the reaction(s):
- Kolbe electrolytic reaction
 - Etard reaction
 - Fitting reaction
 - Wittig reaction
17. Sodium nitrate on heating at around 500°C gives:
- Na_2O_2
 - O_2
 - NaNO_2
 - NO_2
18. The statement(s) which is(are) correct for Na and K:
- They maintain osmotic pressure inside the cell
 - They neutralize negative charge on macromolecules in the cell

- Na^+ & K^+ are present in equal amounts inside and outside the cell
- Na^+ & K^+ are present in different amounts inside and outside the cell

19. Consider the following flow sheet diagram and answer the questions:



- (i) The compound B is:
- Na_2CO_3
 - NaHCO_3
 - NH_4HCO_3
 - NH_4Cl
- (ii) The compound C is:
- NH_4Cl
 - $(\text{NH}_4)_2\text{CO}_3$
 - NH_4HCO_3
 - NaHCO_3
- (iii) The compound E is:
- $(\text{NH}_4)_2\text{CO}_3$
 - Na_2CO_3
 - NH_4HCO_3
 - NH_4Cl

ANSWER**SINGLE ANSWER**

1. (b) 2. (d) 3. (a) 4. (c) 5. (b) 6. (c) 7. (b) 8. (c) 9. (b) 10. (c)
 11. (b) 12. (a) 13. (d) 14. (b)

MULTIPLE ANSWER

15. (c, d) 16. (c) 17. (b, c) 18. (a, b, d)

FLOW SHEET DIAGRAM

119. (i) \rightarrow (b); (ii) \rightarrow (a) (iii) \rightarrow (b)

CHAPTER 11: GROUP – 2 (II_A) [BE, MG, CA, SR, BA, RA]

OBJECTIVE QUESTIONS (ONE CORRECT)

- Active constituent in bleaching powder is:
 (a) $\text{Ca}(\text{OCl})\text{Cl}$ (b) $\text{Ca}(\text{OCl}_2)_2$
 (c) $\text{Ca}(\text{OCl})_2$ (d) $\text{Ca}(\text{ClO}_3)_2$
- MgCl_2 solution when treated with sodium salt of unknown anion gives white precipitate only on boiling. The anion of sodium salt may be:
 (a) CO_3^{2-} (b) HCO_3^-
 (c) NO_3^- (d) SO_4^{2-}
- The purpose of curing cement plaster with water is:
 (a) To keep it cool
 (b) To simply hydrate mortar
 (c) To change CaO to $\text{Ca}(\text{OH})_2$
 (d) To develop inter locking between hydrated silicates
- Which of the following is not an ore of magnesium?
 (a) Magnesite (b) Dolomite
 (c) Magnetite (d) Carnalite
- One mol magnesium nitride on reaction with excess water gives:
 (a) One mol of NH_3
 (b) One mol of HNO_3
 (c) Two mol of $\text{H}_2\text{N} - \text{OH}$
 (d) Two mol NH_3
- When BaO_2 reacts with dil H_2SO_4 , the oxidation states of the most electronegative elements in the products is:
 (a) $-1, -2$ (b) $0, -1$
 (c) $-2, 0$ (d) -1 only
- The property that increases down group 2 metals is:
 (a) Rate of reaction with H_2
 (b) Charge-radius ratio
 (c) Solubility of chlorides
 (d) $\Delta H_{(\text{Hyd})}$ of M^{2+} ions
- The metal that does not produce H_2 with cold water is:
 (a) Ba (b) Mg
 (c) Ca (d) Sr
- The thermal stability of $\text{MgCO}_3(\text{I})$, $\text{CaCO}_3(\text{II})$, $\text{Na}_2\text{CO}_3(\text{III})$ and $\text{BeCO}_3(\text{IV})$ decreases in the order:
 (a) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (b) $\text{IV} > \text{I} > \text{II} > \text{III}$
 (c) $\text{III} > \text{IV} > \text{II} > \text{I}$
 (d) $\text{IV} > \text{II} > \text{III} > \text{I}$
- Asbestos is:
 (a) Na and Ca silicate
 (b) Al and Na silicate
 (c) Al and Mg silicate
 (d) Mg and Ca silicate
- The solubility of MCO_3 compounds of group-2 metals decreases down the group due to:
 (a) decrease in inter-ionic force
 (b) decrease in lattice energy of MCO_3
 (c) increase in entropy of solution process
 (d) decrease in hydration energy of cations
- The purpose of adding gypsum in cement is to:
 (a) Slow down the process of setting
 (b) Make the process of setting fast
 (c) Mix cement better with concrete and sand
 (d) Dissolve calcium aluminate in cement
- Cement is a mixture of compounds. Which of the following compounds is present maximum in cement:
 (a) Ca_3SiO_5 (b) Ca_2SiO_4
 (c) $\text{Ca}_3\text{Al}_2\text{O}_6$ (d) SiO_2
- The chloride that crystallises with lowest number of water molecules is:
 (a) BeCl_2 (b) MgCl_2
 (c) SrCl_2 (d) BaCl_2

MULTIPLE CHOICE (ONE OR MORE THAN ONE CORRECT)

15. Which of the following metal(s) dissolve in liquid NH_3 ?
 (a) Be (b) Ca
 (c) Mg (d) K
16. The correct statement(s) for group-2 metals is (are):
 (a) The melting point of Ca is greater than Mg
 (b) The melting point of Mg is greater than Ca
 (c) The reducing power of Ca is greater than Mg
 (d) The oxides BeO and MgO are amphoteric
17. Which of the following ore(s) contain(s) Ca?
 (a) Fluorspar (b) Epson salt
 (c) Anhydrite (d) Carnallite
18. The metal(s) which fail(s) flame test is (are):
 (a) Cu (b) Mg
 (c) Sr (d) K
19. The property(ies) of Group-2 metals which increase(s) down the group:
 (a) Solubility of their fluorides
 (b) Solubility of their chlorides
 (c) Rate of reaction with H_2
 (d) Thermal stability of $\text{M}(\text{OH})_2$
20. The compound(s) which has (have) polymeric structure in solid state:
 (a) BeH_2
 (b) CaH_2
 (c) BeCl_2
 (d) CaC_2
21. Magnesium metal is strongly heated with air. The product(s) formed is (are):
 (a) MgO_2
 (b) MgO
 (c) Mg_3N_2
 (d) Mg_2O_2

ANSWER**SINGLE CHOICE**

1. (c) 2. (b) 3. (d) 4. (c) 5. (d) 6. (a) 7. (a) 8. (b) 9. (c) 10. (d)
 11. (d) 12. (a) 13. (a) 14. (d)

MULTIPLE CHOICE

15. (b, d) 16. (a, c) 17. (a, c) 18. (b) 19. (a, c, d) 20. (a, c) 21. (b, c)

CHAPTER 12 : GROUP – 11 (I_B) [COPPER, SILVER AND GOLD]

OBJECTIVE QUESTIONS

- The correct order of ionization energy is
(a) $\text{Cu} > \text{Ag} > \text{Au}$ (b) $\text{Cu} > \text{Au} > \text{Ag}$
(c) $\text{Au} > \text{Cu} > \text{Ag}$ (d) $\text{Ag} > \text{Au} > \text{Cu}$
- Bonding in Cu is
(a) Covalent
(b) Electrovalent
(c) Ionic and covalent
(d) Coordinate covalent
- Which of the following is paramagnetic?
(a) $\text{K}_3[\text{Cu}(\text{CN})_4]$ (b) $\text{K}[\text{Cu}(\text{CN})_2]$
(c) Cu_2Cl_2 (d) $\text{Cu}(\text{NO}_3)_2$
- When Cu_2S and FeS mixture is heated in air the product is
(a) Cu_2S , FeO (b) CuO , FeO
(c) Cu_2O , FeS (d) Cu_2O , FeO
- When a mixture of Cu_2S and Cu_2O are heated the product is
(a) Cu_2S (b) Cu
(c) CuSO_4 (d) CuSO_3
- When excess NH_4OH is added to CuSO_4 solution the colour is
(a) Red (b) Deep blue
(c) Light blue (d) Green
- When excess KCN is added to CuSO_4 solution the colour is
(a) Green (b) Blue
(c) Red (d) Colourless
- Which of the following is used in photography?
(a) CuBr_2 (b) CuBr
(c) AgBr (d) AuCl_3
- Which of the following does not disproportionate in water?
(a) Cu^{2+} (b) Au^{+1}
(c) Cu^{+} (d) Cl_2
- The solubility of AgBr in hypo solution is due to the formation of
(a) $\text{Ag}_2\text{S}_2\text{O}_3$ (b) $[\text{Ag}(\text{S}_2\text{O}_3)]^-$
(c) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ (d) Ag_2SO_3
- Verdigris is
(a) Basic silver acetate
(b) Basic copper acetate
(c) Basic lead acetate
(d) Basic ferric acetate
- Which of the following is expected to be coloured?
(a) CuCl (b) Ag_2SO_4
(c) CuF_2 (d) MgF_2
- The product 'A', in the following reaction is
 $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{A} + \text{H}_2\text{SO}_4 + 2\text{HCl}$
(a) CuSO_4 (b) Cu_2Cl_2
(c) CuCl_2 (d) Cu_2SO_3
- An alloy which does not contain Cu is
(a) Brass (b) Bronze
(c) Solder (d) Bell metal
- Silver sulphide dissolves in NaCN in the presence of O_2 to form the complex.
(a) $\text{Na}[\text{Ag}(\text{CN})_2]$ (b) $\text{Na}_2[\text{Ag}(\text{CN})_4]$
(c) $\text{Na}_3[\text{Ag}(\text{CN})_4]$ (d) All
- Which of the following is colored due to d – d transition?
(a) CuO (b) Cu_2O
(c) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (d) CuS
- Which of the following is coloured and paramagnetic?
(a) Cu_2Cl_2 (b) $\text{Cu}(\text{NO}_3)_2$
(c) $\text{K}[\text{Cu}(\text{CN})_2]$ (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
- Which of the following is not expected to exist?
(a) CuF (b) CuCl
(c) CuBr (d) CuI

ANSWERS

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|--------|---------|
| 1. (c) | 2. (c) | 3. (d) | 4. (a) | 5. (b) | 6. (b) | 7. (d) | 8. (c) | 9. (a) | 10. (c) |
| 11. (b) | 12. (c) | 13. (b) | 14. (c) | 15. (a) | 16. (c) | 17. (b) | 18. (a) | | |

CHAPTER 14 : GROUP – 13 (IIIA) B, AL, GA, IN, TL

OBJECTIVE QUESTIONS (ONLY ONE CORRECT)

- The product of the reaction between B_2H_6 and NH_3 at around $-120^\circ C$ is:
 - $2BH_3(NH_3)$
 - $[BH_2(NH_3)_2]^+ BH_4^-$
 - $[BH_3(NH_3)_2]^+ BH_4^-$
 - $[BH(NH_3)_3]^+ BH_4^-$
- Boric acid (H_3BO_3) is:
 - monoprotic & strong bronsted acid
 - triprotic & strong bronsted acid
 - monoprotic & weak Bronsted acid
 - monoprotic & weak Lewis acid
- Boric acid is weak but its strength can be improved in the presence of which of the following:
 - NaH_2PO_2
 - Borax
 - cis – 1, 2 – diols
 - trans – 1, 2 – diols
- The product A in the following reaction is

$$B_2H_6 + NH_3 \xrightarrow{(1:2)} A$$
 - $B_2H_5(NH_3)$
 - $B_3N_3H_6$
 - $B_2H_4(NH_3)_2$
 - BH_3NH_3
- BF_3 and NH_3 form solid addition compound. Identify the geometry and hybridization of B and N in the adduct:
 - B; planar sp^2 ; N pyramidal sp^3
 - B irregular tetrahedral, sp^3 ; N regular tetrahedral sp^3
 - B irregular tetrahedral, sp^3 ; N irregular tetrahedral sp^3
 - B pyramidal, sp^3 ; N pyramidal sp^3
- B_2H_6 reacts at low temperature with Me_3N to give which of the following:
 - $2BH_3(Me_3N)$
 - $[BH_2(NMe_3)_2]^+ BH_4^-$
 - $[BH(NMe_3)_3]^+ BH_4^-$
 - $[BH_3(NMe_3)_2]^+ BH_4^-$
- The HBH angle involving terminal H atoms in B_2H_6 is around
 - 109.5°
 - 120°
 - 95°
 - 100°
- Anhydrous $AlCl_3$ can be obtained by heating Al_2O_3 with:
 - dry Cl_2
 - dry HCl gas
 - solid KCl
 - C and dry Cl_2
- Boron always forms covalent bond because:
 - it is a p-block element
 - B^{3+} is very small
 - its electronegativity is high
 - its crystal structure is very stable
- Boric acid is weak and can not be titrated directly with NaOH solution. But it can be titrated with NaOH in the presence of:
 - Ethylene glycol
 - Dimethyl amine
 - glycerol
 - ethylmethyl ether
- In which of the following anhydrous $AlCl_3$ will dissolve more:
 - Et_2O
 - C_6H_{12}
 - C_6H_6
 - CH_2Cl_2
- The coordination number of Al in crystalline $AlCl_3$ is:
 - 4
 - 3
 - 6
 - 8
- Which of the following is correct:
 - TlI_3 contain Tl^{3+}
 - TlI_3 is a covalent compound
 - TlI_3 contain Tl^+
 - TlI_3 contain three I^- ions
- The constitution of borax, $Na_2B_4O_7 \cdot 10H_2O$ is:
 - $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
 - $Na_2[B_4O_5(OH)_6] \cdot 7H_2O$
 - $Na_2[B_4O_4(OH)_4] \cdot 8H_2O$
 - $Na_2[B_4O_6(OH)_4] \cdot 8H_2O$

MULTIPLE CHOICE QUESTION

15. Identify the correct choice(s):
 (a) Borax in water forms a basic solution
 (b) Borax in water forms an acidic solution
 (c) Borax on heating with HCl gives boric acid
 (d) Borax on heating with HCl gives sodium meta borate
16. B_2H_6 on reaction with Me_2SO_4 and NaOH form(s):
 (a) $B_2H_3Me_3$ (b) $B_2H_4Me_2$
 (c) B_2H_5Me (d) $B_2H_2Me_4$
17. Anhydrous $AlCl_3$ is used as catalyst in which of the following reaction(s):
 (a) to replace H of C_6H_6 by

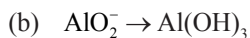
$$\begin{array}{c} O \\ || \\ CH_3 - C - R - Cl \end{array}$$

 (b) to prepare alkane from $CH_3 - C(=O) - R - Cl$
 (c) to prepare branched chain alkanes from straight chain alkane
 (d) to prepare aldehyde from alcohol
18. Which of the following compound(s) imparts green colour to the burner flame?
 (a) $B(OMe)_3$ (b) BF_3
 (c) $EtoK$ (d) $Al(OCHMe_2)_3$
19. The correct choice(s) for boric acid is (are):
 (a) H_3BO_3 is a triprotic acid
 (b) H_3BO_3 is not a protic acid
 (c) H_3BO_3 has H-bonded structure
 (d) H-bonds give a layer structure to H_3BO_3
20. Boric acid can be titrated with NaOH using methyl orange indicator in the presence of which of the following compound(s)
 (a) Catachol
 (b) ethylene glycol
 (c) mannitol
 (d) 1, 3 – cyclopentanol
21. The chemical substance(s) which is (are) not expected to exist:
 (a) B_2Cl_6 (b) Al_2F_6
 (c) Al_2I_6 (d) Al_2Cl_6
22. The correct choice(s) for group-13 elements is (are):
 (a) exhibit oxidation state of + only
 (b) exhibit oxidation state of +3 only
 (c) form electron deficient compounds
 (d) exhibit oxidation states of +1 and +3 both

MATRIX MATCH

23. Match the reactions given in Column I with Chemical facts given in Column II:

Column – I



Column – II

(p) Addition of $CN^-_{(aq)}$

(q) Hydrolysis

- (c) $B_4O_7^{2-} \rightarrow H_3BO_3$ (r) Addition of water
 (d) $AlCl_3 \xrightarrow{sol} Al(OH)_3$ (s) Acidification

ANSWERS

SINGLE ANSWER

1. (b) 2. (d) 3. (c) 4. (b) 5. (c) 6. (a) 7. (d) 8. (d) 9. (b) 10. (c)
 11. (a) 12. (c) 13. (c) 14. (a)

MULTIPLE ANSWER

15. (a, c) 16. (d) 17. (a, c) 18. (a, b) 19. (b, c, d) 20. (a, c) 21. (a, b) 22. (c, d)

MATRIX MATCH

- 23.(a) \rightarrow (q, r); (b) \rightarrow (s); (c) \rightarrow (q, r, s); (d) \rightarrow (p)

CHAPTER 15: GROUP – 14 (IVA) C, Si, Ge, Sn, Pb

OBJECTIVE QUESTIONS (SINGLE CHOICE)

- Which of the following chlorosilane will form linear silicone polymer?
 - Me_3SiCl
 - Me_2SiCl_2
 - MeSiCl_3
 - PhSiCl_3
- Among the type of silicates, in which three O-atoms of $[\text{SiO}_4]^{4-}$ are shared:
 - Sheet silicate
 - Pyrosilicate
 - Three dimensional silicate
 - Linear chain silicate
- The oxide which is neutral, is:
 - SnO
 - ZnO
 - PbO
 - CO
- The correct statements among the following about graphite is:
 - it is electrical conductor all along the structure
 - it is electrical conductor along the layers
 - carbon atoms in graphite are sp^3 hybridized
 - there are localized π -bonds in graphite
- When formic acid is dehydrated over conc. H_2SO_4 , the gaseous product obtained is
 - CO_2
 - SO_2
 - SO_3
 - CO
- A metal forms MCl_2 and MCl_4 both. Mark the correct statement about the chlorides:
 - MCl_4 is more volatile than MCl_2
 - MCl_4 is less volatile than MCl_2
 - MCl_4 is more ionic than MCl_2
 - MCl_4 is less soluble in anhydrous ethanol than MCl_2
- Germanium for electronic use is purified by:
 - Van anke method
 - Kroll process
 - Zone refining
 - Hoof's process
- The most stable oxidation states of tin and lead respectively are:
 - +4, +4
 - +4, +2
 - +2, +4
 - +2, +2
- In the preparation of chlorosilanes by Rochow process, the catalyst is $\text{R}-\text{Cl}+\text{Si} \xrightarrow[\Delta]{?} \text{R}_x\text{SiCl}_{4-x}$ ($x=1, 2, 3$):
 - Fe
 - Co
 - Ni
 - Cu
- Which of the following is piezo-electric material?
 - Mica
 - Asbestose
 - Quartz
 - Calcite
- The type of silicate in which two and three O-atoms of $[\text{SiO}_4]^{4-}$ get shared is:
 - Pyrosilicate
 - Amphibole
 - Pyroxene
 - Sheet silicate
- Mark the correct one for adduct formed by BF_3 and CO ($\text{F}_3\text{B} \leftarrow \text{CO}$):
 - B is sp^3 in the adduct
 - B is almost planar in the adduct
 - the B and C distance is short
 - the adduct is very stable
- Which of the following metal ions can produce cyanogens gas in aqueous solution?
 - Fe^{2+}
 - Mn^{2+}
 - Cu^{2+}
 - Ni^{2+}
- HCN can be produced by the catalytic reaction $\text{CH}_4 + \text{NH}_3 \xrightarrow{\Delta} \text{HCN} + \text{H}_2$. The catalyst in the reaction and the name of the process respectively are:
 - Fe, Dow process
 - Pt, Degusa process
 - Cu, Rochow process
 - Ni, Kroll process
- The Chlorosilane, Me_2SiCl_2 on hydrolysis will produce:
 - $\text{Me}_2\text{Si}=\text{O}$
 - $\text{Me}_2\text{Si}(\text{OH})_2$

- (c) $\text{Me}_2\text{Si} - \text{O} - \text{SiMe}_2$
 (d) $\text{[O} - (\text{Me}_2)\text{Si} - \text{O}]_n$
16. The pair of amphoteric species is:
 (a) H_2CO_3 and HCO_3^- (b) HCO_3^- and H_2O
 (c) H_2O and H_2CO_3 (d) CO_3^{2-} and H_3O^+
17. CO_2 in water forms an equilibrium system. The carbon species present in this equilibrium is:
 (a) CO_2 , HCO_3^- , CO_3^{2-}
 (b) H_2CO_3 , HCO_3^- , CO_2
18. The compound that is used to control the chain length of silicon polymers is:
 (a) Me_3SiCl (b) SiCl_4
 (c) SiF_4 (d) Me_2SiCl_2
19. Thermodynamically most stable form of carbon is:
 (a) graphite (b) diamond
 (c) coke (d) fullerene

MULTIPLE CHOICES

20. The chlorosilane(s) which on hydrolysis can form silicone(s) is (are):
 (a) Me_3SiCl (b) Et_2SiCl_2
 (c) MeSiCl_3 (d) Ph_3SiCl
21. Which of the following oxide(s) is (are) amphoteric?
 (a) B_2O_3 (b) SnO
 (c) SiO_2 (d) SnO_2
22. The compound(s) which is (are) isostructural:
 (a) Me_3N (b) $(\text{Me}_3\text{Si})_3\text{N}$
 (c) $(\text{H}_3\text{Si})_3\text{N}$ (d) $\text{P}(\text{SiH}_3)_3$
23. The type of silicate(s) in which two O-atoms of $[\text{SiO}_4]^{4-}$ is (are) shared
 (a) Cyclic silicates
 (b) Amphiboles
 (c) Sheet silicates
 (d) Pyroxenes
24. The tetrahalide(s) which hydrolyse completely is (are)?
 (a) CCl_4 (b) SiCl_4
 (c) GeCl_4 (d) SnCl_4
25. The basic repeating unit of $(\text{SiO}_3)_n^{2n-}$ is present in which of the following silicate(s):?
 (a) Chain silicate
 (b) Sheet silicate
 (c) Cyclic silicate
 (d) Three dimensional silicate
26. Which of the following chemical species is (are) deadly toxic to human system?
 (a) CO_2 (b) CO
 (c) N_2 (d) CN^-
27. Although electron precise but which of the following is (are) Lewis acid(s):
 (a) CCl_4 (b) SiF_4
 (c) GeCl_4 (d) CF_4

SINGLE DIGIT (0 TO 9) ANSWER TYPE

28. The total number of Si – Si bonds present in $\text{Si}_3\text{O}_9^{6-}$ is _____.
29. The total number of crystalline allotropes of carbon is _____.
30. The total number of chemically equivalent O – atoms in $\text{Si}_2\text{O}_7^{6-}$ is _____.
31. The total number of O – atoms of SiO_4^{4-} being shared to form a sheet silicate is _____.
32. The total number of σ bonds in Mg_2C_3 is _____.

ANSWER

SINGLE ANSWER

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (a) | 3. (d) | 4. (b) | 5. (d) | 6. (a) | 7. (c) | 8. (b) | 9. (d) | 10. (c) |
| 11. (b) | 12. (b) | 13. (c) | 14. (b) | 15. (d) | 16. (b) | 17. (c) | 18. (a) | 19. (a) | |

MULTIPLE ANSWER

- | | | | | | | | |
|------------|------------|------------|------------|------------|------------|------------|------------|
| 20. (b, c) | 21. (b, d) | 22. (b, c) | 23. (a, d) | 24. (b, d) | 25. (a, c) | 26. (b, d) | 27. (b, c) |
|------------|------------|------------|------------|------------|------------|------------|------------|

SINGLE DIGIT TYPE

- | | | | | |
|---------|---------|---------|---------|---------|
| 28. (0) | 29. (4) | 30. (6) | 31. (3) | 32. (2) |
|---------|---------|---------|---------|---------|

CHAPTER 16: GROUP – 15 (V_A) N, P, AS, SB, BI

OBJECTIVE QUESTIONS (ONE CORRECT)

- The oxide of nitrogen which is coloured and solid is:
 - N_2O
 - N_2O_3
 - N_2O_4
 - N_2O_5
- The salt that gives extra pure N_2 on heating is:
 - NH_4NO_2
 - NH_4Cl
 - $Ba(N_3)_2$
 - NH_4NO_3
- Which of the trihalide hydrolyses in water to give a base?
 - $AsCl_3$
 - $BiCl_3$
 - PCl_3
 - NCl_3
- The oxide that is anhydride of nitric acid is
 - N_2O_3
 - N_2O_4
 - N_2O_5
 - N_2O
- The correct decreasing order of boiling points, of MH_3 compounds given below, is
 - $NH_3 > PH_3 > AsH_3$
 - $NH_3 > AsH_3 > SbH_3$
 - $NH_3 > SbH_3 > AsH_3$
 - $SbH_3 > NH_3 > AsH_3$
- The proticity of hypophosphorus acid (H_3PO_2) is
 - 1
 - 2
 - 3
 - 4
- The fertilizer which can increase the acidity of soil by repeated use is:
 - Potassium nitrate
 - Urea
 - Ammonium sulphate
 - Superphosphate of lime
- The number of H atoms directly attached to P in hypophosphorus acid is:
 - Zero
 - One
 - Two
 - Three
- Phosphorus is not a diatomic species like N_2 because:
 - P is less electronegative than N
 - P is less non-metallic than N
 - P is more reactive than N
 - P cannot form effective (p-p) π bond
- The number of P-O bonds in P_4O_6 is:
 - 6
 - 8
 - 10
 - 12
- Which is not a product when PCl_5 reacts with H_2SO_4 ?
 - $POCl_3$
 - PCl_3
 - $ClSO_2OH$
 - SO_2Cl_2
- Calcium cyanamide on reaction with water gives which of the following?
 - $CaCO_3, NH_3$
 - $Ca(HCO_3)_2, NH_3$
 - $Ca(OH)_2, NH_3$
 - $Ca(NO_3)_2, NH_3$
- Which of the following gives precipitate with aqueous NH_3 ?
 - $AgCl$
 - $CuCl_2$
 - $ZnCl_2$
 - $FeCl_3$
- Very dilute HNO_3 ($< 1M$) forms NH_4NO_3 with which of the following metals?
 - Cu
 - Ag
 - Zn
 - Hg
- The anhydride of HNO_2 is:
 - N_2O_3
 - N_2O
 - N_2O_5
 - NO
- The amorphous form of silica is:
 - Mica
 - Asbestos
 - Cristobalite
 - Kieselguhr
- Mark the correct statement for P_4O_{10} :
 - all P-O bonds are equal
 - terminal P-O bonds are shorter than P-O bonds in the cage
 - has 12 P-O bonds
 - P is sp^2 hybridised

18. Which of the following will not give POCl_3 with PCl_5 ?
 (a) H_2O (b) H_2SO_4
 (c) SO_2 (d) CO_2
19. The ammonium compound that gives NH_3 on heating alone is
 (a) NH_4NO_3 (b) NH_4Cl
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) NH_4MnO_4
20. The oxide of nitrogen that contains no N-N bond is:
 (a) N_2O_3 (b) N_2O
 (c) N_2O_5 (d) N_2O_4
21. P_4 is quite reactive. It reacts with X selectively to form P_4O_6 . The X is:
 (a) $\text{O}_2 + \text{NaOH}$ solution (b) Moist O_2
 (c) $\text{C} + \text{O}_2$ (d) $\text{O}_2 + \text{N}_2$
22. Which of the following metals give N_2O on reaction with dil. HNO_3 ?
 (a) Ag (b) Au
 (c) Zn (d) Hg
23. The number of $-\text{OH}$ groups present in hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$) is:
 (a) 2 (b) 3
 (c) 4 (d) 1
24. The number of P-P bonds in cyclotrimetaphosphoric acid is:
 (a) zero (b) one
 (c) two (d) three
25. The XPX angle in MX_3 compounds ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) decreases in the order:
 (a) $\text{PF}_3 > \text{PCl}_3 > \text{PBr}_3$
 (b) $\text{PBr}_3 > \text{PF}_3 > \text{PCl}_3$
 (c) $\text{PBr}_3 > \text{PCl}_3 > \text{PF}_3$
 (d) $\text{PF}_3 > \text{PBr}_3 > \text{PCl}_3$
26. NO and NO_2 both are passed in dil. NaOH solution. The product is:
 (a) NaNO_3 (b) NaNO_2
 (c) N_2O_3 (d) N_3O_4
27. Which of the following is calcium cyanamide?
 (a) CaC_2N (b) CaCN_2
 (c) CaC_2N_2 (d) $\text{Ca}(\text{CN})_2$
28. The N – N distance in N_2H_4 (I), N_2O (II) and N_2O_4 (III) decreases as:
 (a) $\text{III} > \text{I} > \text{II}$
 (b) $\text{I} > \text{II} > \text{III}$
 (c) $\text{I} > \text{III} > \text{II}$
 (d) $\text{II} > \text{I} > \text{III}$
29. Thermodynamically most stable form of phosphorus is:
 (a) red – P (b) white – P
 (c) black – P (d) yellow – P
30. The pair of metals which do not give metal nitrate with concentrated HNO_3 is:
 (a) Fe and Zn (b) Ag and Pt
 (c) Fe and Pt (d) Cu and Zn

MULTIPLE CHOICE (ONE OR MORE CORRECT)

31. The nitrogen oxide(s) which contain(s) N – N bond(s) is (are):
 (a) N_2O_5 (b) N_2O_3
 (c) N_2O (d) N_2O_4
32. The salt(s) which give(s) the same gaseous product on heating alone is (are):
 (a) NH_4NO_3 (b) NH_4NO_2
 (c) NH_4Cl (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
33. The product(s) on heating H_3PO_2 is (are):
 (a) H_3PO_3 (b) H_3PO_4
 (c) PH_3 (d) $\text{H}_4\text{P}_2\text{O}_4$
34. Which of the following statement(s) is (are) correct for P_4O_6 and P_4O_{10} ?
 (a) The P–O–P units in P_4O_6 are six
 (b) The P–O–P units in P_4O_{10} are six
 (c) All P–O bonds in P_4O_{10} are equal
 (d) P is sp^3 in P_4O_{10} and P_4O_6
35. Among the following, the correct statement(s) is (are):
 (a) NH_3 is better donor than PH_3 as lone pair is present in s-type orbital
 (b) NH_3 is better donor than PH_3 as lone pair is present in sp^3 -type orbital

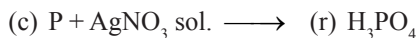
- (c) PH_3 is better donor than NH_3 as lone pair is present in sp^3 -type orbital
 (d) PH_3 is bad donor than NH_3 as lone pair is present in s-type orbital
36. Consider the reaction $\text{P}_4 + \text{NaOH}$ solution $\xrightarrow{\Delta}$. The product(s) in the above reaction is (are):
 (a) PH_3 (b) H_2PO_3^-
 (c) H_2PO_2^- (d) H_2PO_4^-
37. A solution of a colourless salt M on boiling with excess NaOH solution gives a non-flamable gas. The evolution of gas ceases after sometimes. But addition of Zn -dust to the same solution evolves the same gas. The salt(s) M is (are):
 (a) NH_4Cl (b) NH_4NO_2
 (c) CH_3COONa (d) NaNO_3
38. Silver nitrate on heating at moderate temperature give(s):
 (a) O_2 (b) NO
 (c) AgNO_2 (d) N_2O_3
39. The correct statement(s) for H_3PO_2 and H_3PO_3 is (are):
 (a) both are diprotic
 (b) both are triprotic
 (c) H_3PO_2 is monoprotic and H_3PO_3 is diprotic
 (d) H_3PO_3 can form acidic and normal salts

MATRIX MATCH

41. Match the reactions given in Column I with Chemical facts given in Column II:

Column – I**Column – II**

- (a) $\text{P} + \text{NaOH sol.} \xrightarrow{\Delta}$ (p) H_3PO_3
 (b) $\text{P} + \text{conc. HNO}_3 \xrightarrow{\Delta}$ (q) Redox reaction



- (d) $\text{P} + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$ (s) PH_3
 (t) Disproportionation reaction

ANSWERS**SINGLE ANSWER**

1. (b) 2. (c) 3. (d) 4. (c) 5. (d) 6. (a) 7. (c) 8. (c) 9. (d) 10. (d)
 11. (b) 12. (a) 13. (d) 14. (c) 15. (a) 16. (d) 17. (b) 18. (d) 19. (b) 20. (c)
 21. (d) 22. (c) 23. (c) 24. (a) 25. (c) 26. (b) 27. (b) 28. (a) 29. (c) 30. (c)

MULTIPLE ANSWER

31. (b, c, d) 32. (b, d) 33. (b, c) 34. (a, b, d) 35. (b, d) 36. (a, c) 37. (b, d)
 38. (a, c) 39. (c, d)

MATRIX MATCH

40. (a) \rightarrow (q, s, t); (b) \rightarrow (q, r); (c) \rightarrow (p, q, t); (d) \rightarrow (p, q)

CHAPTER 17: GROUP – 16 (VI_A) O, S, SE, TE, PO

OBJECTIVE QUESTIONS (ONE CORRECT)

- In the reaction

$$\text{SnCl}_2 + \text{HCl} + \text{SO}_2 \rightarrow \text{SnCl}_4 + \text{H}_2\text{O} + \text{S}, \text{SO}_2 \text{ is:}$$
 - Reducing agent
 - Oxidizing agent
 - Oxidizing and reducing agents both
 - Neither oxidizing agent nor reducing agent
- Which of the following does not undergo hydrolysis?
 - SF_4
 - H_2S
 - SF_6
 - Na_2S
- The standard state of oxygen is O_2 but of S is S_8 because:
 - Oxygen is more electro-negative than S
 - O is stronger oxidizing agent than S
 - S can not form effective (p-p) π bond
 - S is less non-metallic than oxygen
- S on heating with conc. H_2SO_4 forms:
 - SO_3
 - SO_2
 - $\text{H}_2\text{S}_2\text{O}_3$
 - $\text{H}_2\text{S}_2\text{O}_4$
- Among the MH_2 (M = O, S, Se, Te) compounds, the one with highest boiling point is:
 - H_2Te because of highest molecular mass
 - H_2S because of H – bonding
 - H_2O because of H – bonding
 - H_2Se because of H – bonding
- When sulphur is heated above its melting point, which of the following statement is correct?
 - Its viscosity decreases
 - Its viscosity increases and is maximum at around 200°C
 - Its viscosity decreases and is minimum at around 200°C
 - There is no change in the viscosity of liquid sulphur
- When excess sulphur is boiled with aqueous NaOH , an yellow solution is obtained. The yellow colour is due to:
 - Na_2S
 - $\text{Na}_2\text{S}_2\text{O}_3$
 - Na_2S_5
 - $\text{Na}_2\text{S}_2\text{O}_4$
- Which of the following is expected to have (d-p) π bonding?
 - CO_3^{2-}
 - $\text{B}_4\text{O}_7^{2-}$
 - NO_3^-
 - SO_3^{2-}
- The correct order of HMH angle (M = O, S, N) in the following is:
 - $\text{H}_2\text{S} > \text{H}_3\text{O}^+ > \text{NH}_3$
 - $\text{H}_3\text{O}^+ > \text{NH}_3 > \text{H}_2\text{S}$
 - $\text{NH}_3 > \text{H}_3\text{O}^+ > \text{H}_2\text{S}$
 - $\text{NH}_3 > \text{H}_2\text{S} > \text{H}_3\text{O}^+$
- Among As_2O_3 , SiO_2 , SO_2 and P_4O_6 , the correct order of acidic nature is:
 - $\text{As}_2\text{O}_3 > \text{SO}_2 > \text{P}_4\text{O}_6 > \text{SiO}_2$
 - $\text{P}_4\text{O}_6 > \text{SO}_2 > \text{SiO}_2 > \text{As}_2\text{O}_3$
 - $\text{SO}_2 > \text{P}_4\text{O}_6 > \text{SiO}_2 > \text{As}_2\text{O}_3$
 - $\text{SiO}_2 > \text{SO}_2 > \text{As}_2\text{O}_3 > \text{P}_4\text{O}_6$
- The number of tetrahedral centres in $\text{H}_2\text{S}_2\text{O}_8$ is
 - 4
 - 6
 - 5
 - 8
- S uses which of the d-orbitals for the formation of SF_4 :
 - d_{yz}
 - d_{xz}
 - $d_{x^2-y^2}$
 - d_{z^2}
- The most basic oxide is
 - Sb_2O_3
 - Al_2O_3
 - Bi_2O_3
 - SeO_2
- $[\text{X}] + \text{dil. H}_2\text{SO}_4 \rightarrow [\text{G}]$ Colourless pungent gas
 $[\text{G}] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{Green solution}$
 $[\text{X}]$ and $[\text{G}]$ respectively are:
 - CO_3^{2-} , CO_2
 - S^{2-} , H_2S
 - NO_3^- , NO_2
 - SO_3^{2-} , SO_2
- In which of the following reactions, H_2SO_4 is an oxidizing agent?
 - $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
 - $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$

- (c) $\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{I}_2 + \text{H}_2\text{O}$
 (d) $\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{POCl}_3 + \text{HSO}_3\text{Cl} + \text{HCl}$
16. Which of the following is true for SOCl_2 ?
 (a) It is water stable
 (b) It is a sulphonating agent
 (c) It is a chlorinating agent
 (d) It is a bleaching agent
17. Polysulphides are coloured because of?
 (a) Charge transfer
 (b) d – d transition
- (c) Crystal defect
 (d) F – centres
18. By passing H_2S gas in acidic KMnO_4 , the sulphur product is:
 (a) K_2S (b) MnS
 (c) K_2SO_3 (d) S
19. Which of the following has sp^2 hybridized central atom?
 (a) SiO_4^{4-} (b) $\text{S}_2\text{O}_3^{2-}$
 (c) SO_3^{2-} (d) SO_3

PARAGRAPH TYPE QUESTION

20. A white solid 'S' reacts with dil. H_2SO_4 to form a pungent gas 'B' with off white precipitate 'C'. The precipitate 'C' burns in air to form the gas 'B'. When the gas 'B' is passed in water which contains zinc dust, a new gas 'D' is produced. The gas B reacts with the gas 'D' in water to form another gas 'C'.
- (i) The white solid 'S' is a:
 (a) Sulphite (b) Thiosulphate
 (c) Sulphate (d) Persulphate
- (ii) The gas 'B' is:
 (a) SO_2 (b) H_2S
 (c) SO_3 (d) CO_2
- (iii) The gas 'D' is:
 (a) SO_2 (b) SO_3
 (c) H_2S (d) N_2O
21. A colourless salt M dissolves in water to form a basic solution. The salt on reaction with dil. HCl gives a gas N which does not give a purple solution with sodium pentacyanonitrosyl ferrate (II). But the aqueous solution of the salt M forms a purple solution with the above reagent.
- (i) The salt contains the anion:
 (a) S^{2-} (b) SO_3^{2-}
 (c) $\text{S}_2\text{O}_3^{2-}$ (d) SO_4^{2-}
- (ii) The gas N is
 (a) SO_2
 (b) H_2S
 (c) SO_3
 (d) NO_2
- (iii) The purple colour is due to:
 (a) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NOS}]$
 (b) $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NOS}]$
 (c) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$
 (d) $\text{Na}[\text{Fe}(\text{CN})_5\text{NOS}]$
22. A black solid dissolves slowly in conc. H_2SO_4 to form a gas 'G' which is soluble in benzene, alcohols, ethers etc., and a light pink solution. The pink solution on heating with PbO_2 and HNO_3 forms a purple solution which is discharged by passing SO_2 in it:
- (i) The metal ion expected in black solid is
 (a) Mn^{2+} (b) Zn^{2+}
 (c) Mn^{4+} (d) Fe^{3+}
- (ii) The gas 'G' is:
 (a) O_2 (b) SO_2
 (c) CO_2 (d) NO_2
- (iii) The purple solution is due to the oxoanion:
 (a) MnO_4^{2-} (b) CrO_4^{2-}
 (c) MnO_4^- (d) VO_4^{3-}

MATRIX MATCH

23. Match the molecules in Column I with Chemical facts given in Column II:

| Column – I | Column – II |
|---------------------|---|
| (a) SF_4 | (p) One lone pair at the central atom |
| (b) SOCl_2 | (q) sp^3d^2 hybridization of the central atom |



(r) Easy to hydrolysis

(s) sp^3 hybridised central atom

(t) Difficult to hydrolyse

ANSWER

SINGLE ANSWER

1. (b) 2. (c) 3. (c) 4. (b) 5. (c) 6. (b) 7. (c) 8. (d) 9. (b) 10. (c)
11. (b) 12. (d) 13. (c) 14. (d) 15. (c) 16. (c) 17. (a) 18. (d) 19. (d)

PARAGRAPH ANSWER

20. (i) \rightarrow (b); (ii) \rightarrow (a); (iii) \rightarrow (c) 47. (i) \rightarrow (a); (ii) \rightarrow (b); (iii) \rightarrow (c)
48. (i) \rightarrow (c); (ii) \rightarrow (a); (iii) \rightarrow (c)

MATRIX MATCH

23. (a) \rightarrow (p, r); (b) \rightarrow (p, r, s); (c) \rightarrow (q, t); (d) \rightarrow (r, s)

CHAPTER 18: GROUP 17 (VIIA) HALOGENS F, CL, BR, I AND AT

OBJECTIVE QUESTIONS (ONE CORRECT)

- Which of the following is meta-periodic acid?
(a) HIO_4 (b) H_5IO_6
(c) H_4IO_6 (d) H_6IO_6
- A solution contains KX and CCl_4 . When chlorine gas is passed in the solution, which of these will give a reddish brown solution?
(a) KCl (b) KBr
(c) KI (d) KF
- The halogen that develops a blue colour with starch is:
(a) Cl_2 (b) F_2
(c) Br_2 (d) I_2
- A mixture of KF and HF contains the species:
(a) HF , K^+ and F^- (b) $[\text{KHF}]^-$ and F^-
(c) K^+ , H^+ and F^- (d) K^+ and $[\text{HF}_2]^-$
- Which of the following is a pseudohalide?
(a) $[\text{NNN}]^-$ (b) $[\text{HCOO}]^-$
(c) $[\text{COOO}]^{2-}$ (d) $[\text{SOOO}]^{2-}$
- The correct order of acidity of HClO_4 (I), HClO_2 (II), HClO_3 (III) and HOCl (IV) is:
(a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{II} > \text{I} > \text{III} > \text{IV}$
(c) $\text{I} > \text{III} > \text{II} > \text{IV}$ (d) $\text{III} > \text{I} > \text{II} > \text{IV}$
- Chlorine gas is passed in dil. NaOH . The species present in the solution are:
(a) Cl^- and ClO^-
(b) Cl^- and ClO_2^-
(c) ClO^- and ClO_2^-
(d) ClO_3^- and Cl^-
- The most easily reducible halogen is:
(a) I (b) Br
(c) Cl (d) F
- Halogens have been considered for their different properties indicated against them. which of these is not correct:
(a) $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$
(Oxidising power)
(b) $\text{Br}_2 < \text{F}_2 < \text{Cl}_2$
(Electron affinity)
(c) $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$
(Electronegativity)
(d) $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$
(Bond dissociation energy)
- The $d_{\text{Cl-O}}$ correct decreasing order is represented by:
(a) $\text{ClO}_3^- > \text{ClO}_2^- > \text{ClO}^-$
(b) $\text{ClO}^- > \text{ClO}_2^- > \text{ClO}_3^-$
(c) $\text{ClO}_2^- > \text{ClO}^- > \text{ClO}_3^-$
(d) $\text{ClO}_3^- > \text{ClO}^- > \text{ClO}_2^-$
- Which of the following has maximum number of lone pairs at the central atom?
(a) ClO_3^- (b) ClF_3
(c) ICl_2^- (d) BrF_5
- The salt $\text{Rb}^+[\text{IBrCl}]^-$ on heating gives:
(a) $\text{RbI} + \text{BrCl}$ (b) $\text{RbBr} + \text{ICl}$
(c) $\text{RbCl} + \text{IBr}$ (d) $\text{RbI} + \text{Cl}_2 + \text{Br}_2$
- Among the fluorides, MF_3 ($\text{M} = \text{B}, \text{N}, \text{Al}, \text{Cl}$), the one in which all M-F bond distances are not equal, is:
(a) BF_3 (b) NF_3
(c) AlF_3 (d) ClF_3
- Which of the following halide ion is most easily oxidizable:
(a) F^- (b) I^-
(c) Cl^- (d) Br^-
- Which of the following can be prepared in anhydrous form (or pure form)?
(a) HOCl (b) HOClO
(c) HOClO_2 (d) HOClO_3
- The pair which is isoelectronic, is:
(a) Cl_2O and I_3^- (b) ClO_2^- and IF_2^+
(c) ICl_2^- and ClO_2 (d) ICl_2^+ and I_3^-
- The correct order of polyhalide, pseudohalide and interhalogen is:
(a) IF_2^- , OCN^- , BrF_3
(b) OCN^- , BrF_3 , ICl_2^-
(c) BrF_3 , OCN^- , ICl_2^-
(d) BrF_5 , SCN^- , ICl_2^-

18. All halogens (X_2) are coloured because of:
 (a) Their high electronegativity
 (b) Their high oxidizing power
 (c) Charge transfer
 (d) Their diatomicity
19. The uranium product 'A' in the following reaction is

$$U_{(s)} + ClF_3 \longrightarrow A + ClF$$

 (a) UF_3 (b) UF_5
 (c) UF_7 (d) UF_6
20. The bond angle $ClOCl$ in ClO_3^- , ClO_2 and OCl_2 increases in the order:
 (a) $ClO_3^- < OCl_2 < ClO_2$
 (b) $ClO_2 < ClO_3^- < OCl_2$
 (c) $OCl_2 < ClO_2 < ClO_3^-$
 (d) $OCl_2 < ClO_3^- < ClO_2$
21. BrF_5 reacts with water to give:
 (a) FO^- and BrO^- (b) F^- and BrO_3^-
 (c) F^- and BrO_2^- (d) F^- and BrO_4^-

MULTIPLE CHOICE (MORE THAN ONE CORRECT)

22. When chlorine gas is passed in hot concentrated $NaOH$, the change in its oxidation state is from:
 (a) 0 to +3 (b) 0 to -1
 (c) 0 to +5 (d) 0 to +7
23. The species in which the central atom involves d_{z^2} only for hybridization is (are):
 (a) ClF_3 (b) IF_4^+
 (c) ICl_4^- (d) IF_7
24. Which of the following can convert I_2 into iodic acid?
 (a) conc. HNO_3 (b) Br_2
 (c) HCl (d) Cl_2

MATRIX MATCH

25. Match species given in Column I with structural facts given in Column II:

| Column – I | Column – II |
|---------------|--|
| (a) ClF_3 | (p) Two lone pairs at the central atom |
| (b) ICl_4^- | (q) Linear geometry |

- (c) IF_4^+ (r) Square planar geometry
 (d) IF_2^- (s) All bond angles 90°
 (t) Trigonal bipyramidal structure

ANSWERS**SINGLE ANSWER**

1. (a) 2. (b) 3. (d) 4. (d) 5. (a) 6. (c) 7. (c) 8. (d) 9. (d) 10. (b)
 11. (c) 12. (c) 13. (d) 14. (b) 15. (d) 16. (b) 17. (a) 18. (c) 19. (d) 20. (a)
 21. (b)

MULTIPLE CHOICE

22. (b, c) 23. (a, b) 24. (a, d)

MATRIX MATCH

25. (a) \rightarrow (p, t); (b) \rightarrow (r, s); (c) \rightarrow (t); (d) \rightarrow (q)

CHAPTER 19: GROUP – 18, THE NOBLE GASES

OBJECTIVE QUESTIONS (ONE CORRECT)

- The statement that is true for SF_4 and XeF_4 is:
 - both are isostructural
 - both have equal number of lone pairs at the central atom
 - they are not isostructural
 - FMF angle in both are equal
- The species that has maximum number of lone pair electrons at the central atom is:
 - XeOF_2
 - XeO_3
 - XeO_2F_2
 - XeF_6
- The product A in the following reaction is

$$\text{XeF}_6 + \text{SiO}_2 \longrightarrow \text{A} + \text{SiF}_4$$
 - XeOF_3
 - XeOF_4
 - XeO_2F_2
 - XeO_2F
- The oxyfluoride of Xe which is paramagnetic is
 - XeOF_2
 - XeOF_4
 - XeOF_3
 - XeO_2F
- In which of the following all FMF (M = central atom) angles are of 90° :
 - SF_4
 - SiF_4
 - XeF_4
 - BeF_4^{2-}
- The correct melting point decreasing order is:
 - $\text{XeF}_6 > \text{XeF}_4 > \text{XeF}_2$
 - $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$
 - $\text{XeF}_6 > \text{XeF}_2 > \text{XeF}_4$
 - $\text{XeF}_2 > \text{XeF}_6 > \text{XeF}_4$
- Which of the following is most soluble in water:
 - Ne
 - Kr
 - Xe
 - Ar

MULTIPLE CHOICE (MORE THAN ONE CORRECT)

- When XeF_4 reacts with water, the product(s) is (are):
 - Xe
 - XeOF_3
 - XeO_4
 - XeO_3
- Consider the reaction

$$\text{XeF}_4 + \text{H}_2\text{O} \longrightarrow \text{A} \xrightarrow[\text{(High pH)}]{\text{NaOH}} \text{B}$$
 The products A and B are:
 - XeO_3
 - XeOF_2
 - HXeO_4^-
 - XeO_2F_2

PARAGRAPH TYPE QUESTION

- The elements of group-18 are monoatomic under normal conditions. The extremely low boiling point of lower members are due to weak dispersion forces between them. Helium has lowest boiling point of known natural chemical substances. Lower members are highly inert.

The first noble gas known to form true chemical compounds is Xe. It reacts directly only with F_2 to form fluorides. The tetrafluoride XeF_4 reacts violently with water to form XeO_3 . All compounds of Xe follow VSEPR theory.

 - The structure of XeO_3 is:
 - Trigonal planar
 - Trigonal Pyramidal
 - T-Shaped
 - Square planar
 - Argon is widely used in welding due to its
 - high calorific value
 - high flammability
 - extremely low reactivity with metal
 - ability to low melting point of metal
 - XeF_2 and XeF_4 are expected to be:
 - reducing
 - unreactive
 - fluorinating
 - basic

MATRIX MATCH

11. Match compounds in Column I with structural features given in Column II:

| Column – I | Column – II |
|---------------------|--|
| (a) XeO_3 | (p) Square pyramid sp^3d^2 |
| (b) XeOF_4 | (q) Trigonal pyramidal, sp^3 |

(r) Trigonal bipyramidal, sp^3d

(s) T-shaped,

(t) Explosive

ANSWERS

SINGLE ANSWER

1. (c) 2. (a) 3. (b) 4. (c) 5. (c) 6. (b) 7. (c)

MULTIPLE CHOICE

8. (a, d) 9. (a, c)

PARAGRAPH TYPE QUESTION

10. (i) \rightarrow (b); (ii) \rightarrow (c); (iii) \rightarrow (c)

MATRIX MATCH

11. (a) \rightarrow (q, t); (b) \rightarrow (p); (c) \rightarrow (r, s); (d) \rightarrow (r)

CHAPTER 20: ANALYTICAL CHEMISTRY (SALT ANALYSIS)

OBJECTIVE QUESTIONS (ONE CORRECT)

1. Sodium pentacyano nitrosyl ferrate (II) forms purple solution with:
 - (a) NO_3^-
 - (b) S^{2-}
 - (c) NO_2^-
 - (d) I^-
2. When excess KCN is added in copper (II) sulphate solution, the product is:
 - (a) $[\text{Cu}(\text{CN})_2]^-$
 - (b) $[\text{Cu}(\text{CN})_4]^{2-}$
 - (c) $[\text{Cu}(\text{CN})_4]^{3-}$
 - (d) $[\text{Cu}(\text{CN})_6]^{4-}$
3. The pair of ions which can not be separated by H_2S in dil HCl medium is:
 - (a) Mn^{2+} , Cu^{2+}
 - (b) Zn^{2+} , Cu^{2+}
 - (c) Al^{3+} , Hg^{2+}
 - (d) Bi^{3+} , Hg^{2+}
4. A salt solution is first treated with fresh solution of FeSO_4 and conc. H_2SO_4 is added in it. A deep brown colour develops. The salt contains the anion:
 - (a) NO_3^-
 - (b) Cl^-
 - (c) SO_3^{2-}
 - (d) $\text{S}_2\text{O}_3^{2-}$
5. The sulphide which is not soluble in 50% HNO_3 is:
 - (a) MnS
 - (b) ZnS
 - (c) HgS
 - (d) FeS
6. A red solid gives violet vapours on heating. It is insoluble in water but dissolves in water in the presence of excess of KI to give a colourless solution. The red solid is:
 - (a) Pb_3O_4
 - (b) HgO
 - (c) HgI_2
 - (d) BiI_3
7. A solution when treated with $\text{K}_4[\text{Fe}(\text{CN})_6]$, produces brown precipitate. The solution may contain the metal ion:
 - (a) $\text{Fe}^{2+}_{(\text{aq})}$
 - (b) $\text{Mn}^{2+}_{(\text{aq})}$
 - (c) $\text{Cu}^{2+}_{(\text{aq})}$
 - (d) $\text{Zn}^{2+}_{(\text{aq})}$
8. The compound which can test a liquid that is H_2O_2 is:
 - (a) FeCl_3
 - (b) K_2CrO_4
 - (c) HNO_3
 - (d) HClO_4
9. An inorganic compound X gives I_2 with KI, O_2 gas with acidic KMnO_4 and brown precipitate with alkaline KMnO_4 . The compound X is:
 - (a) SnCl_2
 - (b) H_2S
 - (c) H_2O_2
 - (d) $\text{Na}_2\text{S}_2\text{O}_3$
10. A solution contains Fe^{3+} , Al^{3+} , Zn^{2+} and Mn^{2+} . Ammonium chloride and NH_4OH are added to the solution. Mark the correct statement:
 - (a) Zn^{2+} and Mn^{2+} hydroxides will precipitate
 - (b) Al^{3+} and Fe^{3+} hydroxides will precipitate
 - (c) Al^{3+} and Mn^{2+} hydroxides will precipitate
 - (d) Fe^{3+} and Mn^{2+} hydroxides will precipitate
11. An aqueous solution of Mohr's salt and CrCl_3 is heated with excess Na_2O_2 (or $\text{NaOH} + \text{H}_2\text{O}_2$) and filtered. The substances obtained are:
 - (a) An yellow filtrate and brown residue
 - (b) An yellow filtrate and green residue
 - (c) A colourless filtrate and brown residue
 - (d) A green filtrate and brown residue
12. Passing H_2S gas into a mixture of Hg^{2+} , Zn^{2+} , Cu^{2+} and Mn^{2+} ions in an acidic aqueous medium, will precipitate:
 - (a) MnS and CuS
 - (b) MnS and ZnS
 - (c) CuS and HgS
 - (d) HgS and ZnS
13. Which of the following reagent will separate Zn^{2+} in one step from a solution that contains Al^{3+} , Ca^{2+} and Zn^{2+} ?
 - (a) $\text{HCl} + \text{H}_2\text{S}$
 - (b) $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$
 - (c) $\text{NH}_4\text{OH} + \text{H}_2\text{S}$
 - (d) $\text{NH}_4\text{OH} + \text{CH}_3\text{COONH}_4$
14. A solution contains Mg^{2+} . It is treated with Na_2HPO_4 in the presence of NH_4Cl and aqueous NH_3 . The product is:
 - (a) $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - (b) MgHPO_4
 - (c) MgNaPO_4
 - (d) $\text{Mg}_3(\text{PO}_4)_2$
15. Dimethyl glyoximate and NH_4OH form red precipitate with which of the following metal ion:
 - (a) Zn^{2+}
 - (b) Ca^{2+}
 - (c) Ni^{2+}
 - (d) Mn^{2+}

MULTIPLE CHOICE QUESTIONS

16. A mixture of NH_4Cl and aqueous NH_3 will precipitate:
 (a) Al^{3+}
 (b) Ca^{2+}
 (c) Zn^{2+}
 (d) Bi^{3+}
17. Which of the statement(s) is (are) correct?
 (a) Cu^{2+} gives brown precipitate with potassium ferrocyanide
 (b) Fe^{3+} gives blue precipitate with potassium ferrocyanide
 (c) Fe^{2+} gives blue precipitate with potassium ferricyanide
 (d) Fe^{3+} gives blue precipitate with potassium ferricyanide
18. The metal ion(s) is (are) precipitated by H_2S in dil. HCl medium:
 (a) Bi^{3+}
 (b) Al^{3+}
 (c) Cu^{2+}
 (d) Zn^{2+}
19. H_2O_2 form(s) blue colour in acid medium with:
 (a) K_2CrO_4
 (b) K_2MnO_4
 (c) KMnO_4
 (d) $\text{K}_2\text{Cr}_2\text{O}_7$
20. Aqueous solution of Chrome alum and FeSO_4 are heated with excess of Na_2O_2 . The product(s) is (are):
 (a) an orange solution
 (b) an yellow solution
 (c) a brown precipitate
 (d) a white precipitate

PARAGRAPH QUESTIONS

21. A metal nitrate when treated with KI gives black precipitate A, which dissolves in excess KI to form an orange solution B. Also the black precipitate on boiling with water gives an orange precipitate C in metal nitrate is
 (i) The metal M is:
 (a) Al^{3+}
 (b) Cr^{3+}
 (c) Bi^{3+}
 (d) Fe^{3+}
 (ii) The orange solution (B) is due to
 (a) BiI_3
 (b) BiI_4^-
 (c) BiI_5^-
 (d) BiI_6^-
 (iii) The orange solid (C) is:
 (a) BiO_2I_2
 (b) BiOI_3
 (c) BiOI
 (d) BiO_2I
22. A fresh acidic solution of FeSO_4 forms a deep brown complex with NO_3^- ion. The reaction are

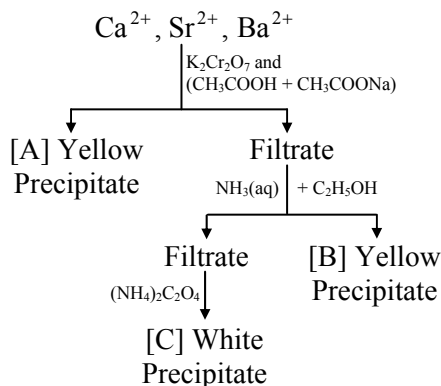
$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{X} + [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$$

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{X} \longrightarrow \text{Y} + \text{H}_2\text{O}$$
 (i) The compound X is:
 (a) N_2O
 (b) NO
 (c) NO_2
 (d) N_2O_2
- (ii) The complex Y is:
 (a) $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$
 (b) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{3+}$
 (c) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$
 (d) $[\text{Fe}(\text{H}_2\text{O})_3(\text{NO})_3]^{2+}$
23. Consider the following changes and answer the questions:
- (A + B) Mixture $\xrightarrow[\Delta]{\text{NaOH(solution)}} \text{Gas(G)}$
- $\xrightarrow[\text{KOH}]{\text{K}_2[\text{HgI}_4]} \text{Brown ppt. (H)}$
- $\xrightarrow[\text{conc. H}_2\text{SO}_4/\Delta]{\text{solid K}_2\text{Cr}_2\text{O}_7} \text{Deep red vap (P)}$
- (i) The deep red vapour P is:
 (a) CrO_2Cl_2
 (b) CrOCl_2
 (c) CrO_2Cl
 (d) CrOCl
- (ii) The brown precipitate H is:
 (a) $\text{Hg}(\text{NH}_2)\text{I}$
 (b) $\text{HgO} \cdot \text{HgNH}_2\text{I}$
 (c) $\text{Hg}_2\text{NH}_2\text{I}$
 (d) $\text{Hg}_2(\text{NH}_2)_2\text{I}_2$

(iii) The Gas G is:

- (a) NO (b) N₂O
(c) NH₃ (d) Cl₂

24. A solution contains Ca²⁺, Sr²⁺ and Ba²⁺ ions. Some chemical reactions are given below. Answer the following questions:



(i) The white precipitate C is:

- (a) CaC₂O₄
(b) SrC₂O₄
(c) BaC₂O₄
(d) (NH₄)₂Ca(C₂O₄)₂

(ii) The yellow ppt A is:

- (a) CaCrO₄
(b) SrCrO₄

(c) BaCrO₄

(d) Ba₂Cr₂O₇

(iii) The yellow ppt. B is:

- (a) SrCrO₄ (b) SrCr₂O₇
(c) CaCrO₄ (d) BaCrO₇

25. A solution contains Cu²⁺, Al³⁺ and Mn²⁺. It is desired to separate them.

(i) Which of the following reagent will separate Cu²⁺ from the others?

- (a) NH₄Cl + NH₄OH
(b) NH₄OH + H₂S
(c) H₂S + HCl
(d) dil. HCl only

(ii) For Mn²⁺ to separate the reagent is

- (a) H₂S + H₂SO₄
(b) NH₄OH + H₂S
(c) NH₄Cl + NH₄OH
(d) dil. H₂SO₄ only

(iii) For Al³⁺ to separate from the others, the reagent is:

- (a) NH₄Cl + (NH₄)₂CO₃
(b) NH₄OH + HCl
(c) NH₄OH + NH₄Cl
(d) NH₄OH + H₂S

ANSWERS

SINGLE ANSWER

1. (b) 2. (c) 3. (d) 4. (a) 5. (c) 6. (c) 7. (c) 8. (b) 9. (c) 10. (b)
11. (a) 12. (c) 13. (c) 14. (a) 15. (c)

MULTIPLE CHOICE

16. (a, d) 17. (a, b, c) 18. (a, c) 19. (a, d) 20. (b, c)

PARAGRAPH TYPE QUESTION

21. (i) → (c); (ii) → (b); (iii) → (c)
22. (i) → (b); (ii) → (c)
23. (i) → (a); (ii) → (b); (iii) → (c)
24. (i) → (a); (ii) → (c); (iii) → (a)
25. (i) → (c); (ii) → (b); (iii) → (c)