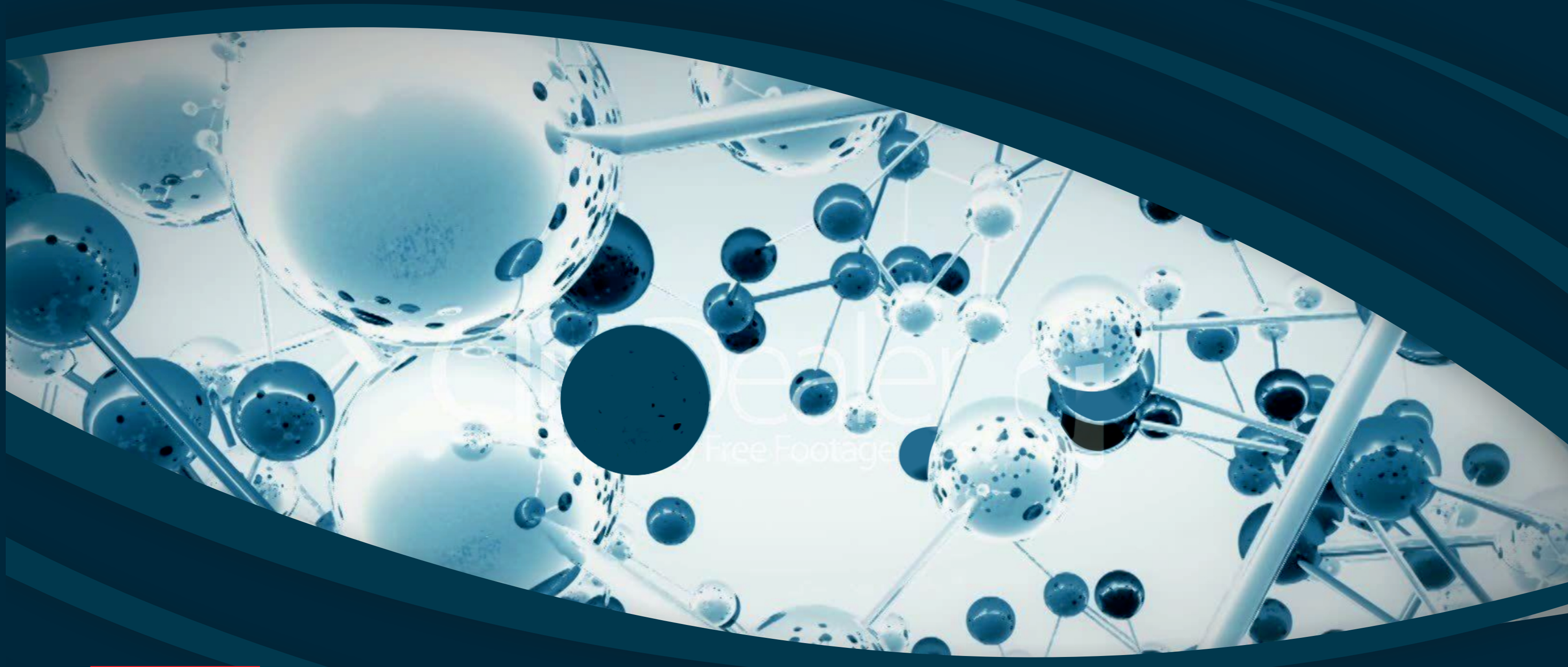
CHEMISTRY
MODULE-III

INORGANIC CHEMISTRY

for

JEE

(MAIN & ADVANCED)



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McGraw Hill Education (India) Private Limited
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Inorganic Chemistry for JEE

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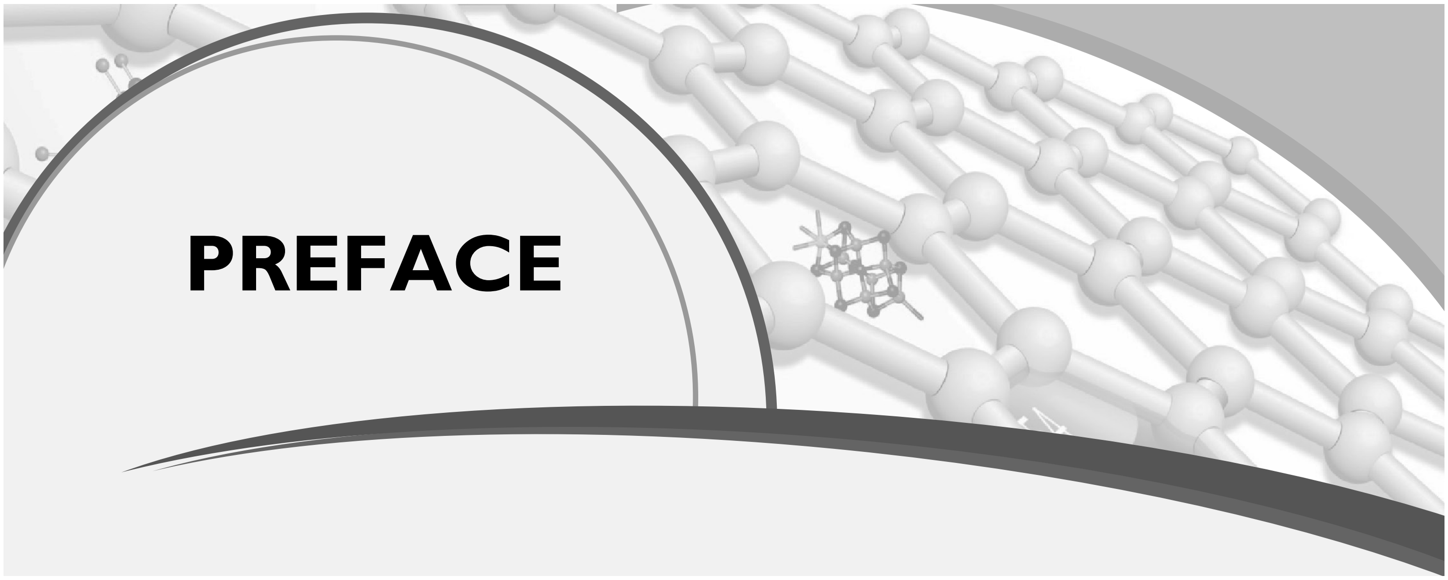
PREFACE



It gives me immense pleasure to present the first edition of this book for JEE aspirants. This is an outcome of teaching experience gained through years of interaction with students preparing for JEE.

The objective of this book is to provide proper guidance and relevant material to the JEE aspirants. The topics and problems of this book are framed in a way that they touch the required level of depth for each topic.

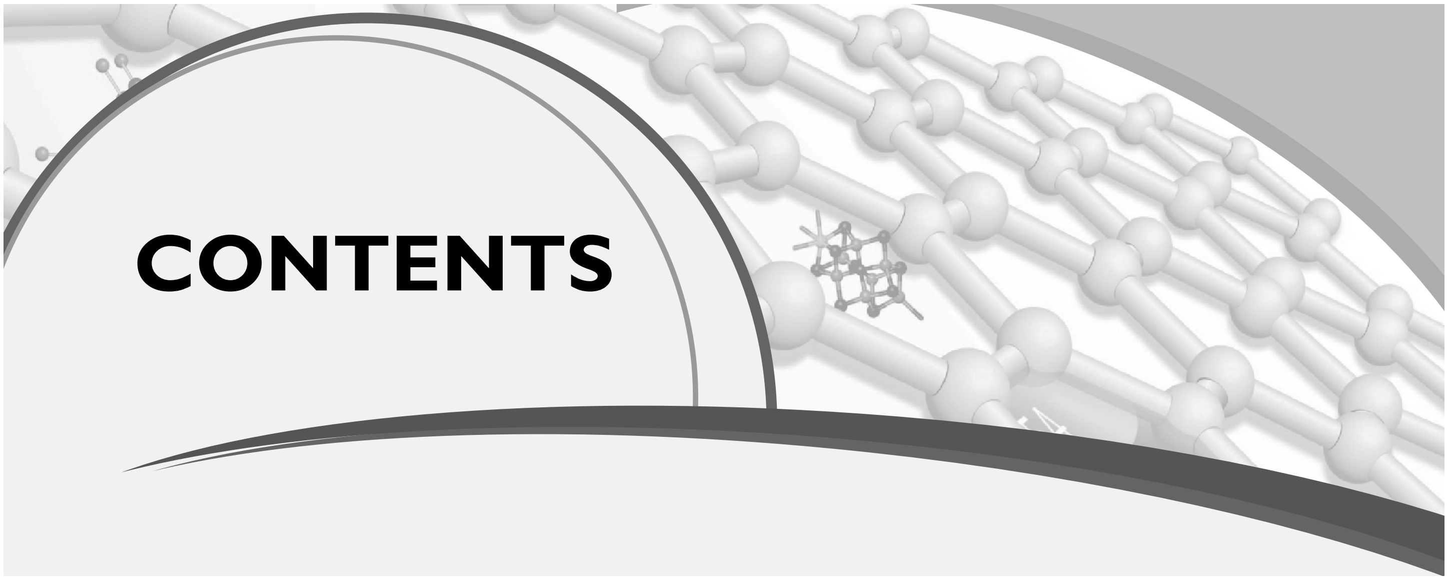
All the chapters of this book have key concepts, solved examples, three levels of problems and previous years' questions to provide a quick revision to the aspirants.

The details of the salient points are given below:

- KEY CONCEPTS – Efforts have been made to highlight the important theories in short form.
- SOLVED EXAMPLES – Improve the problem-solving capacity of the aspirants in a short span of time.
- LEVEL-I– are the problems based on basic concepts useful for JEE Main Exam.
- LEVEL-II– are the conceptual problems with wide application of topics which are useful for JEE Main Exam.
- LEVEL-III– are the problems based on comprehension (passage), integer answer types, column matching type and one or more than one correct answer types to make the students familiar with JEE ADVANCED pattern.
- PREVIOUS YEARS' QUESTIONS FOR JEE (Main & Advanced) –covers previous years' questions asked in IIT-JEE, AIEEE and JEE Main Exam.

I have tried my best to keep this book free from errors. Last but not the least, constructive criticism and valuable suggestions from the readers will be highly appreciated to make this book more precise, accurate and useful.

– Author



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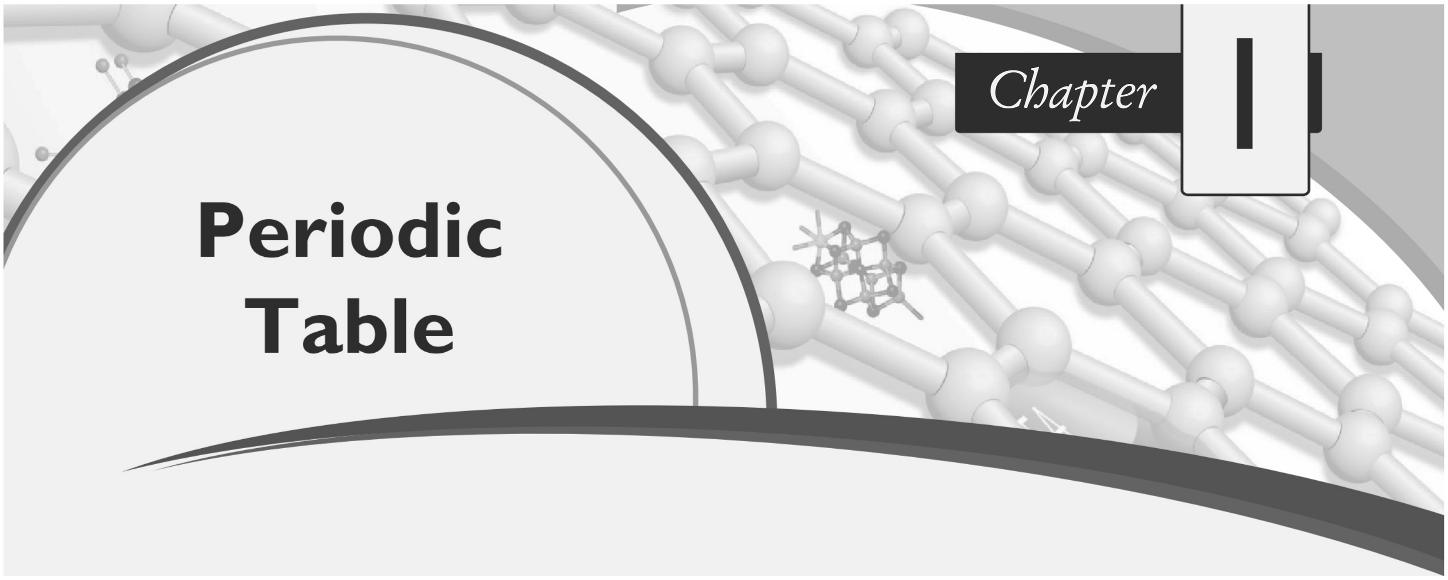


Chapter 1

Periodic Table

Key Concepts

IMPORTANT FACTS TO REMEMBER

1. Lowest electronegativity : Cs
2. Highest electronegativity : F
3. Highest ionization potential : He
4. Lowest ionization potential : Cs
5. Lowest electron affinity : Noble gases
6. Highest electron affinity : Chlorine
7. Least electropositive element : F
8. Lowest melting point metal : Hg
9. Highest melting point and boiling point metal : W (Tungsten)
10. Lowest melting point and boiling point non-metal : He
11. Notorious element : Hydrogen
12. Lightest element : Hydrogen
13. Smallest atomic size : H
14. Largest atomic size : Cs
15. Largest anionic size : I^-
16. Smallest cation : H^+
17. Most electropositive element : Cs
18. Element with electronegativity next to Fluorine : Oxygen
19. Group containing maximum number of gaseous elements in the periodic table : Zero group(18th)
20. Total number of gaseous elements in the periodic table : 11(H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, Rn)
21. Total number of liquid elements in the periodic table : 6 (Ga, Br, Cs, Hg, Fr, Unb)
22. Smallest anion : F^-
23. Liquid element of radioactive nature : Fr
24. Total number of radioactive elements in the periodic table : 25
25. Volatile d-block elements : Zn, Cd, Hg, Unb
26. Element containing no neutron : H
27. Most abundant element in earth's crust : Oxygen
28. Rarest element on earth : At (astatine)
29. Most abundant metal in crust earth : Al
30. Element having maximum tendency for catenation in periodic table : Carbon
31. Non-metal having highest melting point, boiling point : Carbon (diamond)
32. Metals showing highest oxidation state : Os (+8)
33. Most electrovalent compound : CsF
34. Most stable carbonate : Cs_2CO_3
35. Strongest base : CsOH
36. Strongest basic oxide : Cs_2O
37. Best electricity conductor among metals : Ag

38. Best electricity conductor among non-metals : Graphite
39. Most poisonous element : Pu (Plutonium)
40. Liquid non-metal : Br
41. Element kept in water : Phosphorous
42. Elements kept in kerosene : IA group element (except Li)
43. Elements sublime on heating : I_2
44. Noble metals : Au, Pt etc.
45. Amphoteric metal : Be, Zn, Al, Sn, Pb
46. Amphoteric metalloid : Si
47. Metalloids elements : Si, As, Te, At, Ge, Sb
48. Non-metals having metallic lusture : Graphite, Iodine
49. Heaviest naturally occurring element : Uranium
50. Poorest conductor of electricity : Diamond
51. Hardest naturally occurring element : Diamond
52. Lightest solid metal : Li
53. Amphoteric oxides : BeO, Al_2O_3, ZnO, PbO, SnO, SnO_2, Sb_2O_3, As_2O_3, etc.
54. Neutral oxides of non metals : NO, CO, H_2O, N_2O
55. Dry bleacher : H_2O_2
56. Dry ice : Solid CO_2
57. First man-made element : ${}_{43}Te$ (Technicium)
58. Smallest period : I^{st} (2 elements)
59. Largest period in periodic table : 6^{th} (32 elements)
60. Largest group in periodic table : IIIB (32 elements)
61. Most abundant d-block metal : Fe
62. Most abundant s-block metal : Ca
63. Highest density (metals) : Os, Ir
64. Highest density (non-metals) : Boron
65. Most abundant gas in atmosphere : Nitrogen
66. Most abundant element in the universe : Hydrogen

MODERN PERIODIC TABLE

i. It was proposed by Henry Moseley.

ii. Modern periodic table is based on atomic number.

iii. Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays. He found out that $\sqrt{v} \propto Z$ where v = frequency of X-rays

From this experiment, Moseley concluded that the physical and chemical properties of the elements are periodic function of their atomic number. It means that when the elements are arranged in the increasing order of their atomic number elements having similar properties after a regular interval. This is also known as **'Modern periodic Law'**.

iv. **Modern periodic Law –** The physical and chemical properties of elements are a periodic function of the atomic number.

LONG FORM/PRESENT FORM OF MODERN PERIODIC TABLE

i. It consist of 7 horizontal periods and 18 vertical columns (groups)

ii. According to IUPAC 18 vertical columns are named as 1^{st} to 18^{th} group.

iii. The co-relation between the groups in long form of periodic table and in modern form of periodic table are given below.

IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

iv. Elements belonging to same group having same number of electrons in the outermost shell so their properties are similar.

DESCRIPTION OF PERIODS

Period	*n*	*Sub-shell*	*No.of elements*	*Element*	*Name of period*
1	1	1s	2	${}_1H$, ${}_2He$	Shortest
2	2	2s, 2p	8	${}_3Li$-${}_{10}Ne$	I Short
3	3	3s, 3p	8	${}_{11}Na$-${}_{18}Ar$	II Short

4	4	4s, 3d, 4p	18	$_{19}$K-$_{36}$Kr	I Long
5	5	5s, 4d, 5p	18	$_{37}$Rb-$_{58}$Xe	II Long
6	6	6s, 4f, 5d, 6p	32	$_{55}$Cs-$_{86}$Rn	Longest (very long)
7	7	7s, 5f, 6d, 7p	26	$_{87}$Fr-$_{112}$Unb	Incomplete

DESCRIPTION OF GROUPS

1st/IA/Alkali metals:

General electronic configuration = ns^1 (n = Number of shell)

Number of valence shell e^- = 1

2nd/IIA/Alkaline earth metals:

General electronic configuration = ns^2

Number of valence shell e^- = 2

13th/IIIA/Boron family:

General electronic configuration = ns^2np^1

Number of valence shell e^- = 3

14th/IVA/Carbon family:

General electronic configuration = $ns^2\,np^2$

Number of valence shell e^- = 4

15th/VA/Nitrogen Family/Pricogens: (Used in fertilizer as urea)

General electronic configuration = $ns^2\,np^3$

Number of valence shell e^- = 5

16th/VIA/Oxygen family/Chalcogens: (Ore forming)

General electronic configuration = $ns^2\,np^4$

Number of valence shell e^- = 6

17th/VIIA/Halogen family/Halogens: (Salt forming)

General electronic configuration = $ns^2\,np^5$

Number of valence shell e^- = 7

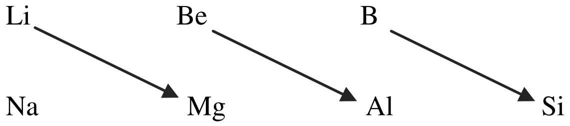
18th/Zero group/Inert gases/Noble gases:

General electronic configuration = $ns^2\,np^6$ (except He)

Number of valence shell e^- = 8

SOME IMPORTANT POINTS

(i) 2nd period elements (Li, Be, B) show diagonal relationship with 3rd period elements (Mg, Al, Si). Due to almost similar ionic potential (Ionic potential = charge/Radius) value they show similarily in properties.



(ii) 3rd period elements (Na, Mg, Al, Si, P, S, Cl) are called typical elements because they represent the properties of other element of their respective group.

(iii) In 6th period all types of elements are included (s, p, d and f)

(iv) No inert gas in 7th period.

(v) Normal elements present in all periods.

(vi) Atomic number of last inert gas element is 86.

(vii) Long form modern periodic table can be divided into four portions:

1. Left portion (IA and IIA) – s-block.
2. Right portion (IIIA to VIIA + zero group) – p-block.
3. Middle portion (IIIB to VIIB + VIII + IB and IIB) – d-block.
4. Bottom portion (IIIB) – f-block elements

NORMAL OR REPRESENTATIVE ELEMENTS

i. The elements in which ultimate orbit is incomplete while penultimate orbits are complete are called as normal elements.

ii. Their general electronic configuration is:

$$\underbrace{\overset{\text{IA}}{ns^1}\qquad \overset{\text{IIA}}{ns^2}}_{ns^{1-2}}\qquad \underbrace{\overset{\text{IIIA}}{ns^2np^1}\quad \overset{\text{IVA}}{ns^2np^2}\quad \overset{\text{VA}}{ns^2np^3}\quad \overset{\text{VIA}}{ns^2np^4}\quad \overset{\text{VIIA}}{ns^2np^5}}_{ns^2\,np^{1-5}}$$

TRANSITION ELEMENTS

The elements in which both ultimate (n) as well penultimate shells (n-1) are incomplete either in atomic state or in some oxidation state are called as transition elements.

Note: According to this concept Zn, Cd, Hg and Unb are not transition elements because they do not have incomplete penultimate shell either in atomic state or in some oxidation state.

Group number: IIIB to VIIB + VIII + IB and IIB

Periods: 4th to 7th

i. General electronic configuration is $(n-1)d^{1-10}\,ns^{1\text{ or }2}$

ii. Total number of d-block elements = 40

Total number of transition elements = 36 (Except Zn, Cd, Hg and Unb)

Note: All transition elements are d-block but all d-block elements are not transition elements.

INNER-TRANSITION ELEMENTS

The elements in which all the three shells, i.e. ultimate (n), penultimate (n-1) and pre or antipenultimate (n-2) shells, are incomplete are called as inner-transition elements.

i. General electronic configuration is:
$(n-2)f^{1-14}\,(n-1)d^{0 \text{ or } 1}\,ns^2$

ii. These are 28 in number.

iii. Group – IIIB

iv. Period – 6th and 7th

v. Inner transition elements are divided into two series:

(a) Lanthanoid series/Rare earth elements/ Lanthenones (Ce_{58}–Lu_{71} 14 elements)

(b) Actinoid series/Man-made elements/Actinones (Th_{90}–Lw_{103} 14 elements)

PERIODIC PROPERTIES

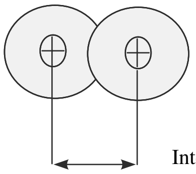
Atomic radius

1. Atomic radius of an element cannot be determined because atoms never exist in their free state and position of their outermost e^- is uncertain.
2. Atomic radius is determined in bonded state

Type of Radius

1. Covalent Radius (r_c)

a. Such type of radius is determined if a single covalent bond is present between two similar atoms.



$$r_c = \frac{d_{a-a}}{2}$$

b. If a single bond is present between two different atoms,

$d_{a-b} = r_a + r_b - 0.09\,(\Delta EN)$, Å

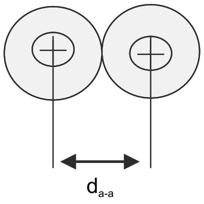
(Bond length)

r_a = covalent radius of A

r_b = covalent radius of B

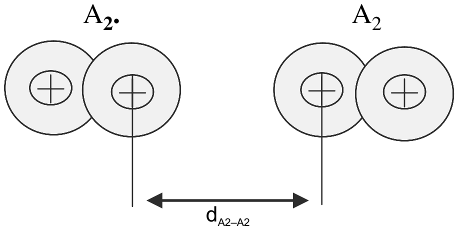
ΔEN = difference in electronegativity of A and B

2. Metallic radius (r_m): Such type of radius is determined if atoms are bonded with metallic bond.



$$r_m = \frac{d_{a-a}}{2}$$

3. van der Waal's radius (r_v): Such type of radius is determined if molecules are bonded with van der Waal's force of attraction.



$$r_v = \frac{d_{A2-A2}}{2}$$

$$\boxed{r_v > r_m > r_c}$$

Note: Noble gases are monoatomic molecules bonded with van der Waal's force of attraction hence, for noble gases, van der Waal's radius is considered.

4. Ionic radius (radius of ions):

a. A cation is always smaller than its parent atom because it has greater Z_{eff} than its parent atom. As positive oxidation state increases, radius decreases.

$$Mn > Mn^{+2} > Mn^{+7}$$

b. An anion is always larger than its parent atom because the anion has lower Z_{eff} than its parent atom. As negative oxidation state increases, radius increases.

$$O < O^- < O^{-2}$$

Isoelectronic species

1. Species (atoms, molecules or ions) having same number of electrons are known as isoelectronic.

e.g	Si	N_2	CO	CN^-	NO^+
	$14e^-$	$14e^-$	$14e^-$	$14e^-$	$14e^-$

2. Order of radius in monoatomic isoelectronic species:

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

In isoelectronic species, as atomic number increases, radius decreases. It is due to increment in Z_{eff}.

Periodicity in atomic radius

1. <u>In periods:</u>

a. As we move left to right in a period, when Z_{eff}

increase in the atomic radius decrease except in noble gases.

$Li > Be > B > C > N > O > F << Ne$

$Na > Mg > Al > Si > P > S > Cl << Ar$

b. Order of radius in 3d- series:

$Sc > Ti > V > Cr < Mn > Fe \simeq Co \simeq Ni < Cu < Zn$

2. In groups:
   a. As we move top to bottom in a group, when number of shell increase the atomic radius increases

      $Li < Na < K < Rb < Cs$

      $F < Cl < Br < I$
   b. Exception (in d-block):

      4d series ≃ 5d series (due to lanthanoid contraction)
   c. Exception(in p-block): $Al > Ga$

      Note: Radius mainly depends on number of shells.

      Some exceptions are:

      $Li^+ \quad > \quad Mg^{+2}$

      0.76Å   0.72Å

      $H^- \quad > \quad F^-$

      1.40Å   1.33Å

Lanthanoid contraction

1. In lanthanoid series, as atomic number increases, atomic and ionic radius gradually decreases. It is called as lanthanoid contraction.
2. Cause: As me move from Ce to Lu, nuclear charge (Z) increases and $1e^-$ is successively added into inner 4f-subshell. Since $f\text{-}e^-$ produces almost negligible screening effect hence, screening coefficient (σ) remains almost constant and Z_{eff} increases thus, radius decreases. (due to poor screening of $4f\text{-}e^-$ on outer e^-)
3. Effect of lanthanoid contraction is also present from $_{72}Hf$ to $_{82}Pb$. It is also called as post lanthanoid contraction or lanthanoid contraction. Due to this, these element have greater Z_{eff} than expected (its due to poor screening by $14e^-$ present in 4f-subshell).

Order of radius (along the group)

a. In d-block: 4d series ≃ 5d Series

(Z_{eff} high)

$Zr \simeq Hf$

$Pd \simeq Pt$

$Y < La$ (No lanthanoid contraction)

b. In p-block:

$In \simeq Tl$

$Sn \simeq Pb$

Ionization Potential (IP) or Ionization Energy (IE)

(a) It is the energy required to remove an e^- from outermost shell of isolated (free) gaseous atom.

(b) This process is endothermic.

$$M_{(g)} + \text{IE of } M \rightarrow M^+_{(g)} + e^-; \Delta H = IE$$

Factors affecting IE

(i) Z_{eff}: $IE \propto Z_{eff}$

(ii) Atomic size: $IE \propto \dfrac{1}{\text{At. Size}}$

(iii) Penetration power of orbitals: $s > p > d > f$

(iv) Electronic configuration of outermost subshell:

a. Elements having fully filled or half filled outermost subshell have greater IE than expected.

(b) Such elements in a period have greater IE than adjacent elements.

1	2	13	14	15	16	17	18
ns^1	ns^2	np^1	np^2	np^3	np^4	np^5	np^6
	↑			↑			↑
	(fully filled)			(half filled)			(fully filled)

$1 < 2 > 13 < 14 < 15 > 16 < 17 < 18$

$1 < 13 < 2 < 14 < 16 < 15 < 17 < 18$

Order of IE in second period:

$Li < \underbrace{B < Be} < C < \underbrace{O < N} < F < Ne$

Order of IE in third period:

$Na < \underbrace{Al < Mg} < Si < \underbrace{S < P} < Cl < Ar$

Periodicity in IE

1. In periods: as we move from left to right, in general, IE increases. (except for fullyfilled and half filled elements)
2. In groups: as we move top to bottom in a group, in general, IE decreases. (it is due to increase in atomic size)

Exception: (a) due to lanthanoid contraction,

In d-block:

4d series < 5d series

Z_{eff} high

$Zr < Hf$

$Pd < Pt$

$Y > La$ (No lanthanoid contraction)

In p-block:
$In < Tl$
$Sn < Pb$
(b) $Al < Ga$
(Z_{eff} high)

General order of IE is:

s-block < f-block < d-block < p-block

Successive IE

1. Successive IE always increases because during successive removal of e^- z_{eff} increases and size decreases.

   $M_{(g)} + IE_1 \rightarrow M^+_{(g)} + e^-; \quad \Delta H = + IE_1$
   $M^+_{(g)} + IE_2 \rightarrow M^{+2}_{(g)} + e^-; \quad \Delta H = + IE_2$
   $M^{+2}_{(g)} + IE_3 \rightarrow M^{+3}_{(g)} + e^- ; \quad \Delta H = + IE_3$

   $IE_1 < IE_2 < IE_3 <$ - - - - - - -

   Energy required to remove n^{th} e^- = IE_n

   Energy required to remove ne^- = ($IE_1 + IE_2$ + ------------- IE_n)
2. IE_2 of M = IE_1 of M^+
   IE_3 of M = IE_2 of M^+ = IE_1 of M^{+2}
3. Successive IE always increases but if during successive removal of e- electronic configuration becomes stable than rate of increment in successive I.E. is much more than expected.

   Mg = (Ne) $3s^2$

   $IE_1 < IE_2 << IE_3$ (because third electron is removed from fulfilled electronic configuration)

Order of IE_2 in second period:

IE_2 of M = IE_1 of M^+

Li^+	Be^+	B^+	C^+	N^+	O^+	F^+	Ne^+
$1s^2$	$2s^1$	$2s^2$	$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$
↑ fully filled		↑ fully filled			↑ half filled		

Be < C < B < N < F < O < Ne < Li

(in a particular period alkali metal has highest IE_2 because it has very high Z_{eff})

Order of IE_3 in second period:

IE_3 of M = IE_1 of M^{2+}

Li^{+2}	Be^{+2}	B^{+2}	C^{+2}	N^{+2}	O^{+2}	F^{+2}	Ne^{+2}
$1s^1$	$1s^2$	$2s^1$	$2s^2$	$2p^1$	$2p^2$	$2p^3$	$2p^4$
	fully filled		fully filled			half filled	

B < N < C < O < Ne < F < Li < Be

(in a particular period alkaline earth metal has highest IE_3 because it has very high Z_{eff})

Electron affinity/e-gain enthalpy

1. It is the energy released when an e^- is added to outermost shell of an isolated gaseous atom.
2. This process in generally exothermic. (ΔH = -ve)

   $X_{(g)} + e^- \rightarrow X^-_{(g)}$ + EA of X ; $\quad \Delta H = -EA$
   ↑
   e- gain enthalpy

   $\Delta H = -EA$

   $-\Delta H = EA$

   $\boxed{\text{negative } e^- \text{ gain enthalpy} = EA}$

   EA of X = IE of X^-
3. (a) Elements having fully filled or half filled outermost sub-shell do not add another e- hence, their EA is generally zero.

   (b) If we still add e- to such elements, process becomes endothermic and formed anion becomes unstable.

   $Y_{(g)} + e- \rightarrow Y^-_{(g)} - EA; \Delta H = + EA$

   (group 2,18 and N)
4. EA_1 process is generally exothermic while all higher EA processes are always endothermic because anions resist addition of another e^-.

   $X_{(g)} + e^- \rightarrow X^-_{(g)} + EA_1; \Delta H = -EA_1$
   (Except group 2, 18, N)
   $X^-_{(g)} + e^- \rightarrow X^{-2}_{(g)} - EA_2 ; \Delta H = EA_2$
   $X^{-2}_{(g)} + e^- \rightarrow X^{-3}_{(g)} - EA_3 ; \Delta H = EA_3$

Periodicity in EA

1. In periods: In general as we move from left to right EA increases.

   In period (2):

   Ne < Be < N < B < Li < C < O < F

   In period (3):

   Ar < Mg < Al < Na < P < Si < S < Cl
2. In groups: In general as we move from top to bottom in a group EA decreases.

Note: Second period elements have lower EA than expected. They have exceptionally small size. Hence, incoming e^- feels more repulsion than expected and net attraction becomes less than expected so their EA becomes less than expected.

Order of EA in various groups:

Cl > F > Br > I

S > Se > Te > O

$N < P < As < Bi < Sb$

$Si > C > Ge > Sn > Pb$

$Al > Ga > In > Tl > B$

Electronegativity (EN)

1. Tendency of an atom to attract bonded e^- pair towards itself in a bond is known as EN of that atom.
2. Noble gases do not form interatomic bond hence their EN is assumed as zero.

Factors affecting EN:

1. Z_{eff}:

$$EN \propto Z_{eff}$$

2. Atomic size: $EN \propto \frac{1}{\text{atomic size}}$
3. Oxidation state:
   (a) As positive oxidation state increases, EN increases.

   $A < A^+ < A^{+2}$

   $K\underline{\overset{+7}{Mn}}O_4 > \underline{\overset{+4}{Mn}}O_2$

   (b) As negative oxidation state increases, EN decreases.

   $B > B^- > B^{-2}$

   $H_2\underline{\overset{-2}{O}} < H_2\underline{\overset{-1}{O_2}} < \underline{\overset{+2}{O}}F_2$
4. % s-character: As % s-character increases, EN increases.

sp	sp^2	sp^3
50%	33.33%	25%

Order: $sp > sp^2 > sp^3$

Periodicity in EN

1. In periods: As we move from left to right in a period, Z_{eff} increases hence, EN increases. (Except Noble gases)

   $Li < Be < B < C < N < O < F$

   $Na < Mg < Al < Si < P < S < Cl$
2. In groups: As we move top to bottom in a group, atomic size increases hence, EN decreases.

   $F > Cl > Br > I$

a. Exception: $Al < Ga$ (High Z_{eff})

b. Exception: Due to lanthanoid contraction,

d-block:

4d-series < 5d-series (high Z_{eff})

$Zr < Hf$

$Y > La$ (No lanthanoid contraction)

p-block:

$In < Tl$

$Sn < Pb$

Measurement of EN

1. Mulliken's scale:

$$X_m = \frac{IE + EA}{2} \text{ (both are in eV/atom)}$$

2. Pauling's scale:

$$\Delta EN = | X_A - X_B | = 0.208\sqrt{(E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B})})}$$

Bond energies in kcal/mol

OR,

$$= 0.1017\sqrt{(E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B})})}$$

Bond energies in kJ/mol

$$X_p \simeq \frac{X_m}{2.8}$$

3. Allred-Roshow scale:

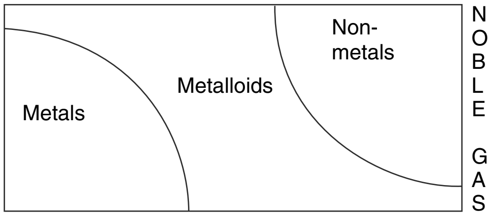
$$X = \frac{0.359\, Z_{eff}}{r^2} + 0.744 \text{ (r = covalent radius (in A°))}$$

Application of EN

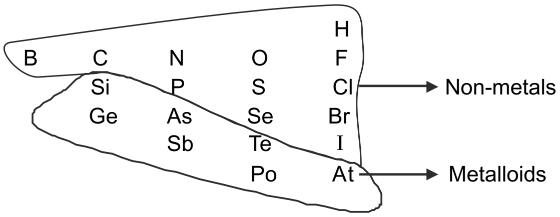
1. Metallic and Non-metallic properties:

$$\text{Metallic property} \propto \frac{1}{EN}$$

$$\text{Non-metallic property} \propto EN$$



Metalloids or semi-metals: elements which can both gain or loose e^-.



s-block → Metals

d and f-block → Metals

p-block → Non-metals, metalloids, metals and noble gases.

2. Nature of bond:

Nature of interatomic bond depends on ΔEN.

ΔEN	Nature of bond	
0	Pure covalent	Covalent
0.1 – 0.8	Covalent	
0.9 – 1.6	Polar Covalent	
1.7	50% ionic and 50% covalent	
1.8 or more	Ionic	

$\%$ ionic character $= 16\,(\Delta EN) + 3.5\,(\Delta EN)^2$

(Henery – Smith formula)

3. Nature of hydride:

Hydrides: Binary compounds having one element H.

eg. CH_4, H_2S, HCl etc.

(along the group)

C	N	O	F	i. Size of central atom (M) increases
Si	P	S	Cl	ii. Bond length of M-H bond increases
Ge	As	Se	Br	iii. H^+ loosing tendency increases
Sn	Sb	Te	I	iv. Acidic strength increases

(along the period)

i. EN of Central atom (M) increases

ii. ΔEN of M-H bond increases

iii. Bond polarity(or ionic character) of M-H bond increases

iv. Tendency to loose H^+ in water increases

v. acidic strength increases

Order of Acidic Strength:

$HF < HCl < HBr < HI$

$CH_4 < NH_3 < H_2O < HF$

$CH_4 < H_2S < HI$

4. Nature of hydroxides and oxides:

a. oxides form hydroxides in water hence, the nature of oxides and hydroxides of an element is similar.

b. Acidic strength of oxides and hydroxides $\propto$ EN of central atom

Order of acidic strength:

$ClOH > BrOH > IOH$

$MgO > CaO > SrO > BaO$

$Na_2O < MgO < Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$

$\overset{+2}{\underline{Mn}O} < \overset{+4}{\underline{Mn}O_2} < \overset{+7}{\underline{Mn}_2O_7}$

$\overset{+1}{\underline{N}_2O} < \overset{+2}{\underline{N}O} < \overset{+3}{\underline{N}_2O_3} < \overset{+5}{\underline{N}_2O_5}$

c. Non-metallic oxides are generally acidic. (Some are neutral)

Neutral oxides are these which do not react with both acid and base

eg. CO, NO, N_2O, H_2O

d. Metallic oxides are generally basic. (Some are amphoteric)

Amphoteric oxides are those which react with both acid and base.

eg. s-block: <u>BeO</u>

d-block: TiO_2, VO_2, CrO_2, Cr_2O_3, MnO_2, Mn_3O_4, ZnO etc.

p-block: Al_2O_3, Ga_2O_3, SnO, SnO_2, PbO, PbO_2, As_2O_3, Sb_2O_3 etc.

Some metallic oxides like CrO_3, Mn_2O_7 etc are acidic in nature.

Some other periodic properties

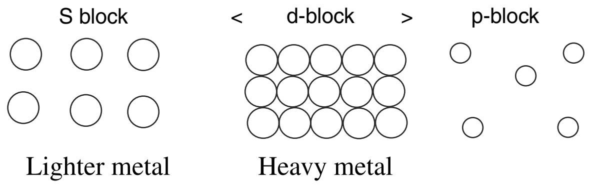
1. Atomic density:

(a) In groups: Down the group both atomic mass and atomic volume increases but increment in mass is much more than volume. Hence, atomic density increases.

Exception: Density of Na > K

Mg > Ca

(b) In periods:



2. Melting point and boiling point:

(a) In periods: The general order is,

s-block < d-block > p-block

(b) In groups: Down the group the general order is:

s-block	d-block	groups 13 and 14	groups15 to18
decreases	increases	decreases	increases

Solved Examples

1. Which of the following is incorrect match?

(a) Z = 48, group = IIB , period No. = 5th

(b) (Xe) $4f^7\ 5d^1\ 6s^2$, group = IIIB , period = 6th

(c) (Rn) $6d^2\ 7s^2$, group = IVB, period = 7th

(d) Z = 56, group = IIA , period = 6th

Sol.(c) Element, having Z = 48, is Cd

It is member of group 12 or IIB and period 6th

Element having electronic configuration (Xe) $4f^7\ 5d^1\ 6s^2$ is a lanthanoid. All lanthanoids belong to group IIIB and period 6th.

Element having electronic configuration (Rn) $6d^2\ 7s^2$ is an actinoid. All actinoids belong to group IIIB and period 7th.

Element, having Z = 56, is Ba. It is member of group 2 or IIA and period 6th.

2. Which of the following metals give inflammable gas with both acid and base?

(a) Na and Zn (b) Mg and Al

(c) Mg and Be (d) Zn and Al

Sol.(d) Amphoteric metals like Be, Zn, Al, Sn, Pb etc give H_2 gas (inflammable) with both acid and base.

3. Which of the following have an incorrect order of ionization energy:

(a) Pb (IE) > Sn (IE)

(b) Na^+ (IE) > Mg^+ (IE)

(c) Li^+ (IE) < O^+ (IE)

(d) Be^+ (IE) < C^+ (IE)

Sol.(c) Due to lanthanoid contraction Pb has greater effective nuclear charge (z_{eff}) than Sn hence,

Pb (IE) > Sn (IE)

Na^+ has electronic configuration of noble gas hence,

Na^+ (IE) > Mg^+ (IE)

Li^+ has electronic configuration of noble gas hence,

Li^+ (IE) > O^+ (IE)

C^+ has greater effective nuclear charge (z_{eff}) than Be^+ hence,

Be^+ (IE) < C^+ (IE)

4. Which set of ions have same magnetic moment?

(a) Co^{+2}, Cr^{+3}, V^{+3}

(b) Mn^{+2}, Fe^{+3}, Cr^+

(c) Ni^{+2}, Mn^{+2}, Co^{+2}

(d) Fe^{+2}, Mn^{+2}, Co^{+2}

Sol.(b)

Ion	Electronic configuration	No. of unpaired e^-
Co^{+2}	(Ar) $4s^0\ 3d^7$	3
Cr^{+3}	(Ar) $4s^0\ 3d^3$	3
V^{+3}	(Ar) $4s^0\ 3d^2$	2
Mn^{+2}	(Ar) $4s^0\ 3d^5$	5
Fe^{+3}	(Ar) $4s^0\ 3d^5$	5
Cr^+	(Ar) $4s^0\ 3d^5$	5
Ni^{+2}	(Ar) $4s^0\ 3d^8$	2
Fe^{+2}	(Ar) $4s^0\ 3d^6$	4

Ions, having similar number of unpaired e^- , have same magnetic moment.

5. The correct order of acidic strength of the following is:

(a) $SO_2 > P_2O_3 > SiO_2 > Al_2O_3$

(b) $P_2O_3 > SO_2 > SiO_2 > Al_2O_3$

(c) $P_2O_3 > Al_2O_3 > SO_2 > SiO_2$

(d) $Al_2O_3 > SiO_2 > P_2O_3 > SO_2$

Sol.(a) Acidic strength of oxides depends on electronegativity of central atom. As electronegativity of central atom increases acidic strength also increases.

Correct order of acidic strength is:

$SO_2 > P_2O_3 > SiO_2 > Al_2O_3$

6. Ionization energy of F^- is 320 kJ mol^{-1}. The electron gain enthalpy of fluorine would be:

(a) – 320 kJ mol^{-1}

(b) – 160 kJ mol^{-1}

(c) + 320 kJ mol^{-1}

(d) + 160 kJ mol^{-1}

Sol.(a) Ionization energy of F^- is 320 kJ mol^{-1}

F^- (g) + 320 kJ mol^{-1} → F (g) + e^-; $\Delta H = 320$ kJ mol^{-1}

Equation for electron gain enthalpy of F is:

F(g) + e^- → F^- (g) + 320 kJ mol^{-1}; $\Delta H = –320$ kJ mol^{-1}

7. The value of IE_1, IE_2, IE_3, and IE_4 of an atom are 7.5 eV, 25.6 eV, 48.6 eV and 170.6 eV respectively. The electronic configuration of the atom will be:

(a) $1s^2\, 2s^2\, 2p^6\, 3s^1$

(b) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^1$

(c) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$

(d) $1s^2\, 2s^2\, 2p^6\, 3s^2$

Sol.(b) The biggest jump occurs from IE_3 to IE_4

$IE_3 << IE_4$

$(IE_n) \quad (IE_{n+1})$

n(Valence e^-) = 3

Hence, the electronic configuration of the atom will be $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^1$.

8. The correct order increasing radii is:

(a) Be^{2+}, Mg^{2+}, Na^+ (b) K^+, Ca^{2+}, S^{2-}

(c) O^{2-}, F^-, N^{3-} (d) S^{2-}, O^{2-}, As^{3-}

Sol.(a) Correct order of increasing radii are:-

(a) $Be^{+2} < Mg^{+2} < Na^+$

(b) $Ca^{+2} < K^+ < S^{-2}$

(c) $F^- < O^{-2} < N^{-3}$

(d) $O^{-2} < S^{-2} < As^{3-}$

9. What will be the distance between H and Cl atom in HCl. The radius of hydrogen is 0.37 Å and the radius of chlorine is 1.67 Å?

(According to the concept of covalent radius)

(a) 2.04Å (b) 1.96Å

(c) 2.12Å (d) 1.0Å

Sol.(b) Bond length of single covalent bond = $r_A + r_B - 0.09\,(\Delta EN)$

Bond length $(d_{H-cl}) = r_H + r_{cl} - 0.09\,(\Delta EN)$

$r_H = 0.37Å$; $r_{cl} = 1.67Å$ and $\Delta EN = 3.0 - 2.1 = 0.9$

$d_{H-cl} = 0.37 + 1.67 - 0.09\,(0.9)$

or, $d_{H-cl} = 2.04 - 0.08 = 1.96Å$

10. The ionization energy of sodium is 495 kJ mol^{-1}. How much energy is needed to convert atoms present in 2.3 mg of sodium into sodium ions?

(a) 4.95 J (b) 49.5 J

(c) 495 J (d) 0.495 J

Sol.(b) Ionization energy of Na = 495 kJ/mol

No. of moles of Na in 2.3 mg

$$= \frac{2.3 \times 10}{23} = 10^{-4} \text{ moles}$$

For 1 mol, energy needed is 495 kJ

Hence, for 10^{-4} mol, energy needed is $495 \times 10^3 \times 10^{-4}$ J = 49.5 J

11. The correct order of the second ionization potential of carbon, nitrogen, oxygen and fluorine is

(a) C > N > F > O (b) O > N > F > C

(c) O > F > N > C (d) F > O > N > C

Sol.(c) IE_2 of neutral element is IE_1 of cation having single positive charge. Hence, for order of IE_2, first put +1 charge to each element then write electronic configuration.

C^+	N^+	O^+	F^+
$1s^2\, 2s^2\, 2p^6$	$1s^2\, 2s^2\, 2p^2$	$1s^2\, 2s^2\, 2p^3$	$1s^2\, 2s^2\, 2p^4$
		↑ Half filled	

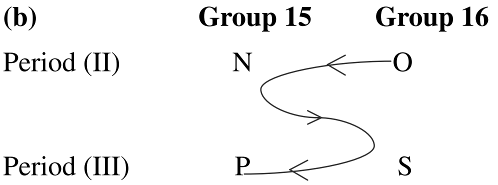
From left to right in a period, IE_1 increases and fulfilled or half filled elements have greater IE_1 than adjacent elements. Hence, correct order of IE_2 is: C > N > F > O

12. The electronegativity of the following elements increases in the order:

(a) S < P < N < O (b) P < S < N < O

(c) N < O < P < S (d) N < P < S < O

Sol. (b)



Correct order of electro negativity is:

P < S < N < O

13. The formation of the oxide ion, $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothermic step as shown below :

$O(g) + e^- \rightarrow O^-(g);\ \Delta_{eg}H = -141\ kJmol^{-1}$

$O^-(g) + e^- \rightarrow O^{2-}(g);\ \Delta_{eg}H = +780\ kJmol^{-1}$

Thus process of formation of O^{2-} in gas phase is unfavorable even O^{2-} is isoelectronic with neon. It is due to the fact that :

(a) Oxygen is more electronegative.

(b) Addition of electron in oxygen results in larger size of the ion.

(c) Electron repulsion outweighs the stability gained by achieving noble gas configuration.

(d) O^- ion has comparatively smaller size than oxygen atom.

Sol.(c) Process of formation of O^{2-} ion in gaseous phase is unfavorable because O^- ion (anion) resists addition of another e^- due to repulsion hence, electron repulsion outweighs the stability gained by achieving noble gas configuration.

14. Which is the correct in the following -

(a) Radius of Cl atom is 0.99 Å, while that of Cl^+ ion is 1.54 Å

(b) Radius of Cl atom is 0.99 Å, while that of Na atom is 1.54 Å

(c) Radius of Cl atom is 0.99 Å, while that of Cl^- ion is 0.81 Å

(d) Radius of Na atom is 0.95 Å, while that of Na^+ ion is 1.54 Å

Sol.(b) The atomic radius decreases along the period. Also cations are always smaller than their parent atom and anions are always larger than their parent atom.

15. Which oxide of 'N' is isoelectronic with CO_2:

(a) NO_2 (b) NO

(c) N_2O (d) N_2O_2

Sol.(c) N_2O is isoelectronic with CO_2. Both have 22 electrons.

16. Arrange Ce^{3+}, La^{3+}, Pm^3 and Yb^{3+} in increasing order of their size -

(a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$

(b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$

(c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$

(d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

Sol.(a) Lanthanide contraction is observed in these ions, i.e., ionic radius decreases as atomic number increases.

17. In which of the following compounds chromium shows maximum radius:-

(a) $K_2Cr_2O_7$ (b) CrO_2Cl_2

(c) $Cr_2(SO_4)_3$ (d) $CrCl_2$

Sol.(d) In $CrCl_2$, oxidation state of chromium is +2 (minimum). Thus it will have maximum radius. As positive oxidation state increases, radius decreases.

18. The IP_1, IP_2, IP_3, IP_4, and IP_5 of an element are 7.1, 14.3, 34.5, 46.8, 162.2 eV respectively.

The element is likely to be-

(a) Na (b) Si

(c) F (d) Ca

Sol.(b) The jump in IP values exist in IP_5 and thus removal of fifth electron occurs from inner shell. Thus element contains four electrons in its valence shell. It means the element belongs to the group 14.

19. Following are ground state electronic configuration of some neutral atoms:

(a) $1s^2\,2s^2\,2p^3$ (b) $1s^2\,2s^2\,2p^5$

(c) $1s^2\,2s^2 2p^6\,3s^1$ (d) $1s^2\,2s^2\,2p^6$

(i) Which of the following would have lowest IE?

(ii) Arrange them in increasing order of IE

Sol. (i) Three electrons in 2p subshell (i.e. half filled) indicate for its greater stability while 6 electrons in 2p indicate for its maximum stability. Thus electronic configuration (c) having 1 electron in 3s would require minimum IE

(ii) $c < a < b < d$ (increasing order of IE)

20. The atomic number of three elements A, B and C are a, a+1 and a+2, C is an alkali metal. In a compound of A and C, the nature of bonding is-

(a) Co-ordinate (b) Covalent

(c) Ionic (d) Metallic

Sol.(c) If C is alkali metal, A should be halogen (non-metal). Between metal and non-metal ionic bond is present.

Exercise

LEVEL I

1. X^{2-} is isoelectronic with "O_2^{+}" and has Z + 1 neutron (Z is atomic number of X^{2-}) then:
- (a) Mass number of X^{2-} is 27
- (b) Mass number of X^{2-} is 57
- (c) Atomic number of X^{2-} is 28
- (d) Number of proton X^{2-} is 15

2. Which of the following statements is not correct regarding hydrogen atom ?
- (a) It resembles halogens in some properties
- (b) It resembles alkali metals in some properties
- (c) It can be placed in 17th group of periodic table
- (d) It can not be placed in first group of periodic table

3. If an atom has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$, it will be place in:

(a) Second group (b) Third group

(c) Fifth group (d) Sixth group

4. Among the following, the element with the lowest atomic number that has a ground-state electronic configuration of $(n-1)\ d^5\ ns^1$ is located in the:

(a) Fifth period (b) Sixth period

(c) Fourth period (d) Third period

5. In species X^{2+} the mass number is 20 and number of neutrons are 10 then calculate the number of electrons in species X^{2+}:

(a) 4 (b) 7

(c) 6 (d) 8

6. The elements which are characterised by the outer shell configuration ns^1, ns^2 and $ns^2\ np^1$ to ns^2np^5 are collectively called as:
- (a) Transition elements
- (b) Representative elements
- (c) Lanthanides
- (d) Inner-transition elements

7.

Column - I (Type of element)	**Column – II (Outer electronic configuration)**
(A) Inert gas elements	(i) ns^{1-2} and $ns^2\ np^1$ to ns^2np^5
(B) Representative elements	(ii) $1s^2$ and $ns^2\ np^6$
(C) Transition elements	(iii) $(n-2)\ f^{1-14}\ (n-1)d^{0-1}\ ns^2$
(D) Inner- transition elements	(iv) $(n-1)\ d^{1-10}\ ns^{1\text{ or }2}$

- (a) A- i, B-ii,C-iii, D-iv
- (b) A-ii, B-i, C-iii, D-iv
- (c) A-ii, B-i, C-iv, D-iii
- (d) A-i, B-ii, C-iv, D-iii

8. Which of the following is an incorrect match?
- (a) Z = 65, group = IIIB, period – 6th
- (b) Z = 46, group = VIIIB, period – 5th
- (c) Z = 108, group = XB, period – 8th
- (d) Z = 57, group = IIIB, period – 6th

9. The element with atomic number 56 is likely to have the same outer shell configuration as the element with atomic number:

(a) 12 (b) 18

(c) 14 (d) 24

10. Electronic configuration of species M^{2+} is $1s^2$, $2s^2$, $2p^6$, $3s^2$,$3p^6$,$3d^6$ and its atomic weight is 56. The number of neutrons in the nucleus of species M is:

(a) 32 (b) 26

(c) 30 (d) 28

11. Which is correct order of ionic mobility in aqueous medium?
- (a) $Li^+ < Na^+ < K^+$
- (b) $Na^+ < Mg^{2+} < Al^{3+}$
- (c) $Al^{3+} < Na^+ < Mg^{2+}$
- (d) $Li^+ > Na^+ > K^+$

12. Which one of the following is not a characteristic of p-block elements?
- (a) The last electrons in them enters into a p-orbital
- (b) They mostly form acidic oxides
- (c) Down the group, stability of lower oxidation state increases
- (d) They mostly form basic oxides

13. Which of the following species has a value of magnetic moment, $\mu = \sqrt{35}$?

(a) Cr^{3+} (b) Mn^{2+}

(c) Fe^{2+} (d) Cu^{2+}

14. The paramagnetic species among the following is:

(a) Na^+ (b) Zn^{2+}

(c) Cu^+ (d) Fe^{3+}

15. All of the following possess complete d-subshells except:

(a) Ag^+ (b) Cu^{2+}

(c) Ga^{3+} (d) Zn^{2+}

16. Calculate the 'X' in Mn^{x+} if μ=3.87 BM

(a) 2 (b) 3

(c) 4 (d) 5

17. The first element of a group in many ways differs from the other heavier members of the group. This is due to:

(a) the small size

(b) the high electronegativity and high ionization potential

(c) the unavailability of d-orbitals

(d) all of the above

18. Be and AI show diagonal relationship hence, both have:

(a) almost same of electronegativity

(b) amphoteric nature of oxides

(c) approximately same polarizing power of respective cations

(d) all the properties above

19. Which of the following set contains pair of elements that do not belong to same group but show chemical resemblance?

(a) Hf, Zr (b) K, Rb

(c) Be, Al (d) B, Al

20. Which of the following set of magic numbers is not correct for given group?

(a) 18, 18, 32 ⇒ IIIB

(b) 8, 8, 18, 18, 32 ⇒ VIA

(c) 18, 32, 32 ⇒ IB

(d) 8, 8, 18, 18, 32 ⇒ IIA

21. Correct order of ionic radius of following isoelectronic species is:

(a) $Se^{-2} > Br^- > Kr > Rb^+ > Sr^{+2}$

(b) $S^{-2} > Cl^- > K^+ > Ar > Ca^{+2}$

(c) $N^{-3} > O^{-2} > Ne > F^- > Ca^{+2}$

(d) $F^- > Ne > Na^+ > Al^{+3} > Mg^{+2}$

22. Which of the following has the largest ionic radius?

(a) Be^{2+} (b) Mg^{2+}

(c) Ca^{2+} (d) Sr^{2+}

23. The correct order of the size of C, N, P and S is:

(a) N < C < P < S (b) C < N < P < S

(c) N < C < S < P (d) C < N < S < P

24. Which of the following pair of elements have almost similar atomic radii?

(a) Zr, Hf (b) Cu, Ag

(c) Sc, Ti (d) Pd, Ni

25. In which of the following compounds, manganese shows maximum radius?

(a) MnO_2 (b) $KMnO_4$

(c) MnO (d) $K_3\ (Mn(CN)_6)$

26. Ionization enthalpies tend to decrease going down any column of main group elements because------------ going down the column.

(a) Nuclear charge increases

(b) Number of shielding electrons increases

(c) Atomic size increases

(d) Effective nuclear charge increases

27. The ionization potential of nitrogen is more than that of oxygen because of:

(a) Greater attraction of electrons by the nucleus

(b) Extra stability of the half-filled p-orbitals

(c) Smaller size of nitrogen

(d) More penetration effect

28. Which of the following transition involve maximum amount of energy?

(a) $M^-_{(g)} \rightarrow M_{(g)}$ (b) $M^-_{(g)} \rightarrow M^+_{(g)}$

(c) $M^+_{(g)} \rightarrow M^{2+}_{(g)}$ (d) $M^{2+}_{(g)} \rightarrow M^{3+}_{(g)}$

29. Which of the following process refers to IE_2 of X?

(a) $X_{(g)} \rightarrow X^{2+}_{(g)}$ (b) $X^+_{(g)} \rightarrow X^{2+}(g)$

(c) $X^+_{(aq)} \rightarrow X^{2+}_{(g)}$ (d) $X_{(g)} \rightarrow X^+_{(g)}$

30. Which of the following statement concerning ionization energy is not correct?

(a) The IE_2 is always more than the first.

(b) Within a group, there is a gradual increase in ionization energy because nuclear charge increases.

(c) Ionization energy of Be is more than B.

(d) Ionization energy of noble gases are high.

31. Lanthanide contraction is related with:
(a) Sharp decrease in atomic size in lanthanide series
(b) Slow or gradual decrease in atomic size in lanthanide series
(c) Constancy in atomic size
(d) All the above

32. Relation between electron gain enthalpy and electron affinity is:
(a) $\text{EA} = \Delta H_{\text{e.g.}}$ (b) $\text{EA} = 2\Delta H_{\text{e.g.}}$
(c) $\text{EA} = -2\Delta H_{\text{e.g.}}$ (d) $\text{EA} = -\Delta H_{\text{e.g.}}$

33. The process requiring absorption of energy is:
(a) $N \rightarrow N^-$ (b) $F \rightarrow F^-$
(c) $Cl \rightarrow Cl^-$ (d) $H \rightarrow H^-$

34. Second and successive electron gain enthalpy of an element
(a) is always negative (energy is released)
(b) is always positive (energy is absorbed)
(c) can be positive or negative
(d) is always zero

35. Of the following pairs, the one containing examples of metalloid elements is:
(a) B and Al (b) Ga and Ge
(c) Al and Si (d) As and Sb

36. The group in the periodic table that contains the elements in all the different physical states at room temperature is:
(a) VA (b) IA
(c) VIIA (d) IVA

37. Elements of which group form anions most readily?
(a) Oxygen family (b) Nitrogen family
(c) Halogens (d) Alkali metals

38. What is the percentage of ionic character in CsF: (according to Henry-Smith formula)
{EN of Cs = 0.7 and EN of F = 4.0}
(a) 100% (b) 10%
(c) 90.9% (d) 99%

39. In halogens, which of the following decrease from iodine to fluorine?
(a) Bond length
(b) Electronegativity
(c) The ionization energy of the element
(d) Oxidizing power

40. As we proceed from top to bottom in the periodic table:
(a) hydroxides are more basic
(b) oxyacids are less acidic
(c) neither (a) and (b) of the above
(d) Both (a) and (b) of the above

41. Among the following oxides, which is least acidic?
(a) Al_2O_3 (b) B_2O_3
(c) CO_2 (d) NO_2

42. Which of the following oxides is neutral?
(a) SiO_2 (b) CO
(c) ZnO (d) SnO_2

43. What is the nature of Al_2O_3 and B_2O_3?
(a) Acidic, Acidic
(b) Acidic, Amphoteric
(c) Amphoteric, Amphoteric
(d) Amphoteric, Acidic

44. Correct order of acidic strength is:
(a) $SiH_4 > PH_3 > CH_4 > HCl$
(b) $HCl > PH_3 > CH_4 > SiH_4$
(c) $HCl > SiH_4 > PH_3 > CH_4$
(d) $HCl > PH_3 > SiH_4 > CH_4$

45. Which of the following oxide is acidic?
(a) N_2O_5 (b) Mn_2O_7
(c) CrO_3 (d) All

LEVEL II

1. An element X belongs to fourth period and fifteenth group of the periodic table. Which one of the following is true regarding the outer electronic configuration of X? It has:
A. Partially filled d-orbitals and completely filled s-orbital
B. Completely filled s-orbital and completely filled p-orbitals
C. Completely filled s-orbital and half filled p-orbitals
D. Half filled d-orbitals and completely filled s-orbital
(a) A,B & C (b) Only A & B
(c) A, B & D (d) Only C

2. Vishal Thakur went to meet his friend Sumit, Where he saw that his friend was doing the study of a particular chemistry book. But he could not find the theoretical value of bond length in H-F but he found that r_H and r_F are 0.37 Å and 0.72 Å respectively and eletronegativity of F and H are 4.0 and 2.1 respectively. What is bond length of H-F bond?

(a) 1.09 (b) 1.784

(c) 0.92 (d) 0.46

3. Choose the correct order of ionic radius for the following species:

(a) $Cl^- > I^- > Te^{2-} > Ar^+$

(b) $Te^{2-} > I^- > Cl^- > Ar^+$

(c) $I^- > Te^{2-} > Cl^- > Ar^+$

(d) $I^- > Cl^- > Ar^+ > Te^{2-}$

4. Which statement is correct?

(a) Tl^+ ion is more stable than Tl^{3+}

(b) Pb^{4+} salts act as good oxidizing agents

(c) Bi^{5+} salts act as good oxidizing agents

(d) All of these

5. Among the elements Ca, Mg, P and Cl, the order of increasing atomic radii is:

(a) Mg < Ca < Cl < P

(b) Cl < P < Mg < Ca

(c) P < Cl < Ca < Mg

(d) Ca < Mg < P < Cl

6. Element X belongs to 4th period. It contains 18 and 1 electron in the penultimate and ultimate orbit. The element X should be:

(a) Normal element

(b) Transition element

(c) Inert gas

(d) Inner-transition element

7. General electronic configuration of outermost and penultimate shell is $(n-1)s^2\ (n-1)p^6\ (n-1)d^x\ ns^2$. If n = 4 and x = 5, then number of protons in the nucleus will be :

(a) > 25 (b) < 24

(c) 25 (d) 30

8. Select correct statement:

(a) La and Ac belong to f-block

(b) An element having atomic number 31 belongs to 3rd period

(c) General outermost shell e^- configuration of d-block element is $ns^{1-2}\ (n-1)d^{1-10}$

(d) All actinoids are man made elements

9. A°/2 atoms of X(g) are converted into $X^+(g)$ by absorbing energy E_1. A°/2 ions of $X^+(g)$ are converted into $X^-(g)$ with release of energy E_2. Hence ionization energy and electron affinity of X(g) are:

(a) $\frac{2E_1}{A°}$, $\frac{2(E_1 - E_1)}{A°}$

(b) $\frac{2E_1}{A°}$, $\frac{2(E_2 - E_1)}{A°}$

(c) $\frac{(E_1 - E_2)}{A°}$, $\frac{2E_2}{A°}$

(d) None of these

10. Which represents correct order of acidic strength?

(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(b) $K_2O > ZnO > NO_2$

(c) NaOH < KOH < RbOH < CsOH

(d) $CH_4 < NH_3 < H_2O < HF$

11. Which of the following statements is incorrect?

(a) Cesium is the most electropositive element while F is the most electronegative element

(b) Cl has the highest -ve electron gain enthalpy out of all the elements

(c) Electron gain enthalpy of N as well as that of noble gases is positive

(d) In any period, the atomic radius of the noble gas is lowest

12. Which of the following is correct order of decreasing acidic character?

(i) $ClO_2 > SO_2 > SiO_2 > CO_2$

(ii) $ClO_2 > SO_2 > SiO_2 > SnO_2$

(iii) $N_2O_3 > P_2O_3 > As_2O_3 > Bi_2O_3$

(iv) $N_2O_5 > P_2O_5 > As_2O_5 > Bi_2O_5$

(a) i, ii, iii (b) ii, iii, iv

(c) i, iii, iv (d) i, ii, iv

13. Which of the following conclusions are correct regarding the element having atomic number equal to 113?

(i) It is present in the 8th period of the modern periodic table

(ii) It is present in the group 13 in the periodic table

(iii) It is a p-block element

(iv) Oxidation states of this element may be +1 or +3.

(a) i, iii, iv (b) ii, iii, iv

(c) i, ii, iv (d) i, iv

14. Which of the following statement(s) is(are) correct?

(a) The electronic configuration of Cr is (Ar) $3d^4$ $4s^2$ (Atomic number of Cr = 24)

(b) Cr is a representative element.

(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type.

(d) The oxidation state of nitrogen in HN_3 is –3.

15. Find the formula of halide of a metal whose successive ionization energies are x, 2x, 5x, 20x, 25x kJ mol^{-1} respectively.

(a) MX (b) MX_2

(c) MX_3 (d) M_2X

16. Which is/are true statement(s) about s-block elements?

(a) Metals are obtained by the electrolysis of fused chlorides

(b) Only one type of valency, +1 for IA and +2 for IIA, is shown

(c) Oxides are basic except BeO

(d) all of the above are correct statements

17. Which of the following statement(s) is/are correct?

(i) Vander waal's radius of iodine is more than its covalent radius

(ii) All isoelectronic ions belong to the same period of the periodic table

(iii) IE_1 of N is higher than that of O while IE_2 of O is higher than that of N

(iv) he 1^{st} electron gain enthalpy of Cl is negative while second is positive

(a) i, ii (b) i, ii, iii

(c) i, iii, iv (d) i, ii, iii, iv

18. Consider the following electronic configuration of an element (P):

$(Xe)4f^{14}5d^16s^2$

Then correct statement about element (P) is:

(a) It belongs to 6th period and 1st group

(b) It belongs to 6th period and 2nd group

(c) It belongs to 6th period and 3rd group

(d) None of these

19. The set representing the correct order of ionic radius is:

(a) $Na^+ > Mg^{2+} > Al^{3+} > Li^+ > Be^{2+}$

(b) $Na^+ > Li^+ > Mg^{2+} > Al^{3+} > Be^{2+}$

(c) $Na^+ > Mg^{2+} > Li^+ > Al^{3+} > Be^{2+}$

(d) $Na^+ > Mg^{2+} > Li^+ > Al^{3+} > Be^{2+}$

20. In the compound M-O-H, the M-O bond will be broken in water if:

(a) Δ (EN) of M and O < Δ (EN) of O and H

(b) Δ (EN) of M and O = Δ (EN) of O and H

(c) Δ (EN) of M and O > Δ (EN) of O and H

(d) Cannot be predicated according Δ (EN) data

21. Consider the following changes:

$M(s) \rightarrow M(g)$ .... (i)

$M(s) \rightarrow M^{2+}(g) + 2e^-$ .... (ii)

$M(g) \rightarrow M^+(g) + e^-$ .... (iii)

$M^+(g) \rightarrow M^{2+}(g) + e^-$ .... (iv)

$M(g) \rightarrow M^{2+}(g) + 2e^-$ .... (v)

The second ionization energy of M could be calculated from the energy values associated with:

(a) i+iii+iv (b) ii-i+iii

(c) i+v (d) v-iii

22. Consider the following conversions:

(i) $O_{(g)} + e^- \rightarrow O^-_{(g)}, \Delta H_1$

(ii) $F_{(g)} + e^- \rightarrow F^-_{(g)}, \Delta H_2$

(iii) $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}, \Delta H_3$

(iv) $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}, \Delta H_4$

That according to given information the incorrect statement is:

(a) ΔH_3 is more negative than ΔH_1 and ΔH_2

(b) $\Delta H_1$is less negative than ΔH_2

(c) ΔH_1, ΔH_2 and ΔH_3 are negative whereas ΔH_4 is positive

(d) ΔH_1 and ΔH_3 are negative whereas ΔH_2 and ΔH_4 are positive

23. Ionic radii of:

(a) ${}^{35}Cl^- > {}^{37}Cl^-$ (b) $Mn^{7+} > Ti^{4+}$

(c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$

24. The correct order of relative stability of half filled and completely filled sub-shell is:

(a) $p^3 > d^5 < d^{10} < p^6$ (b) $d^5 > p^3 < d^{10} < p^6$

(c) $d^5 < p^3 < d^{10} < p^6$ (d) $p^3 > d^{10} < d^5 < p^6$

25. The five successive ionization energies of an element are 800, 2427, 3658, 25024 and 32824 kJ Mol^{-1} respectively. The number of valence electron is:

(a) 3 (b) 5

(c) 1 (d) 2

26. What is the order of ionization energies of the coinage metal?

(a) Ag > Cu > Au (b) Cu > Ag > Au

(c) Cu < Ag < Au (d) Au > Cu > Ag

27. IE_2 for an element is invariably higher than IE_1 because:

(a) It is difficult to remove electron from cation

(b) The size of the cation is smaller than its atoms

(c) Z_{eff} is more for cation

(d) All the above

28. Two p-block elements x (outer configuration $ns^2 np^3$) and z (outer configuration $ns^2 np^4$) occupy neighbouring positions in a period. Using this information which of the following is correct with respect to their ionization potential I_x and I_z?

(a) $I_x > I_z$

(b) $I_x < I_z$

(c) $I_x = I_z$

(d) Relation between I_x and I_z is uncertain

29. Fluorine has the highest electronegativity among the group on the pauling scale, but the electron affinity of fluorine is less than that of chlorine because:

(a) The atomic number of fluorine is less than that of chlorine

(b) Fluorine being the first member of the family behaves in an unusual manner

(c) Chlorine can accommodate an electron better than fluorine by utilising its vacant 3d orbital

(d) Small size, high electron density and an increased electron repulsion make addition of an electron to fluorine less favourable than that in the case of chlorine

30. Select correct statement about radius of an atom:

(a) Values of vanderwaal's radii are larger than those of covalent radii because the vanderwaal's forces are much weaker than the forces operating between atoms in a covalently bonded molecule.

(b) The metallic radii are smaller than the vander waal's radii, since the bonding forces in the metallic crystal lattice are much stronger than the vander waal's forces.

(c) Both (a) & (b)

(d) None of these

31. Which represents alkali metals (i.e. 1st group metals) based on IE_1 and IE_2 values in kJ mol^{-1}?

		IE_1	IE_2
(a)	X	500	1000
(b)	Y	600	2000
(c)	Z	550	7500
(d)	M	700	1400

32. Match the correct atomic radius with the element:

S.No.	Element	Code	Atomic radius (pm)
(i)	Be	(p)	74
(ii)	C	(q)	88
(iii)	O	(r)	111
(iv)	B	(s)	77
(v)	N	(t)	66

(a) (i)–r, (ii)–q, (iii)–t, (iv)–s, (v)–p

(b) (i)–t, (ii)–s, (iii)–r, (iv)–p, (v)–q

(c) (i)–r, (ii)–s, (iii)–t, (iv)–q, (v)–p

(d) (i)–t, (ii)–p, (iii)–r, (iv)–s, (v)–q

33. Electronic configurations of four element A, B, C and D are given below:

(i) $1s^2\ 2s^2\ 2p^6$ (ii) $1s^2\ 2s^2\ 2p^4$

(iii) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (iv) $1s^2\ 2s^2\ 2p^5$

Which of the following is the correct order of increasing tendency to gain electron ?

(a) i < iii < ii < iv (b) i < ii <iii < iv

(c) iv < ii < iii < i (d) iv < i < ii < iii

34. Which of the following is the wrong statement?

(a) All the actinoid elements are radioactive.

(b) Alkali and alkaline earth metals are s-block elements.

(c) Pnictogens and halogens are p-block elements.

(d) The first member of the lanthanoid series is lanthanum

35. Which is true statement(s)?

(a) Larger the value ionization enthalpy, easier is the formation of cation.

(b) Larger the value of electron affinity, easier is the formation of anion.

(c) Larger the value of ionization energy as well as electron affinity, smaller is the Mulliken electronegativity of atom.

(d) Larger the Z_{eff}, larger is the size of atom.

36. The lithium ion (Li^+) and hydride ion (H^-) are isoelectronic ions. Which statement about these systems is true?

(a) Chemical properties of these ions are identical since they are isoelectronic.

(b) Li^+ is a stronger reducing agent than H^-

(c) More energy is needed to ionize H^- than Li^+

(d) Radius of H^- is larger than that of Li^+

37. The correct order of increasing first ionization energy is:

(a) Ca < K < Ne < P < F

(b) F < Ca < Ne < P < K

(c) K < Ca < P< F < Ne

(d) Ne < F < P < Ca < K

38. The number of d-electrons in Fe^{2+} (atomic number = 26) is not equal to that of:

(a) p-electrons in $_{10}Ne$

(b) s-electrons in $_{12}Mg$

(c) d-electrons in Fe

(d) p-electrons in Cl^-

39. Which of the following transition results in increase in magnetic moment value?

(a) $Mn^{2+} \rightarrow Mn^{4+}$ (b) $Ni^{2+} \rightarrow Ni^{4+}$

(c) $Cu^{2+} \rightarrow Cu^{+}$ (d) $Zr \rightarrow Zr^{2+}$

40. The compound of vanadium with chlorine has magnetic moment 1.73 BM. The vanadium chloride has the formula:

(a) VCl_2 (b) VCl_3

(c) VCl_4 (d) VCl_5

41. Which of the following order of radius is not correct?

(a) $Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$

(b) $Mg^{+2} < Na^+ < Al < F^-$

(c) K > Ca > Mg > Li

(d) $O < O^{-2} < F < F^-$

42. Correct trend of first ionization energy in group-13 is:

(a) B > Al > Ga > In > Tl

(b) B > Al > Ga > Tl > In

(c) B > Tl > Ga > Al > In

(d) B > Ga > Al > In > Tl

43. Which has the lowest anion to cation size ratio?

(a) LiF (b) NaF

(c) Csl (d) CsF

44. Select the incorrect statement:

(a) Size of H^- is larger than F^-

(b) Rb is more electropositive compared to Ca

(c) Na^+ is more electronegative than the Na

(d) $Cl^-$is more electronegative than that of F

45. Four elements P, Q, R and S have atomic number Z-1, Z, Z+1 and Z+2 respectively. If Z is 17, then bond between which pair of elements will be least covalent:

(a) S and Q (b) P and R

(c) S and R (d) S and P

LEVEL III

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Select the correct statement(s):

(a) Alkali metals have lowest IE in respective period.

(b) Noble gases have highest IE in respective period.

(c) EA_1 of N < EA_1 of O

(d) $F^-$is the strongest reducing agent among halide ions.

2. The electronic configuration of given species (X) is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This can be its:

(a) Cationic form X^+ (b) Anionic form X^-

(c) Excited state (d) Ground state

3. In which of the following arrangements, the order is according to the property indicated against it?

(a) IE_1: O > N > C > B

(b) $\Delta_{eg}H$ (with – ve sign): Cl > F > Br > I

(c) Metallic radius: Rb > K > Na > Li

(d) Ionic size: $F^- > Na^+ > Mg^{2+} > Al^{3+}$

4. In which of the following arrangements, the order is according to the property indicated against it?

(a) Basic strength: $SbH_3 > AsH_3 > PH_3 > NH_3$

(b) IE_1: N > O > C > B

(c) Oxidising power: $PbO_2 > SnO_2 > SiO_2 > CO_2$

(d) Acid strength: HI > HBr > HCl > HF

5. Which of the following orders is (are) correct for size?

(a) Al ≈ Ga (b) $Te^{2-} > I^{-} > Cs^{+} > Ba^{2+}$

(c) $Cr^{3+} < Cr^{6+}$ (d) Pd ≈ Pt

6. Which of the following statements is/are correct?

(a) The second ionization enthalpy of oxygen element is greater than that of fluorine element.

(b) The third ionization enthalpy of phosphorus is greater than that of aluminium.

(c) The first ionization enthalpy of aluminium is slightly greater than that of gallium.

(d) The second ionization enthalpy of copper is greater than that of zinc.

7. Which of the following is/are correct order(s)of electron affinity?

(a) $N < C < O < F$ (b) $P < Si < S < Cl$

(c) $Si < P < S < Cl$ (d) $C < N < O < F$

8. Which of the following is correct order of electronegativity?

(a) $Cs > Rb > Na$ (b) $Li < Be < B$

(c) $C < N < O$ (d) $Cl > F > Br$

9. Poor shielding of nuclear charge by d or f- orbital electrons is responsible for which of the following facts?

(a) Atomic radius of Nb (4d- series) is comparable to that of Ta (5d- series).

(b) The 1st ionization enthalpy of copper is less than that of zinc.

(c) The value of electron gain enthalpy is more negative for sulphur than for oxygen.

(d) The 1st ionization energy for gold is greater than that of silver.

10. Which of the following is/are true order(s)?

(a) $B^{+} < B < B^{-}$	Size
(b) $I < Br < Cl < F$	Electron gain enthalpy (with negative sign)
(c) $O^{2-} < O < O^{+}$	Z_{eff}
(d) $Na < Al < Mg < Si$	Ionization potential

11. Select the endothermic step(s):

(a) $S^{-}_{(g)} + e^{-} \rightarrow S^{2-}_{(g)}$

(b) $Ne_{(g)} + e^{-} \rightarrow Ne^{-}_{(g)}$

(c) $N_{(g)} + e^{-} \rightarrow N^{-}_{(g)}$

(d) $Al^{2+}_{(g)} \rightarrow Al^{3+}_{(g)} + e^{-}$

COMPREHENSIONS TYPE QUESTIONS

Read the following passage carefully and answer the question.

Comprehension # 1 (Q. 12 to 14)

It is not possible to measure the atomic radius precisely since the electron cloud surrounding the atom does not have a sharp boundary. One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and then dividing by two. For metals we define the term "metallic radius" which is taken as half the internuclear distance separating the metal cores in the metallic crystal. The van der Waal's radius represents the overall size of the atoms which includes its valence shell in a non bonded situation. It is the half of the distance between two similar atoms in separate molecules in a solid. The atomic radius decreases across a period and increases down the group. Same trends are observed in case of ionic radius of the species having same number of electrons depends on the number of protons in their nuclei. Sometimes, atomic and ionic radii give unexpected trends due to poor shielding of nuclear charge by d- and f-orbital electrons.

12. Which of the following relations is correct, if considered for the same element ?

(a) $R_{\text{Van der Waal}} > R_{\text{Covalent}} > R_{\text{Metallic}}$

(b) $R_{\text{Covalent}} > R_{\text{Metallic}} > R_{\text{Van der Waal}}$

(c) $R_{\text{Van der Waal}} > R_{\text{Metallic}} > R_{\text{Covalent}}$

(d) $R_{\text{Metallic}} > R_{\text{Covalent}} > R_{\text{Van der Waal}}$

13. K^{+}, Cl^{-}, Ca^{2+}, S^{2-} ions are isoelectronic. The decreasing order of their size is:

(a) $Ca^{2+} > K^{+} > Cl^{-} > S^{2-}$

(b) $S^{2-} > Cl^{-} > K^{+} > Ca^{2+}$

(c) $K^{+} > Cl^{-} > Ca^{2+} > S^{2-}$

(d) $S^{2-} > Cl^{-} > Ca^{2+} > K^{+}$

14. Select the INCORRECT option regarding atomic/ ionic sizes:

(a) $Zn > Cu$ (b) $Pb^{2+} > Pb^{4+}$

(c) Zr ≈ Hf (d) $N^{3-} < Al^{3+}$

Comprehension # 2 (Q. 15 to 17)

Effective nuclear charge (Z_{eff}) is the net attractive force on electrons under Consideration and is equal to:

$Z_{eff} = Z - \sigma$ (nuclear charge – screening constant). Z_{eff} or σ is calculated by Slater's formula, as given.

If one electron is present in the outermost orbit, there will be no screening in that orbital. Each electron contribute, 0.35 (total electrons minus one electron) present in the outermost shell.

A contribution of 0.85 for each electron is taken in the (n-1)th shell.

For all other electrons contribution is 1 for each electron.

15. The screening constant (σ) for 4s electron of Mn (Z = 25) will be :

(a) 18.00	(b) 4.25
(c) 18.35	(d) 21.40

16. Which of the following statement is wrong?

(a) IE_1 of Ga > Al, due to imperfect shielding of 3d-orbitals in Ga.

(b) IE_1 of Ga > Al, due to perfect shielding of 3d-orbitals in Ga.

(c) The atomic size of Ga and Al are almost same because of poor shielding effect of electrons in d-orbitals as the effective nuclear increases in Ga.

(d) IE_1 of group 16 elements is less than that of group 15 elements.

17. Which of the following statement is wrong?

(a) The number of lobes in d-orbitals are 4.

(b) IE_1 of element increases along the period.

(c) IE_1 of the group 3 elements is more than that of the group 2 elements

(d) IE_1, IE_2 and IE_3 of an element are 9.5, 18.5 and 154.4 eV predict that the element has either two s-electrons or two p-electrons in the valence shell.

Comprehension # 3 (Q. 18 to 20)

The energy required to remove an electron from the outermost shell of an isolated gaseous atom is known as IE_1 of that atom. Similarly, the energy required for the removal of the electron from the unipositive ion, dipositive ion and tripositive ion are known as IE_2, IE_3 and IE_4 respectively, and are called successive ionization energies. The magnitude of the charge depends on the size of the orbital of electron. Electrons in smaller orbitals are on average close with each other and have more repulsion. Thus for Be ($2s^2$), the IE_1 and IE_2 are 9.3 and 18.2 eV atom^{-1}, whereas for Ca ($4s^2$), the vales are 6.1 and 11.9 eV.

18. The correct order of arrangement of the first ionization energies of C, N, O and F (in decreasing values) is:

(a) C > N > O > F	(b) O > N > F > C
(c) O > F > N > C	(d) F > N > O > C

19. Four elements have the following first ionization energies in kJ mol^{-1} : 762, 709, 59 and 558. The elements are Ga, Ge, In and Sn (not in order). Which of these elements has the ionization energy of 762 kJ mol^{-1}?

(a) In	(b) Ga
(c) Sn	(d) Ge

20. Among the following ionization reactions, which one will have the maximum value of ionization energy?

(a) $Be \rightarrow Be^+$	(b) $Be^+ \rightarrow Be^{2+}$
(c) $Sr \rightarrow Sr^+$	(d) $Sr^+ \rightarrow Sr^{2+}$

Comprehension # 4 (Q. 21 to 23)

Energy is released when an electron is added to neutral isolated gaseous atom in its ground state to give monoanion and this is known as EA_1 or $\Delta_{eg}H_1$. Greater is the amount of energy released the greater will be EA. EA is expressed in eVatom^{-1} or kJ mol^{-1}

21. EA values of N and P are exceptionally low, because:

(a) Both N and P have half-filled p-orbitals in the valence shell.

(b) The atom is more stable than the corresponding anion.

(c) The electronic configuration of the anion N^- and P^- is relatively more stable than the corresponding atom.

(d) Both (b) and (c).

22. Select the correct statements (More than one correct):

(a) EA_1 and $\Delta_{eg}H_1$ of an atom of element have same magnitude

(b) $\Delta_{eg}H_1$(-ve) of Al > B

(c) $\Delta_{eg}H_1$(-ve)of P > N

(d) $\Delta_{eg}H_1$(-ve) of S > O

23. Select the correct statements (More than one correct):

(a) $\Delta_{eg}H_1$of noble gases have large positive values.

(b) $\Delta_{eg}H_1$ of noble gases have large negative values.

(c) $\Delta_{eg}H_1$ if helium (He) is the lowest of all the noble gases.

(d) $\Delta_{eg}H_1$ of Ar is lower than that of Ne.

SINGLE AND DOUBLE VALUE INTEGER TYPE QUESTIONS

24. Most stable oxidation state of thallium is +n. What is the value of n?

25. Total number of elements which have more ionization energy as compare to their next higher atomic number elements. Li, Be ,B, C, N, O, F, Ne

26. How many elements are more electropositive than Cl?
B, N, O, S, P, At, H, Li

27. Total number of elements which have only single oxidation state (other than zero) in their corresponding stable compounds: Cs, Ba, F, Zn, Be, Al, Sr, Ga, Pb

28. How many pairs in their first species have lower ionization energy than second species?

(a) N and O　(b) Li and Li^+

(c) O and S　(d) Ba and Sr

(e) I and I^-　(f) Be and B

(g) Br and K

MATCHING THE COLUMN TYPE QUESTIONS

29.

	Column I		Column II
a.	Na > Mg > Al > B	p.	Oxidizing nature
b.	F > N > C > B > Si	q.	Lowest IE_1
c.	F > O > Cl > N	r.	Metallic character
d.	Out B, C, Al and Si, C have	s.	Non-metallic character
		t.	Highest IE_1

30.

	Column I		Column II
a.	N_2O	p.	Normal oxide
b.	Na_2O	q	Neutral oxide
c.	Ga_2O_3	r.	Suboxide
d.	C_3O_2	s.	Basic oxide
e.	Mn_3O_4	t.	Amphoteric oxide
f.	SnO_2	u.	Mixed oxide

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. The correct order of acidic strength is:

(a) $Cl_2O_7 > SO_2 > P_4O_{10}$

(b) $CO_2 > N_2O_5 > SO_3$

(c) $Na_2O > MgO > Al_2O_3$

(d) $K_2O > CaO > MgO$

(III-JEE, 2000)

2. The correct order of radii is:

(a) N < Be < B　(b) $F^- < O^{2-} < N^{3-}$

(c) Na < Li < K　(d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

(III-JEE, 2000)

3. The set representing the correct order of first ionization potential is:

(a) K > Na > Li　(b) Be > Mg > Ca

(c) B > C > N　(d) Ge > Si > C

(III-JEE, 2001)

4. Identify the least stable ion amongst the following:

(a) Li^-　(b) Be^-

(c) B^-　(d) C^-

(III-JEE, 2002)

5. Identify the correct order of acidic strengths of CO_2, CuO, CaO, H_2O is:

(a) $CaO < CuO < H_2O < CO_2$

(b) $H_2O < CuO < CaO < CO_2$

(c) $CaO < H_2O < CuO < CO_2$

(d) $H_2O < CO_2 < CaO < CuO$

(IIT-JEE, 2002)

6. Statement-1: Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

Statement-2: The higher oxidation states for the group 14 elements are more stable for the heavier members for the group due to inert pair effect.

(a) Statement-1 is True, Statement-2 is true, Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is true, Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

(III-JEE, 2008)

7. Which of the following represent the correct order of increasing IE_1 for Ca, Ba, S, Se and Ar?
(a) S < Se < Ca < Ba < Ar
(b) Ba < Ca < Se < S < Ar
(c) Ca < Ba < S < Se < Ar
(d) Ca < S < Ba < Se < Ar

(III-JEE, 2013)

8. The correct order of ionic radius is:
(a) Ce > Sm > Tb > Lu (b) Lu > Tb > Sm > Ce
(c) Tb > Lu > Sm > Ce (d) Sm > Tb > Lu > Ce

(AIEEE, 2002)

9. Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} have ionic radii in the increasing order as:
(a) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(b) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(c) $La^{3+} = Ce^{3+} < Pm^{3+} < Yb^{3+}$
(d) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$

(AIEEE, 2002)

10. According to the modern Periodic Law of elements, the variation in properties of elements is related to their?
(a) Nuclear masses
(b) Atomic numbers
(c) Nuclear neutron-proton number ratio
(d) Atomic masses

(AIEEE, 2003)

11. The reduction in atomic size with increase in atomic number is a characteristic of elements of:
(a) d-block
(b) f-block
(c) Radioactive series
(d) High atomic masses

(AIEEE, 2003)

12. Which one of the following groups represents a collection of isoelectronic species? (Atomic number of Cs is 55 and of Br is 35)
(a) N^{3-}, F^-, Na^+ (b) Be, Al^{3+}, Cl^-
(c) Ca^{2+}, Cs^+, Br (d) Na^+, Ca^{2+}, Mg^{2+}

(AIEEE, 2003)

13. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) respectively 23, 24, 25 and 26. Which one of these may be expected to have the higher second ionization enthalpy?
(a) Cr (b) Mn
(c) Fe (d) V

(AIEEE, 2003)

14. Which one of the following sets of ions represents the collection of isoelectronic species?
(a) K^+, Cl^-, Mg^{2+}, Sc^{3+}
(b) Na^+, Ca^{2+}, Sc^{3+}, F^-
(c) K^+, Ca^{2+}, Sc^{3+}, Cl^-
(d) Na^+, Mg^{2+}, Al^{3+}, Cl^-

(AIEEE, 2004)

15. Which one of the following ions has the highest value of ionic radius?
(a) O^{2-} (b) B^{3+}
(c) Li^+ (d) F^-

(AIEEE, 2004)

16. Among Al_2O_3, SiO_2, P_2O_3 and SO_2 the correct order of acid strength is:
(a) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$
(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
(c) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$
(d) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

(AIEEE, 2004)

17. The formation of the oxide ion requires first an exothermic and then an endothermic step as shown below:

$O(g) + e^- = O^-(g)\ \Delta H^\circ = -142\ \text{kJ mol}^{-1}$

$O^-(g) + e^- = O^{2-}(g)\ \Delta H^\circ = 844\ \text{kJ mol}^{-1}$

This is because of:
(a) O^- ion will tend to resist the addition of another electron
(b) Oxygen has high electron affinity
(c) Oxygen is more electronegative
(d) O^- ion has comparatively larger size than oxygen atom

(AIEEE, 2004)

18. Which among the following factors is the most important in making fluorine the strongest oxidizing halogen?
(a) Hydration enthalpy
(b) Ionization enthalpy
(c) Electron affinity
(d) Bond dissociation energy

(AIEEE, 2004)

19. Pick out the isoelectronic structure from the following:
I. $^+CH_3$ II. H_3O^+
III. NH_3 IV. CH_3^-
(a) I and II (b) III and IV
(c) I and III (d) II, III and IV

(AIEEE, 2005)

20. Which of the following factors may be regarded as the main cause of lathanoid contraction?

(a) Poor shielding of one of 4f electron by another in the subshell.

(b) Effective shielding of one of 4f electrons by another in the subshell.

(c) Poorer shielding of 5d electrons by 4f electrons

(d) Greater shielding of 5d electrons by 4f electrons

(AIEEE, 2005)

21. In which of the following arrangements the order is NOT according to the property indicated against it?

(a) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ - Increasing ionic size

(b) B < C < N < O - Increasing first ionisation enthalpy

(c) I < Br < F < Cl - Increasing electron gain enthalpy (with negetive sign)

(d) Li < Na < K < Rb - Increasing metallic redius

(AIEEE, 2005)

22. The lanthanide contraction is responsible for the fact that:

(a) Zr and Y have about the same radius.

(b) Zr and Nb have similar oxidation state.

(c) Zr and Hf have about the same radius.

(d) Zr and Zn have same oxidation state.

(AIEEE, 2005)

23. Which of the following oxides is amphoteric in character?

(a) SnO_2 (b) SiO_2

(c) CO_2 (d) CaO

(AIEEE, 2005)

24. The increasing order of the first ionization enthalpies of the elements B, P, S and F (lowest first) is:

(a) F < S < P < B (b) P < S < B < F

(c) B < P < S < F (d) B < S < P < F

(AIEEE, 2006)

25. Which one of the following sets of ions represents a collection of isoelectronic species?

(a) $N^{3-}, O^{2-}, F^-, S^{2-}$

(b) $Li^+, Na^+, Mg^{2+}, Ca^{2+}$

(c) $K^+, Cl^-, Ca^{2+}, Sc^{3+}$

(d) $Ba^{2+}, Sr^{2+}, K^+, Ca^{2+}$

(AIEEE, 2006)

26. Lanthanoid contraction is caused due to:

(a) The same effective nuclear charge from Ce to Lu

(b) The imperfect shielding on outer electrons by 4f electrons from the nuclear charge

(c) The appreciable shielding on outer electrons by 4f electrons from the nuclear charge

(d) The appreciable shielding on outer electrons by 5d electrons from the nuclear charge

(AIEEE, 2006)

27. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?

(a) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens

(b) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group

(c) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group

(d) In both alkali metals and the halogens the chemical reactivity decreases with increases in atomic number down the group

(AIEEE, 2006)

28. The set representing the correct order of ionic radius is:

(a) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$

(b) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$

(c) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$

(d) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$

(AIEEE, 2009)

29. The correct sequence which shows decreasing order of the ionic radii of the elements is:

(a) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$

(b) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$

(c) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$

(d) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

(AIEEE, 2010)

30. The outer electronic configuration of Gd (Atomic number 64) is:

(a) $4f^3\ 5d^5\ 6s^2$ (b) $4f^8\ 5d^0\ 6s^2$

(c) $4f^4\ 5d^4\ 6s^2$ (d) $4f^7\ 5d^1\ 6s^2$

(AIEEE, 2011)

31. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9,17, 35 and 53 respectively is:

(a) F > Cl > Br > I (b) Cl > F > Br > I

(c) Br > Cl > I > F (d) I > Br > Cl > F

(AIEEE, 2011)

32. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?

(a) $Al_2O_3 < MgO < Na_2O < K_2O$

(b) $MgO < K_2O < Al_2O_3 < Na_2O$

(c) $Na_2O < K_2O < MgO < Al_2O_3$

(d) $K_2O < Na_2O < Al_2O_3 < MgO$

(AIEEE, 2011)

33. The increasing order of the ionic radii of the given isoelectronic species is:

(a) Cl^-, Ca^{2+}, K^+, S^{2-} (b) S^{2-}, Cl^-, Ca^{2+}, K^+

(c) Ca^{2+}, K^+, Cl^-, S^{2-} (d) K^+, S^{2-}, Ca^{2+}, Cl^-

(AIEEE, 2012)

34. Which of the following presents the correct order of second ionization enthalpies of C, N, O and F?

(a) O > N > F > C (b) F > O > N > C

(c) C > N > O > F (d) O > F > N > C

(JEE Main Online 2012)

35. Which among the following elements has the highest ionization enthalpy?

(a) Nitrogen (b) Boron

(c) Carbon (d) Oxygen

(JEE Main Online 2012)

36. Electron gain enthalpy with negative sign of fluorine is less than that of chlorine due to:

(a) High ionization enthalpy of fluorine

(b) Smaller size of chlorine atom

(c) Smaller size of fluorine atom

(d) Bigger size of 2p orbital of fluorine

(JEE Main Online 2013)

37. The order of increasing sizes of atomic radii among the elements O, S, Se and As is:

(a) As < S < O < Se (b) Se < S < As < O

(c) O < S < As < Se (d) O < S < Se As

(JEE Main Online 2013)

38. What is the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?

(a) Ca < S < Ba < Se < Ar

(b) S < Se < Ca < Ba < Ar

(c) Ba < Ca < Se < S < Ar

(d) Ca < Ba < S < Se < Ar

(JEE Main, 2013)

39. The first ionization potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be:

(a) -2.55 eV (b) -5.1 eV

(c) -10.2 eV (d) +2.55 eV

(JEE Main, 2013)

40. Similarity in chemical properties of the atoms of elements in a group of the periodic table is most closely related to:

(a) Atomic numbers

(b) Atomic masses

(c) Number of principal energy levels

(d) Number of valence electrons

(JEE Main Online 2014)

41. Which of the following arrangements represents the increasing order (smallest to largest) of ionic radii of the given species O^{2-}, S^{2-}, N^{3-}, P^{3-}?

(a) $O^{2-} < N^{3-} < S^{2-} < P^{3-}$ (b) $O^{2-} < P^{3-} < N^{3-} < S^{2-}$

(c) $N^{3-} < O^{2-} < P^{3-} < S^{2-}$ (d) $N^{3-} < S^{2-} < O^{2-} < P^{3-}$

(JEE Main Online 2014)

42. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively:

(a) 1.36, 1.40 and 1.71 (b) 1.36, 1.71 and 1.40

(c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40

(JEE Main, 2015)

43. Which of the following atoms has the highest first ionization energy?

(a) Na (b) K

(c) Sc (d) Rb

(JEE Main, 2016)

Answer Key

LEVEL I

1. (a) 2. (d) 3. (c) 4. (c) 5. (d) 6. (b) 7. (c) 8. (c) 9. (a) 10. (c)
11. (a) 12. (d) 13. (b) 14. (d) 15. (b) 16. (c) 17. (d) 18. (d) 19. (c) 20. (b)
21. (a) 22. (d) 23. (c) 24. (a) 25. (c) 26. (c) 27. (b) 28. (d) 29. (b) 30. (b)
31. (b) 32. (d) 33. (a) 34. (b) 35. (d) 36. (c) 37. (c) 38. (c) 39. (a) 40. (d)
41. (a) 42. (b) 43. (d) 44. (d) 45. (d)

LEVEL II

1. (d) 2. (c) 3. (b) 4. (d) 5. (b) 6. (b) 7. (c) 8. (c) 9. (b) 10. (d)
11. (d) 12. (d) 13. (b) 14. (c) 15. (c) 16. (d) 17. (c) 18. (c) 19. (b) 20. (c)
21. (d) 22. (d) 23. (d) 24. (c) 25. (a) 26. (d) 27. (d) 28. (a) 29. (d) 30. (c)
31. (c) 32. (c) 33. (a) 34. (d) 35. (b) 36. (d) 37. (c) 38. (d) 39. (b) 40. (c)
41. (d) 42. (c) 43. (d) 44. (d) 45. (a)

LEVEL III

1. (a,b,c) 2. (a,d) 3. (b,c,d) 4. (b,c,d) 5. (a,b,d) 6. (a,b,d) 7. (a,b) 8. (b,c)
9. (a,d) 10. (a,c,d) 11. (a,b,c,d) 12. (c) 13. (b) 14. (d) 15. (d) 16. (b)
17. (c) 18. (d) 19. (d) 20. (b) 21. (a) 22. (a,b,c,d) 23. (a,d) 24. (1)
25. (2) 26. (6) 27. (7) 28. (2)
29. a →r; b →s; c →p;d →t
30. a →q,r; b →p,s; c →t; d →r; e → u; f →t

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (a) 2. (b) 3. (b) 4. (b) 5. (a) 6. (c) 7. (b) 8. (a) 9. (b) 10. (b)
11. (b) 12. (a) 13. (a) 14. (c) 15. (a) 16. (d) 17. (a) 18. (a) 19. (d) 20. (c)
21. (b) 22. (c) 23. (a) 24. (d) 25. (c) 26. (b) 27. (b) 28. (a) 29. (d) 30. (d)
31. (b) 32. (a) 33. (c) 34. (d) 35. (a) 36. (c) 37. (d) 38. (c) 39. (b) 40. (d)
41. (a) 42. (c) 43. (c)

Hints and Solutions

LEVEL I

1. **(a)** Number of e^- in $O_2^+ = 15$ = number of e^- in X^{2-}

Atomic number of X^{2-} is 13 (z)

Number of neutrons = Z+1 = 14

Mass number of $X^{2-} = 13 + 14 = 27$

2. **(d)** Hydrogen resembles halogens in some properties and also resembles alkali metals in some properties. So, it can be placed in first or 17th group.

3. **(c)** This element belongs to d-block

Group number of d-block = (ns + (n – 1) d)

= 2 + 3 = 5

4. **(c)** Cr belongs to fourth period.

5. **(d)** Mass number (proton + neutron) of $X^{2+} = 20$

Number of neutrons = 10

Hence, Number of protons of $X^{2+} = 10$

Number of e^- in $X^{2+} = 8$

6. **(b)** Elements of group 1, 2 and 13 to 17 are called as representative elements.

7. **(c)** Inert gas elements → $1s^2$ and $ns^2\ np^6$

Representative elements → $ns^{1\text{-}2}$ and $ns^2\ np^1$ to $ns^2\ np^5$

Transition elements → $(n-1)\ d^{1\text{-}10}\ ns^{1 or 2}$

Inner – transition elements → $(n-2)\ f^{1\text{-}14}\ (n-1)\ d^{0\text{-}1}\ ns^2$

8. **(c)** Z = 108, group number Viii B , period – 7th

9. **(a)** The element, with atomic number 56, belongs to group 2 (alkaline earth metal). The element, with atomic number 12, also belongs to group 2.

10. **(c)** e^- configuration of $M^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

e^- configuration of $M = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

= atomic number is 26

Atomic weight of M = 56

Number of neutrons = 56 – 26 = 30

11. **(a)** $\text{Ionic mobility} \propto \dfrac{1}{\text{Size in aqueous medium}}$

Order of size in aqueous medium:

$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)}$

Order of ionic mobility:

$Li^+_{(aq)} < Na^+_{(aq)} < K^+_{(aq)}$

12. **(d)** p-block elements mostly form acidic oxides not basic oxides.

13. **(b)**

Ion	e^- configuration	Number of unpaired e^-	μ
Cr^{+3}	$(Ar)\ 4s^\circ\ 3d^3$	3	$\sqrt{15}$
Mn^{+2}	$(Ar)\ 4s^\circ\ 3d^5$	5	$\sqrt{35}$
Fe^{+2}	$(Ar)\ 4s^\circ 3d^6$	4	$\sqrt{24}$
Cu^{+2}	$(Ar)\ 4s^\circ 3d^9$	1	$\sqrt{3}$

14. **(d)** e^- configuration of $Fe^{+3} = (Ar)\ 4s^\circ\ 3d^5$

It has unpaired e^- hence, it is a paramagnetic species.

15. **(b)** $Ag^+ = (Kr)\ 5s^\circ\ 4d^{10}$

$Cu^{+2} = (Ar)\ 4s^\circ\ 3d^9$

$Ga^{+3} = (Ar)\ 4s^\circ\ 3d^{10}\ 4p^\circ$

$Zn^{+2} = (Ar)\ 4s^\circ\ 3d^{10}$

16. **(c)** μ = 3.87 BM

Hence, number of unpaired e^- in $Mn^{x+} = 3$

$Mn = (Ar)\ 4s^\circ\ 3d^5$

$Mn^{4+} = (Ar)\ 4s^\circ\ 3d^3$

17. **(d)** The first element of a group generally belongs to second period. It has a small size, high ionization potential and electronegativity. It does not have d – orbitals.

18. **(d)** Oxides of Be and Al are amphoteric. They have almost similar electronegativity and polarizing power.

19. **(c)** Be and Al show diagonal relationship.

20. **(b)** Correct set of magic numbers for group VIA is 8,18,18,32.

21. **(a)** For a given series of isoelectronic species, as atomic number increases, radius decreases. $Se^{-2} > Br^- > Kr > Rb^+ > Sr^{+2}$

22. **(d)** Order of ionic radius is:

$Be^{+2} < Mg^{2+} < Ca^{2+} < Sr^{2+}$

23. **(c)** Their relative positions in periodic table,

C N (II period)

P S (III period)

The correct order of size is:

N < C < S < P

24. **(a)** Due to lanthanoid contraction Zr and Hf have almost similar atomic radii.

25. **(c)** As positive oxidation state increases, radius decreases.

+4	**+7**	**+2**	+3
MnO_2	$KMnO_4$	MnO	$K_3[Mn(CN)_6]$

26. **(c)** Down the group, ionization enthalpy decreases. It is due to increment in atomic size.

27. **(b)** Due to extra stability of the half filled p-orbitals, N has greater ionization potential than that of O.

28. **(d)** Order of ionization energy is:

$M^- < M^+ < M^{2+}$

M^{+2} has smallest size and highest effective nuclear charge.

29. **(b)** In IE_2 process, $1e^-$ is removed from $X^+(g)$

30. **(b)** Down the group, IE decreases. It is due to increment in atomic size.

31. **(b)** In lanthanide series, as atomic number increases, atomic radius gradually decreases It is called as lanthanide contraction.

32. **(d)** Electron affinity (EA) = - Δ e.g. (e^- gain enthalpy)

33. **(a)** Outermost sub shell of N is half filled. In process, $N \rightarrow N^-$, absorption of energy takes place.

34. **(b)** Second and successive electron gain enthalpy of an element is always positive because anions resist addition of another e^-.

35. **(d)** As and Sb are metalloids.

36. **(c)** In group VIIA (Halogens),

F_2 and $Cl_2 \rightarrow$ gas

$Br_2 \rightarrow$ liquid

$I_2 \rightarrow$ solid

37. **(c)** Halogens have highest electro negativity.

38. **(c)** percentage ionic character

$$= 16\,(\Delta EN) + 3.5\,(\Delta EN)^2$$
$$= 16\,(3.3) + 3.5\,(3.3)^2$$
$$= 90.9\ \%$$

39. **(a)** In halogens, bond length decreases from iodine to fluorine.

40. **(d)** Acidic strength of oxides and hydroxides $\propto$ Electro negativity of central atom

41. **(a)** Order of acidic strength:

$Al_2O_3 < B_2O_3 < CO_2 < NO_2$

42. **(b)** Neutral oxides are CO, NO, N_2O, H_2O

43. **(d)** $Al_2O_3 \longrightarrow$ Amphoteric

$B_2O_3 \longrightarrow$ Acidic

44. **(d)** In order of acidic strength:

$HCl > PH_3 > SiH_4 > CH_4$

45. **(d)** They all are acidic.

LEVEL II

1. **(d)** The elements 'X' is 'As'. Its electronic configuration is (Ar) $4s^2\ 3d^{10}\ 4p^3$.

2. **(c)** Bond length of H – F $= r_H + r_F - 0.09\,(\Delta EN)$

$$= 0.37 + 0.72 - 0.09\,(1.9)$$
$$= 0.92\ \text{Å}$$

3. **(b)** Order of ionic radius:

$I^- > Cl^-$

$Te^{2-} > I^-$ (They are isoelectronic)

4. **(d)** Due to inert pair effect the more common oxidation state for Tl, Pb and Bi are +1, +2 and +3 respectively.

5. **(b)** The relative positions of these elements in periodic table:-

Mg	P	Cl
Ca		

Order of atomic radius:-

Ca > Mg

Mg > P > Cl

6. **(b)** The element 'X' is 'Cu'. Its electronic configuration is (Ar) $4s^1\ 3d^{10}$. In third shell $18e^-$ and in fourth shell $1e^-$ is present.

7. **(c)** The electronic configuration of element is $3s^2\ 3p^6\ 3d^5\ 4s^2$. This element is 'Mn'.

8. **(c)** La and Ac belong to d - block

Element having atomic number 31 belongs to 4th period.

Elements after $_{92}U$ are man-made elements.

9. **(b)** $X(g) + E_1 \rightarrow X^+(g) + e^-$

$\left(\dfrac{A_0}{2}\text{ atoms}\right)$

$\dfrac{A_0}{2}$ atoms absorbs E_1 energy

So, 1 atom absorbs $\dfrac{2E_1}{A_0}$ energy

Hence, ionization energy of X(g) is $\dfrac{2E_1}{A_0}$

$X(g) + \dfrac{2E_1}{A_0} \rightarrow X^+(g) + e^-$...............eq (1)

$X^+(g) + 2e \rightarrow X^-(g) + E_2$

$\left(\dfrac{A_0}{2}\text{ ions}\right)$

$\dfrac{A_0}{2}$ ions release E_2 energy

So, 1 ion releases $\dfrac{2E_2}{A_0}$ energy

Hence, $\underset{\text{(1 ion)}}{X^+(g)} + 2e^- \rightarrow X^-(g) + \dfrac{2E_2}{A_0}$ ....eq(2)

Equation for electron affinity of X(g) is,

$X(g) + e^- \rightarrow X^-(g)$ + EA of X(g).

We can get this equation by adding equation (1) and (2),

$X(g) + e^- \rightarrow X^-(g) + \dfrac{2(E_2 - E_1)}{A_0}$

Hence, electron affinity of X(g) is $\dfrac{2(E_2 - E_1)}{A_0}$.

10. **(d)** In covalent hydrides, as we move left to right in a period acidic strength increases.

11. **(d)** In any period, noble gas has largest atomic radius because for noble gases vander waal's radius is considered.

12. **(d)** Acidic strength of Oxides $\propto$ Electronegativity of central atom.

CO_2 is more acidic than SiO_2 hence, option 'i' is incorrect.

13. **(b)** The elements having atomic number 113 belongs to group 13 and 7th period.

14. **(c)** The electronic configuration of Cr is (Ar) $3d^5\ 4s^1$ and it is a representative element. In HN_3, oxidation state of nitrogen is $-{}^1/_3$.

15. **(c)** The biggest jump in successive ionization energy is from IE_3 to IE_4. Hence, this element has 3 valence e^-.

16. **(d)** In s-block, all oxides are basic except BeO. BeO is an amphoteric oxide. They are obtained by the electrolysis of fused chlorides.

17. **(c)** Na^+ and F^- are isoelectronic but Na belongs to 3rd period while F belongs to 2nd period.

18. **(c)** The element (P) is Lu, which is a lanthanoid. All lanthanoids belong to the 3rd period.

19. **(b)** Ionic radius of Li^+ (0.76Å) is larger than that of Mg^{2+} (0.72Å).

20. **(c)** The bond having greater polarity (or, greater ΔEN) has greater chance of dissociation in water.

21. **(d)** The equation for second ionization energy of M is,

$M^+(g) \rightarrow M^{2+}(g) + e^-$

This equation will be obtained by (V)–(iii)

$$\begin{array}{l} M(g) \rightarrow M^{2+}(g) + 2e^- \\ -\,(M(g) \rightarrow M^+(g) + e^-) \\ \hline M^+(g) \rightarrow M^{+2} + e^- \end{array}$$

22. **(d)** EA_1 process is generally exothermic while EA_2 process is always endothermic. Hence, ΔH_1, ΔH_2 and ΔH_3 are negative whereas ΔH_4 is positive.

23. **(d)** As positive oxidation state increases, radius decreases.

24. **(c)** Completely filled sub-shell is more stable than half filled sub-shell.

25. **(a)** The biggest jump in successive ionization energy is from IE_3 to IE_4. Hence, the number of valence electron is 3.

26. **(d)** Due to lanthanoid contraction 5d-series elements have greater effective nuclear hence, they have higher ionization energy.

27. **(d)** IE_2 for an element is higher than IE_1 because after removal of 1st electron, 2nd electron is removed from the cation. The cation is smaller than its parent atom and it has greater effective nuclear charge (Z_{eff}) than its parent atom.

28. **(a)** Due to extra stability of half-filled p-subshell, elements of group 15 have higher IE than elements of group 16.

29. **(d)** Fluorine has small size, high electron density and an increased electronic repulsion.

30. **(c)** The order of radius is:

$$r_{\text{vander waal}} > r_{\text{metallic}} > r_{\text{covalent}}$$

31. **(c)** Z has biggest jump from IE_1 to IE_2 hence, it has 1 valence e^-.

32. **(c)** The order of radius is:

$Be > B > C > N > O$

33. **(a)** Elements A, B, C and D are Ne, O, Na and F respectively. Their correct order of EA is:

$Ne < Na < O < F$

34. **(d)** The first member of the lanthanoid series is Ce (cerium). Pricogens are group 15 elements.

35. **(b)** Smaller the value of IE, easier is the formation of cation. Larger the value of EA, easier is the formation of anoin.

Electronegativity on Mulliken's scale $= \dfrac{IE+EA}{2}$

$\text{Size} \propto \dfrac{1}{Z_{eff}}$

36. **(d)** For isoelectronic species, as atomic number increases radius decreases.

37. **(c)** The relative order of these elements in periodic table is:

			F	Ne
		P		
K	Ca			

The correct order of IE_1 is:

$K < Ca < P < F < Ne$

38. **(d)** The number of d-electrons in Fe^{2+} ($[Ar]\,4s^0 3d^6$) are 6.

p-electrons in Ne ($1s^2\,2s^2\,2p^6$) are 6.

s-electrons in Mg ($1s^2\,2s^2\,2p^6\,3s^2$) are 6.

d-electrons in Fe ($[Ar]\,4s^2 3d^6$) are 6.

p-electrons in Cl^- ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6$) are 12.

39. **(b)** $Ni^{+2} = [Ar]\,4s^0\,3d^8$ (2 unpaired electrons)

$Ni^{+4} = [Ar]\,4s^0\,3d^6$ (4 unpaired electrons)

40. **(c)** Magnetic moment = 1.73BM

The number of unpaired e^- = 1

$V = [Ar]\,4s^2\,3d^3$

$V^{+4} = [Ar]\,4s^\circ\,3d^1$

In VCl_4, oxidation state of 'V' is '+4'

41. **(d)** The correct order of radius is:

$F < O < F^- < O^{-2}$

42. **(c)** The correct trend of first ionization energy is:

$$B > Al < \underset{\substack{\uparrow \\ \text{Higher} \\ Z_{eff}}}{Ga} > In < \underset{\substack{\uparrow \\ \text{Higher} \\ Z_{eff}}}{Tl}$$

B > Tl > Ga > Al > In (Based on practical values)

43. **(d)** Cs^+ is largest cation and F^- is smallest anion hence, CsF has the lowest anion to cation size ratio.

44. **(d)** F is more electronegative than that of Cl^-. Anions are less electronegative than neutral atoms.

45. **(a)**

Elements	Atomic number
P	16
Q	17
R	18
S	19

The bond between S (alkali metals) and Q (halogens) will be most ionic (least covalent)

LEVEL III

1. (a, b, c) Value of ionization energy increases from left to right in a period.

Hence, alkali metals have lowest IE and noble gases have highest

IE in respective period.

Due to half filled outermost 2p-subshell, N has lower EA_1 than O

2. (a, d) If 'X' Mn then this e^- configuration represent cationic form X^+ (Mn^+)

If 'X' is 'Cr' then this e^- configuration represents ground state.

3.. (b, c, d) The correct order of IE_1 is:

$N > O > C > B$

The remaining orders are correct.

4. (b, c, d) The correct order of basic strength is:

$SbH_3 < AsH_3 < PH_3 < NH_3$

The remaining orders are correct.

5. (a, b, d) As positive charge increases, radius decreases. Hence, Cr^{+3} is larger than Cr^{+6}.

6. (a, b, d) Due to higher effective nuclear charge, Ga has greater first ionization enthalpy than Al.

7. (a, b) The correct orders of electron affinity are:

$N < C < O < F$

$P < Si < S < Cl$

8. (b, c) Down the group, electronegativity decreases. As we move from left to right in a period electronegativity increases.

9. (a, d) Due to poor shielding of nuclear charge by d or f-orbital electrons, 5d-series elements have greater elective nuclear charge.

10. (a, c, d) The correct order of ΔH_{eg}(With negative sign) is:

$Cl > F > Br > I$

The remaining orders are correct.

11. (a, b, c, d) $S^-(g) + e^- \rightarrow S^{2-}(g)$; EA_2 of S

$Ne\ (g) + e^- \rightarrow Ne^-(g)$; EA_1 of Ne

$N\ (g) + e^- \rightarrow N^-(g)$; EA_1 of N

$Al^{2+}(g) + e^- \rightarrow Al^{3+}(g)$; IE_3 of Al

These all steps are endothermic.

12. (c) $r_{\text{Van der Waal}} > r_{\text{Metallic}} > r_{\text{Covalent}}$

13. (b) In isoelectronic series, as atomic number increases, radius decreases.

14. (d) Both N^{3-} and Al^{3+} are isoelectronic. The correct order of radius is:

$N^{3-} > Al^{3+}$

15. (d) $Mn = \underbrace{1s^2\ 2s^2\ 2p^6}_{\text{Other}}\ \underbrace{3s^2\ 3p^6\ 3d^5}_{(n-1)}\ \underbrace{4s^2}_{ns}$

$\sigma = 1 \times 0.35 + 13 \times 0.85 + 10 \times 1$

$= 21.40$

16. (b) IE_1 of Ga > Al, due to imperfect shielding of 3d-orbitals in Ga.

17. (c) IE_1 of the group 2 elements is more than that of the group 3 elements.

18. (d) Order of the first ionization energy is:

$C < O < N < F$

19. (d) Relative positions of these elements in periodic table is:

Ga	Ge
In	Sn

Among these four elements, Ge has highest first ionization energy.

20. (b) Correct orders of ionization energy:

$Be > Sr$

$Be^+ > Sr^+$

$Be^+ > Be$

21. (a) Both N and P have stable half-filled p-orbitals in the outermost shell.

22. (a, b, c, d) $|\ EA_1\ | = |\Delta_{eg}H_1\ |$

Second period elements have lower EA_1 than third period elements.

23. (a, d) Noble gases have stable outermost shell e^- configuration hence, $\Delta_{eg}H_1$ of noble gases have large positive values.

24. Due to inert pair effect, the most stable oxidation stable of Tl is +1.

25. Order of ionization energy is:

$Li < Be > B < C < N > O < F < Ne$

26. B, S, P, At, H, Li

27. Cs, Ba, F, Zn, Be, Al, Sr

28.

$$\left.\begin{array}{l}\text{Li and Li}^+ \ (\text{Li} < \text{Li}^+) \\ \text{Ba and Sr (Ba} < \text{Sr)}\end{array}\right\} \text{Order of ionization energy}$$

29. a → r b → s c → p d → t

30. a → q, r b → p, s c → t d → r
e → u f → t

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **(a)** Acidic strength of oxides ∝ electronegativity of central atom.

2. **(b)** In isoelectronic species, as atomic number increases radius decreases.

3. **(b)** Down the group ionization potential decreases.

4. **(b)** Alkaline earth metals anion are unstable because they have fully filled outermost sub-shell.

5. **(a)** Acidic strength of oxides ∝ electronegativity of central atom.

6. **(c)** The lower oxidation states for the group 14 elements are more stable for the heavier members for the group due to inert pair effect.

7. **(b)** Relative positions of these elements in periodic table,

		S	Ar
Ca	Se		
Ba			

The correct order of increasing IE_1:

$Ba < Ca < Se < S < Ar$

8. **(a)** In lanthanoids, as atomic number increases radius decreases.

9. **(b)** In lanthanoids, as atomic number increases ionic radius decreases.

10. **(b)** The variation in properties of elements is related to their atomic numbers.

11. **(b)** It is due to lanthanoid contraction.

12. **(a)** N^{-3}, F^- and Na^+ all have 10 electrons.

13. **(a)** Electronic configuration of Cr is (Ar) $4s^1\ 3d^5$ after removal $1e^-$, next will be removed from half filled d-subshell.

14. **(c)** K^+, Ca^{+2}, Sc^{+3} and Cl^- all have 18 electrons.

15. **(a)** Correct order of radius:

$B^{3+} < Li^+ < F^- < O^{-2}$

16. **(d)** Acidic strength of oxides ∝ electronegativity of central atom.

17. **(a)** $O^-(g) + e^- \rightarrow O^{-2}(g)$. This process is endothermic because anion will tend to resist the addition of another electron.

18. **(a)** Due to very high hydration enthalpy of F^-, F_2 is strongest oxidizing halogen.

19. **(d)** H_3O^+, NH_3 and CH_3^- all have $10e^-$.

20. **(c)** The main cause of lanthanoid contraction is poor shielding by 4f electrons on outer electrons.

21. **(b)** The correct order of first ionization enthalpy:

$B < C < O < N$

22. **(c)** Due to lanthanoid contraction, 4d and 5d-series elements have almost similar radius.

23. **(a)** SnO_2 is an amphoteric oxide.

24. **(d)** The correct order of first ionization enthalpy:

$S < P$

$B < F$

25. **(c)** K^+, Cl^-, Ca^{+2} and Sc^{+3} all have 18 electrons.

26. **(b)** Cause of lanthanoid contraction is the imperfect shielding on outer electrons by 4f electrons from the nuclear charge.

27. **(b)** Order of reactivity in alkali metals:

$Li < Na < K < Rb < Cs$

Order of reactivity in halogens:

$F_2 > Cl_2 > Br_2 > I_2$

28. **(a)** The correct order of ionic radius is:

$Na^+ > Li^+$

$Li^+ > Mg^{+2}$

$Mg^{+2} > Be^{+2}$

29. **(d)** In isoelectronic species, as atomic number increases ionic radius decreases. The correct order of radius is:

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

30. **(d)** The electronic configuration of Gd (atomic number 64) is:

$[Xe]\ 6s^2\ 4f^7\ 5d^1$

31. **(b)** The correct order of negative e- gain enthalpy (electron affinity) is:

$Cl > F > Br > I$

32. **(a)** Basic strength of oxides $\propto \dfrac{1}{\text{Electronegativity of central atom}}$

33. **(c)** In isoelectronic species, as atomic number increases ionic radius decreases. The order of radius is:

$Ca^{2+} < K^{+} < Cl^{-} < S^{2-}$

34. **(d)** IE of M = IE_1 of M^+

C^+	N^+	O^+	F^+
$2p^1$	$2p^{\mathbf{2}}$	$2p^{\mathbf{3}}$	$2p^4$

The correct order of second ionization enthalpy is:

$C < N < F < O$

35. **(a)** The correct order of ionization enthalpy is:

$B < C < O < N$

36. **(c)** F-atom has smaller size and incoming e^- feels more repulsion from already present e^- in F-atom hence, electron gain enthalpy with negative sign (electron affinity) of fluorine is less than that of chlorine.

37. **(d)** The relative position of elements in periodic table is:

	O
	S
As	Se

The correct order of atomic radius is:

$O < S < Se < As$

38. **(c)** The relative position of elements in periodic table is:

	Se	Ar
Ca	Se	
Ba		

The correct order of first ionization enthalpy is:

$Ba < Ca < Se < S < Ar$

39. **(b)** $Na\,(g) + 5.1\,ev \rightarrow Na^+\,(g) + e^-$

$Na^+\,(g) + e^- \rightarrow Na + 5.1\,ev;\ \Delta H_{eg} = -5.1\,ev$

(e^- gain enthalpy)

40. **(d)** All elements in a group have similar number of valence electrons.

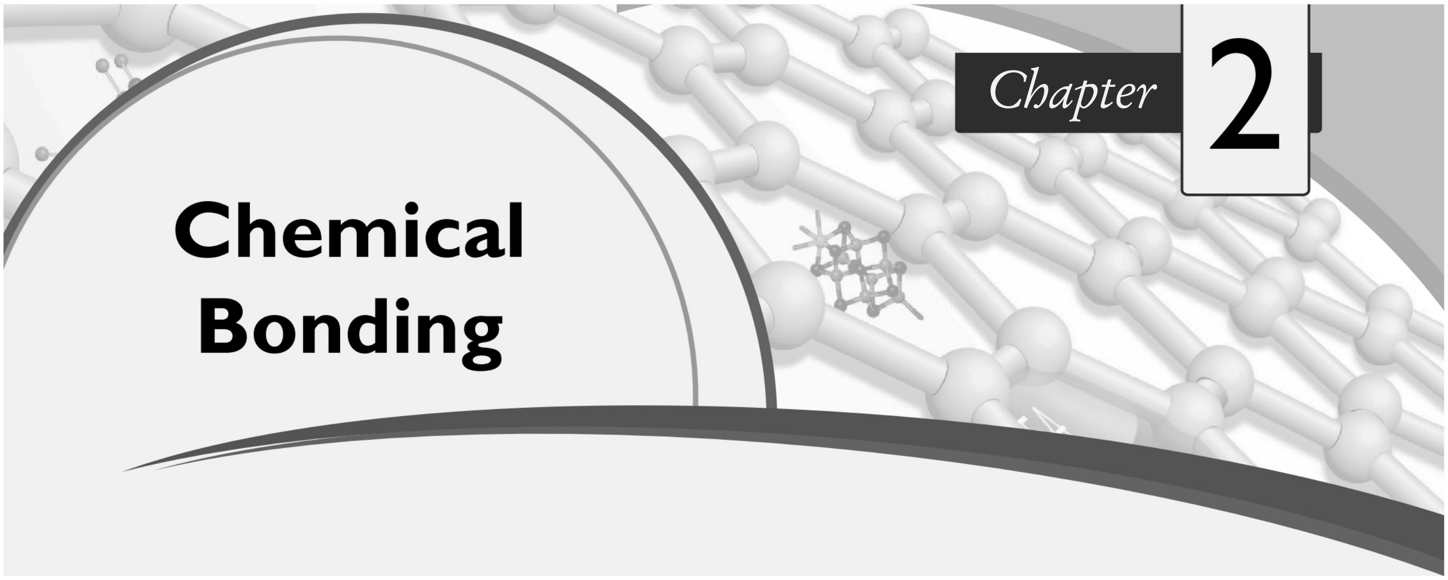
41. **(a)** P^{-3} and S^{-2} are isoelectronic hence, their order of radius is $S^{-2} < P^{-3}$

42. **(c)** N^{-3}, O^{-2} and F^- are isoelectronic hence, their order of radius is

$$\underset{(1.71\,\text{Å})}{N^{-3}} > \underset{(1.40\,\text{Å})}{O^{-2}} > \underset{(1.36\text{Å})}{F^-}$$

43. **(c)** Order of first ionization energy is:

$Sc > Na > K > Rb$



Chapter 2

Chemical Bonding

Key Concepts

INTRODUCTION

The formation of a chemical bond between two atoms implies that the system consisting of these two atoms at stable internuclear distance is energetically more stable than the two isolated atoms. A general study on the reactivity of different elements revealed that noble gases have little tendency to combine with other elements. This leads to the fact that the noble gases have stable outer configuration $(ns)^2$ $(np)^6$ (octet configuration). All other atoms combine to achieve the stable octet configuration either by mutual sharing of electrons (covalent bond) or by complete transfer of electron(s) from one atom to other (ionic bond).

KÖSSEL AND LEWIS THEORY OF CHEMICAL COMBINATION

According to this theory, atoms can combine either by transfer of outer-shell electrons, known as valence electrons, from one atom to another or by sharing the valence electron(s) in order to achieve octet configuration (i.e., a total of eight electrons) in their respective valence shells.

The sharing of electron(s) leads to the formation of covalent bond while transferring of electron(s) leads to the formation of ionic bond between the two involved atoms.

REPRESENTATION OF A BOND BY LEWIS STRUCTURE

In Lewis structure, a bond between the two atoms is shown by Lewis electron-dot symbols in which valence electrons are shown by dots around the letter symbol of the atom. The dots are placed as follows.

Place a single dot on the four sides of the letter symbol followed by the second dot till all the valence-electrons have been accounted for.

Illustrations:

Lithium $(2s^1)$	$\overset{\cdot}{\text{Li}}$	Beryllium $(2s)^2$	$\cdot\ \text{Be}\ \cdot$
Boron $(2s)^2(2p)^1$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{B}}}$	Carbon $(2s)^2(2p)^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot$
Nitrogen $(2s)^2(2p)^3$	$:\overset{\cdot}{\underset{\cdot}{\text{N}}}\cdot$	Oxygen $(2s)^2(2p)^4$	$:\overset{\cdot}{\underset{\cdot}{\text{O}}}:$
Fluorine $(2s)^2(2p)^5$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}\cdot$	Neon $(2s)^2(2p)^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Ne}}}:$

FORMATION OF COVALENT BOND(S)

A covalent bond involves mutual sharing of valence electrons between two atoms. The sharing of two, four and six electron leads to the formation of a single, double and triple bond, respectively.

A covalent bond is formed if the atoms have lesser number of valence electrons as compared to the nearby noble gas which has octet configuration. Such elements are known as electronegative elements. Thus, the criterion of the formation of covalent bond is:

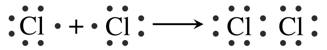
$$\text{Electronegative element + Electronegative element} \longrightarrow \text{Covalent bond}$$

Exception to the octet rule is the hydrogen atom which can accommodate only two electrons which corresponds to the electronic configuration of nearby helium ($1s^2$) atom.

Illustrations:

Formation of Single Bond(s)

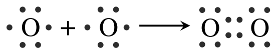
Cl_2



or Cl – Cl

Formation of Double Bond(s)

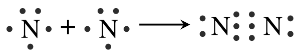
O_2



or O = O

Formation of Triple Bond(s)

N_2



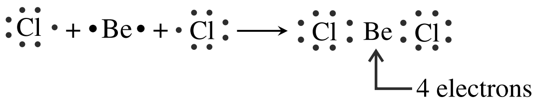
or N ≡ N

EXCEPTIONS TO THE OCTET RULE

The octet rule is generally obeyed by the elements of second and third periods with the following exceptions:-

The Incomplete Octet

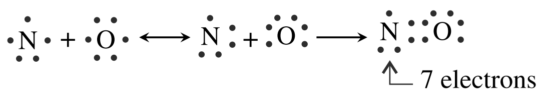
$BeCl_2$



Odd-Electron Molecules

All atoms of a compound containing odd number of electrons will not satisfy octet rule as even number of electrons are required for pairing of electrons.

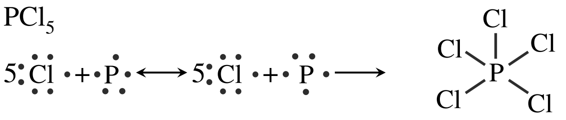
NO



The Expanded Octet

Elements of third period and beyond can accommodate more than 8 electrons due to the availability of vacant d orbitals.

PCl_5

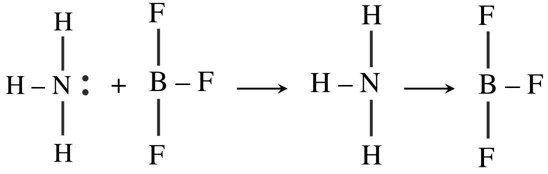


(P has 10 electrons)

COORDINATE COVELENT (OR DATIVE) BOND

If a pair of electrtons shared between two atoms comes exclusively form one of the atoms, the bond formed is said to be a coordinate covelent (or dative) bond. To keep track of electrons, a coordinate covalent bond may be represented by an arrow (⟶). Once a coordinate bond is formed, it behaves like a covalent bond.

$H_3N - BF_3$



Writing a Lewis Structure

The structure of a molecule or ion may be written by following the steps listed below:

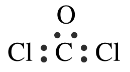
1. Calculate the total number of valence electrons of the atoms in the molecule. For an anion, add the number of negative charges and for a cation, subtract the number of positive charges.
2. Write the skeleton structure of the molecule or ion connecting every bonded pair of atoms by a single bond, i.e., a pair of electron dots.
3. Assign a total of eight electrons in each atom (except hydrogen) surrounding the central atom.
4. Distribute the remaining electrons (if any) as pairs to the central atom.

If there are fewer than eight electrons on the central atom, move one or two pairs of electron from a surrounding atom to form double or triple bond between the two atom. Atoms that often form multiple bond are C, N, O and S.

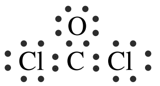
Lewis structure of $COCl_2$

Step 1 Valence electrons are 4 + 6 + 2 × 7 = 24

Step 2 Carbon being the most electropositive atoms occupies the central position to which other atoms are bonded.

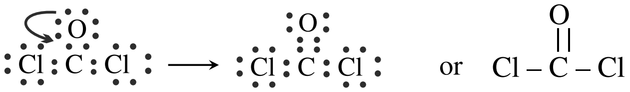


Step 3 Assign 8 electrons each to surrounding atoms



Step 4 There were 24 valence electrons and all of them have been distribuled. However, the central C atom has only 6 electrons. In order that this atom also has 8 electrons, move one pair of elctrons

from O to the bond connecting C atom, thus forming a double bond.



FORMAL CHARGE AND LEWIS STRUCTURE

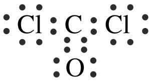
The formal charge an atom is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atoms in a Lewis structure. The equation for computing formal charge is,

$$\text{Formal charge} = \text{Valence electrons on free atom} - \text{Number of (Nonbonding} + \frac{1}{2}\text{ bonding) electrons in a Lewis structure}$$

The sum of the formal charges of atoms in a Lewis structure is equal to the charge on the molecular species.

Illustration

$COCl_2$ molecule Lewis structure



Atom	Valence electrons in a free atom	Electrons in Lewis structure		Formal Charge
		Non-boding	Bonding	
Cl	7	6	2	$7-(6+\frac{1}{2}\times 2)=0$
O	6	4	4	$6-(4+\frac{1}{2}\times 4)=0$
C	4	0	8	$4-(0+\frac{1}{2}\times 8)=0$

UTILITY OF FORMAL CHARGE

Computing formal charge of atoms in a molecule or ion helps deciding a possible Lewis structure of the species. The guiding principles are as follows:

- Amongst the several Lewis structures, the species having the lowest magnitude of formal charge is the preferred structure.
- Amongst Lewis structures having similar distribution of formal charges, the one having negative formal charges one the more elecronegative atoms is the preferred structure.

POLAR COVALENT BOND

Each atom in a molecule has its own ability to attract the bonded pair of electrons. This ability is known as electronegativity. The bonded pair of electrons in homonuclear diatomic molecules (such as H_2, O_2, F_2, Cl_2, etc.) is shared equally by both atoms. This is not correct in the case of heteronuclear diatomic molecules (such as HCl, HF, NO, etc.) The bonded pair of electrons is closer to the atom having larger electronegativity. Consequently, this atom acquires a partial negative charge while the other atom acquires equal partial positive charge. Because of the charge separation, the covalent bond between these two atoms is said to be a polar covalent bond.

DIPOLE MOMENT

The polarization of bonded pair of electrons between two atoms is expressed in terms of physical quantity known as dipole moment (symbol : μ). It is defined as

$$\mu = (\delta q)\,(r)$$

where δq is the partial charge separation between two atoms and r is the distance between the two atoms.

Representation of Dipole Moment

Dipole moment is a vector quantity, i.e., it has magnitude as well as direction. In chemistry, dipole moment is indicated by the crossed arrow as shown in the following.

$$\text{positive end} \longmapsto \text{negative end}$$

that is, it is directed from positive end to the negative end.

Unit of Dipole Moment

In SI system, unit of dipole moment = (unit of δq) (unit of *r*) = Cm

In CGS system, unit of dipole moment = (esu) (cm)

Most molecules have dipole moment of the order of 10^{-18} esu cm. This value of dipole moment is known as 1 debye (written as 1 D).

$$1\text{D} = 10^{-18}\text{ esu cm} = (10^{-18})\left\{(1\text{esu})\left(\frac{1.6\times 10^{-19}\text{C}}{4.8\times 10^{-10}\text{esu}}\right)\right\}$$

$$(10^{-2}\text{ m}) = 3.33\times 10^{-30}\text{ cm}$$

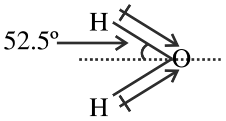
DIPOLE MOMENT OF A POLYATOMIC MOLECULE

Each bond in a molecule has a dipole moment, known as bond moment. The dipole moment of a molecule is obtained by the vector addition of these bond moments.

Illustration

The bond moment of O – H bond is 1.52 D. The bond angle of H_2O is 105°. The dipole moment of H_2O molecule will be

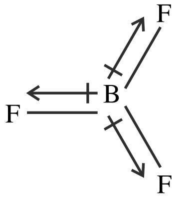
$$\mu_{H_2O} = 2\mu_{OH} \cos(105°/2) = 2\,(1.52\text{ D})\,(0.609) = 1.85\text{ D}$$

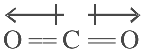


NONPOLAR POLYATOMIC MOLECULE

The dipole moment of a nonpolar polyatomic molecule is zero inspite of the fact that the bond moments of the molecule is not zero. This is due to the fact that the individual bond moments in the molecule is symmetrically placed so that their vector additions is zero.

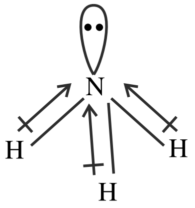
Illustration:

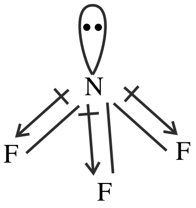




COMPARISON OF DIPOLE MOMENTS OF NH_3 AND NF_3

Both NH_3 and NF_3 have pyramdial shapes with lone pair of electrons on nitrogen atom.





In NH_3, orbital dipole acts in the same direction as the sum of bond vectors of the three N – H bond bonds. In NF_3, orbital dipole acts in the opposite direction to the sum of bond vectors of the three N – F bond bonds. These facts make the dipole moment of NH_3 (μ = 1.57 D) larger than that of NH_3 (μ = 0.24 D).

PERCENT IONIC CHARACTER OF A POLAR BOND

The percent ionic character of a polar bond A – B is defined as:

$$\text{Percent ionic character} = \frac{\mu_{AB}}{\mu_{ionic}} \times 100$$

where μ_{ionic} = (e r_{AB}) corresponds to 100% ionic character of the bond.

Illustration:

The bond moment of O – H bond is 1.52 D. If bond length O – H is 95 pm, its percent ionic character will be

$$\text{Percent ionic character} = \frac{\mu_{OH}}{e\,r_{OH}} \times 100$$

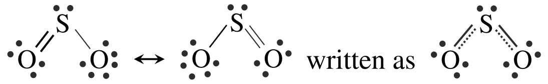
$$= \frac{(1.52\text{D})(3.33\times10^{-30}\text{ Cm / 1D})}{(1.6\times10^{-19}\text{ C})(95\times10^{-12}\text{ m})} \times 100$$

$$= 33.3\ \%$$

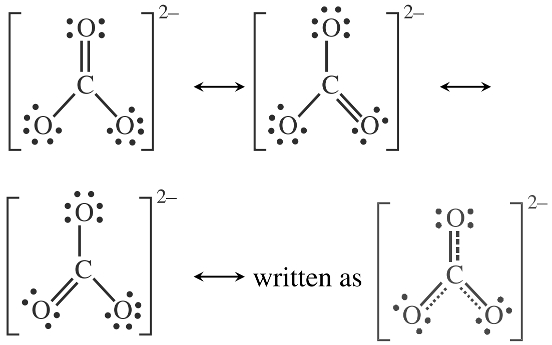
CONCEPT OF RESONANCE

Sometimes, one can write more than one equivalent Lewis structures differing in the distribution if electrons over a given skeleton of atoms in a molecule. None of the individual structures adequately explains the characteristics of the molecule. However, these can be explained if the actual structure of the molecule is considered as the superposition of individual structures. This phenomenon is known as resonance and the individual structures are known as resonating structures. It is represented by a double-headed arrow (↔) inserted between the resonating structures.

Illustrations:

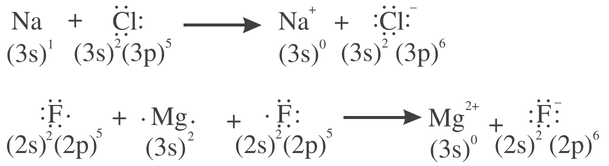


The resonance hybrid of the two Lewis structures makes both the S – O bond lengths equal in size.



FORMATION OF AN IONIC BOND

The transfer of valence electron(s) from one atom of an element to the valence shell of the atom of some other element leads to the formation of positive and negative ions, respectively. The electrostatic attraction between the positive and negative ions results in the formation of an ionic bond between the involved ions.



$$\underset{(3s)^1}{Na} + \underset{(3s)^2(3p)^5}{\ddot{\underset{..}{Cl}}:} \longrightarrow \underset{(3s)^0}{Na^+} + \underset{(3s)^2(3p)^6}{:\ddot{\underset{..}{Cl}}:^-}$$

$$\underset{(2s)^2(2p)^5}{:\ddot{\underset{..}{F}}\cdot} + \underset{(3s)^2}{\cdot Mg \cdot} + \underset{(2s)^2(2p)^5}{\cdot\ddot{\underset{..}{F}}:} \longrightarrow \underset{(3s)^0}{Mg^{2+}} + \underset{(2s)^2(2p)^6}{:\ddot{\underset{..}{F}}:^-}$$

Energies Involved in the Formation of One Molecule of Sodium Chloride

The formation of $Na^+Cl^-(g)$ from Na(g) and Cl(g) involves the following steps.

(i) $Na(g) \longrightarrow Na^+(g) + e^-$ $\quad E_i = 8.24 \times 10^{-19}$ J

(ii) $Cl(g) + e^- \longrightarrow Cl^-(g)$ $\quad E_{ea} = -5.78 \times 10^{-19}$ J

(iii) $Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(g)$ $\quad$ PE

where PE is the potental energy in the formation of ionic bond. This is evaluated by the expression

$$PE = \frac{Q_1Q_2}{(4\pi\varepsilon_0)r}$$

where $Q_1 = Q_2 = 1.60 \times 10^{-19}$C and $r = r_{Na^+} + r_{Cl^-} = 95$ pm + 181 pm = 276 pm. Considering Q_1 and Q_2 as point charges, we have

$$PE = \frac{(1.60\times10^{-19}\,C)(-1.60\times10^{-19}\,C)}{(4)(3.14)(8.854\times10^{-12}\,C^2N^{-1}m^{-2})(276\times10^{-22})}$$

$$= -8.34\times10^{-19} J$$

Hence, for the reaction $Na(g) + Cl(g) \longrightarrow Na^+Cl^-(g)$

$$\begin{aligned} \text{we have } \Delta E &= E_1 + \Delta E_{ea} + PE \\ &= (8.24 - 5.78 - 8.34) \times 10^{-19}\ J \\ &= -5.88 \times 10^{-19}\ J \end{aligned}$$

Comment: The negative value of ΔE indicates that the formation of an isolated ionic bond $Na^+Cl^-(g)$ is feasible as the combination is energetically more stable than Na(g) and Cl(g) taken together.

Essential Requirement for the formation of an ionic bond: For ΔE in Equation (3) to be negative, we must have

(i) Low value of E_i. This is shown by electropositive element(s).

(ii) High value of E_{ea}. This is shown by electronegative element(s).

Hence

$$\underset{\text{element}}{\text{Electropositive}} + \underset{\text{element}}{\text{Electronegative}} \longrightarrow \underset{\text{Bond}}{\text{Ionic}}$$

(eg, elements of Gp.1) (eg, elements of Gp. 17)

Formation of 1 mol of Solid Ionic Compound from Constituent Elements

Taking an example of sodium chloride, we have the following steps in the formation of solid compound.

(i) $Na(s) \rightarrow Na(g)$ $\quad \Delta H_1 = 108$ kJ mol^{-1}

(ii) $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\quad \Delta H_2 = 120$ kJ mol^{-1}

(iii) $Na(g) \rightarrow Na^+(g) + e^-$ $\quad \Delta H_3 = 496$ kJ mol^{-1}

(iv) $Cl(g) + e^- \rightarrow Cl^-(g)$ $\quad \Delta H_4 = -349$ kJ mol^{-1}

$$\text{(v)}\quad \begin{array}{ll} Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s) & \Delta H_5 = -788\,kJ\,mol^{-1} \\ \hline Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+Cl(s) & \Delta H = -313\,kJ\,mol^{-1} \end{array}$$

Since ΔH is negative, the formation of solid NaCl is energetically favorable. From the values of ΔH's listed above, it is obvious that the step (v) is the most favourable step since its highly exothermic nature counter acts the endothermic steps (i) to (iii).

The enthalpy involved in the reversal of step (v), i.e., $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ is known as lattice energy of the ionic solid.

By definition, lattice energy of an ionic solid is the energy required to completely separate one mole of solid ionic compound into gaseous constituent ions. Larger the value of lattice energy, more stable the ionic compound.

The lattice energy is determined indirectly through the use of Born-Haber cycle. The latter involves the steps (i) to (v) listed above for the formation of solid ionic compound. In this cycle, ΔH is determined experimentally. Subtraction of ΔH_1, ΔH_2, ΔH_3 and ΔH_4 from the value of ΔH gives the value of ΔH_5. The lattice energy is negative of the value of ΔH_5.

Fajan Rules: An ionic compound has partial covalent character and vice versa. The partial covalency in an ionic compound my be explained qualitatively with the help of Fajan rules described in the following.

High charge and small size of the cation: Such an ion will exert a greater effect in polarizing anions causing cationic electronic charge to penetrate partially into the anionic electronic cloud resulting into the partial covalent bond character to the ionic bond.

High charge and large size of the anion: The elecronic cloud of such an anion is most easily polarized by the cation because the anionic charge cloud is less influenced by the nuclear charge of the anion.

Electron configuration of the cation: For two cations of the same size and charge, the cations of electronic configuration $(n-1)d^xns^0$ (i.e., transition metal ions) have more polarizing power than the cation of electronic configuration (n – 1)s^2(n–1)p^6 ns^0 (i.e., alkali and alkaline earth metal ions). This is due to less shielding of nucleus by the electronic cloud of transition metal ions as compared to that in the alkali and alkaline metal ions.

Hg^{2+} ion has larger polarizing effect than Ca^{2+} ion. Lithium salts have more covalent chracter than the alkali salts. I^- ion is more easily polarized than Cl^- ion by Ag^+ ion.

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The covalent-bonded molecules have definite shapes which cannot be accounted for by Lewis structures.

A simple theory, known as VSEPR theory, was proposed by Sidgwick and Powell in 1940 and was developed and refined by Nyholm and Gillespie in 1957. The guiding rules of this theory are as follows.

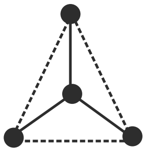
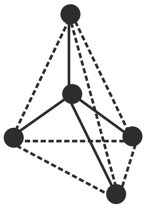
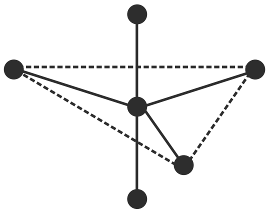
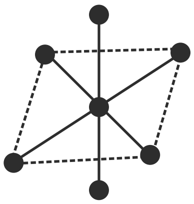
The number of electrons pairs in the valence shell of the central atom of a molecule decides the shape of the molecule. These pairs of electrons occupy the specific positions so as to minimize the mutual electronic repulsion. A multiple bond is treated as if it is a single electron pair.

The repulsive interaction of electron pairs decrease in the order

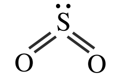
Lone pair (lp) - Lone pair (lp) > Lone pair (lp) - Bond pair (bp) > Bond pair (bp) > Bond pair (bp)

The shapes of molecules as predicted by VSEPR theory are shown in Table.

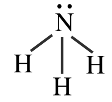
Shapes of some molecules on the basis of VSEPR model

Molecules	Number of valence				Basic shape
	Electrons around the central atom	**Electron pairs**	**Bonding pairs**	**Lone pairs**	
(i) $BeCl_2$	4	2	2	0	Linear 
(ii) BCl_3	6	3	3	0	Triangular planar 
(iii) CH_4 NH_3 H_2O	8 8 8	4 4 4	4 3 2	0 1 2	Tetrahedron 
(iv) PF_4 SF_4 CIF_3	10 10 10	5 5 5	5 4 3	0 1 2	Trigonal bypramid 
(iv) SF_4 IF_5	12 12	6 6	6 5	0 1	Octahedron 

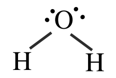
A few examples of molecules containing lone pair electrons along with their geometry are described in the following



Shape : Bent
Bond angle : 109.5°



Shape : Trigonal pyrmidal
Bond angle : 107°



Shape : Bent
Bond angle : 104.5°

VALENCE BOND THEORY

The quantitative description of chemical bond is provided by the quantum mechanical theories. Two theories, namely, valence bond (VB) and molecular orbital (MO) have been developed.

The essential guidelines of VB method are as follows.

(i) A molecule is considered to be a collection of atoms with electrons occupying their respective atomic orbitals.

(ii) The formation of molecule is analysed in terms of interactions amongst electrons-electrons, electrons-nuclei and nuclei-nuclei.

(iii) For a molecule to be stable, the electrostatic attractions must predominate over the electrostatic repulsion. The difference in these two is released in the form of heat. Thus, a molecule is energetically more stable than the individual atoms.

Electron associated with atom H_A can go to the atom H_B and vice versa through the overlap region. Also in the overlap region, there will be some probability of finding both the electrons and thus according to Pauli's exclusion principle, these two electrons must have opposite spins.

STABILITY OF THE MOLECULE

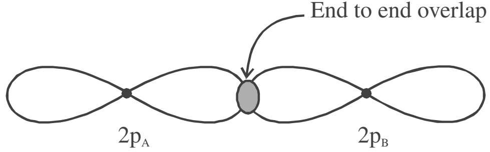
The intervening electronic charge between the two nulcei has an affect of decreasing nuclear repulsion and maximises electron-nuclei attractions. This lead to the stale H_2 molecule.

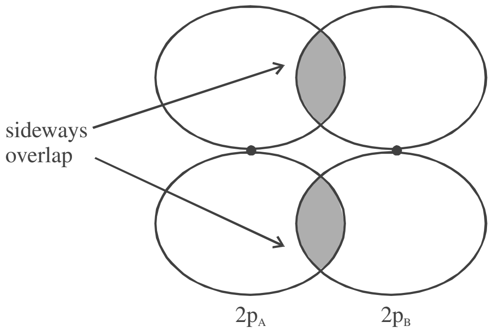
SIGMA AND PI BONDS

In a molecule, two of overlapping of orbitals having directional chracteristics may be distinguished.

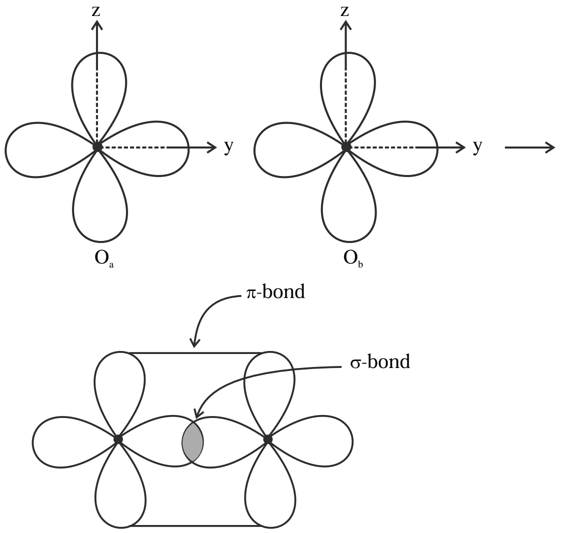
End to End Overlap - Sigma Bond (σ Bond): In this overlapping, the electronic charge is concentrated between the nuclei of bonding atoms.

Sideways Overlap - Pi Bond (π Bond): In this overlapping, the electronic charge is concentrated above the plane of nuclei of the bonding atoms.

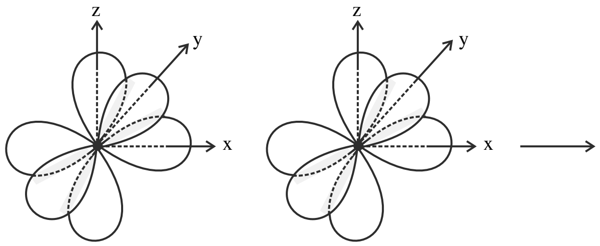


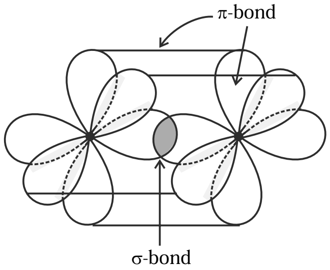


Oxygen molecule: The electronic configuration of oxygen atom is $(1s)^2\ (2s)^2\ (2p_x)\ ^2(2p_y)^1\ (2p_z)\ ^1$. There are two 2p atomic orbital, each containing one electron. Thus it can form two bonds — σ and π bonds.



Nitrogen molecule: The electronic configuration of nitrogen atom is $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$. There are three 2p orbitals, each containing one electron. Thus it can form three bonds—one σ and two π-bonds.





THE CONCEPT OF HYBRIDISATION

According to the valence bond theory,

$_4Be$ ($1s^2$, $2s^2$)	Should form no chemical bond as it does not contain any unpaired electron.
$_5B$ ($1s^2$, $2s^2$, $2p^1$)	Should form a single bond as it contains only one unpaired electron.
$_6C$ ($1s^2$, $2s^2$, $2p_x{}^1$, $2p^1{}_y$)	Should form two bond as it contains two unpaired electron.

Experimentally it is found that Be is divalent, B is trivalent and C is tetravalent.

To explain this, the concept of hybridisation is introduced. In this concept we have,

Two or more atomic orbitals of the same atom mix each other to provide a new set of indentical number of degenerate orbitals. These orbitals, known as hybrid orbitals, are completely identical in size, shape and orientations.

sp^3 Hybridisation: In sp^3 (pronounced as 's-p three') hybridisation, one s orbital and three p orbitals of the same valence shell of an atom combine to give four degenerate equivalent sp^3 hybrid orbitals. These four orbitals are directed towards the four corners of a regular tetrahedron making an angle of 109°28' with respect to each other.

HYBRID ORBITALS INVOLVING D ORBITALS

Three main hybridisation involving d orbitals are as follows :

sp^2d or dsp^2 Hybridisation: The resultant four hybrid orbital lie in a plane with bond angle of 90° with respect to each other.

In dsp^2, d orbital belongs to penultimate shell while in sp^2d, it belong to the valence shell.

sp^3d or dsp^3 Hybridisation: The resultant five hybrid orbitals are directed to the corners of trigonal bipyramid three are in the same plane making an angle 120° with each other, fourth and fifth are directed perpendicular to the plane (one above and the other below).

sp^3d^2 or d^3sp^3 Hybridisation: The resultant six hybrid orbitals are directed to the corners of regular octahedron four are in the same plane making an angle 90° with each other, fifth and sixth are directed perpendicular to the plane (one above and the other below).

sp^3d^3 or d^3sp^3 Hybridisation: The resultant seven orbitals are directed to the corners of a regular pentagonal bipyrimide five are in the same plane and sixth and seventh are directed perpendicular to the plane (one above and the other below).

MOLECULAR ORBITAL THEORY

Molecular orbital theory provides the explanation for the formation of bond in a molecule on the lines very similar to those of atomic orbitals. The essential guidelines of this theory are as follows.

Like atomic orbitals in an atom, there exists molecular orbitals in a molecule. The only difference is that an atomic orbital is a monocentric (i.e., exists around a single nucleus) while a molecular orbitals is a polycentric (i.e., exists around more than one nucleus and thus belongs to the molecule as a whole).

Each molecular orbitals in a molecule describes different electronic behaviour and has a fixed energy.

Electrons in a molecule occupy molecular orbitals in accordance with aufbau principle, Pauli's exclusion principle and Hund's rule.

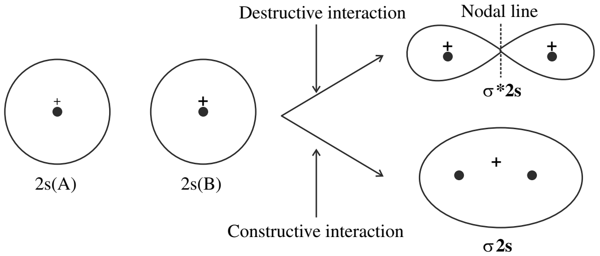
The square of molecular orbital (which a mathematical expression) evaluated at a point around the nuclei of the molecule gives the probability of finding electron at that point.

The shape of a molecular orbital is the region around the nuclei where there exists 90–95% probability of finding the electron.

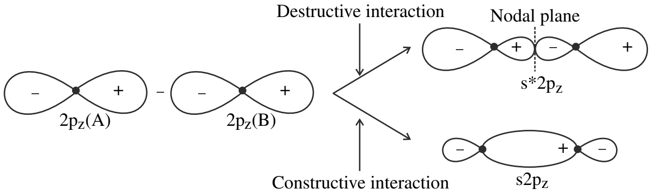
Designation of Molecular orbital: The designation of a molecular orbital starts by starting its σ or π nature followed by the atomic orbitals into which it separates at larger distance. The antibonding orbital is designated by placing an asterisk on the symbol σ or π.

The effective combinations of atomic orbitals of atoms A and B are as follows:

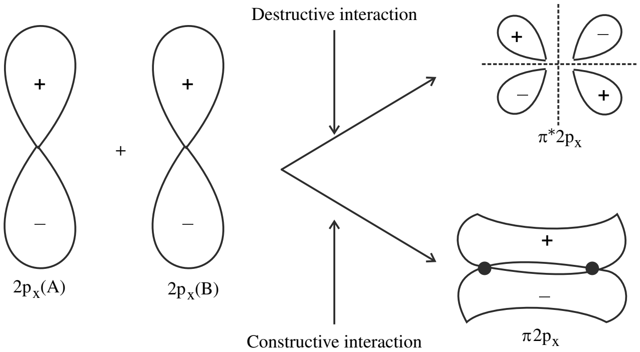
1. Combination Involving 2s(A) and 2s(B)



2. Combination Involving $2s_z$(A) and $2p_z$(B)



3. Combination Involving $2p_x$(A) and $2p_x$(B)

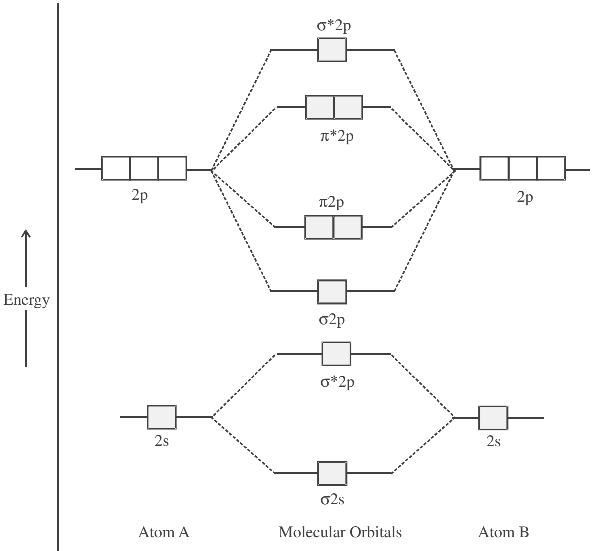


4. Combination Involving $2p_y$(A) and $2p_y$(B)

The molecular orbitals formed are similar to $\pi 2p_x$ and $\pi^* 2p_x$ in the direction of y-axis.

Relative Energies of Molecular Orbitals correlation

Diagram displays the correlation diagram expected for the orbitals of atoms of second period. In this diagram, $E(\sigma 2p) < E(\pi 2p)$ since the end-to-end overlap 2p orbitals is expected to be larger than side-ways overlap.



Correlation diagram for O_2 and F_2

The correlation diagram shown in figure 30 is found to be applicable only for O_2 and F_2 molecules.

The relative energies of molecular orbitals is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

For the molecules Li_2 to N_2, the energies difference in 2s(A) and 2p(A) is not large and thus these two orbitals jointly combine with the orbitals jointly combine with the orbitals 2s(B) and 2p(B). The resultant correlation is modified and is known in figure. The noteable modification is that

$$E(\sigma 2p) > E(\pi 2p)$$

The relative energies of molecular orbitals is

$$\sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

ELECTRONIC STRUCTURE AND MOLECULAR CHARACTERISTICS

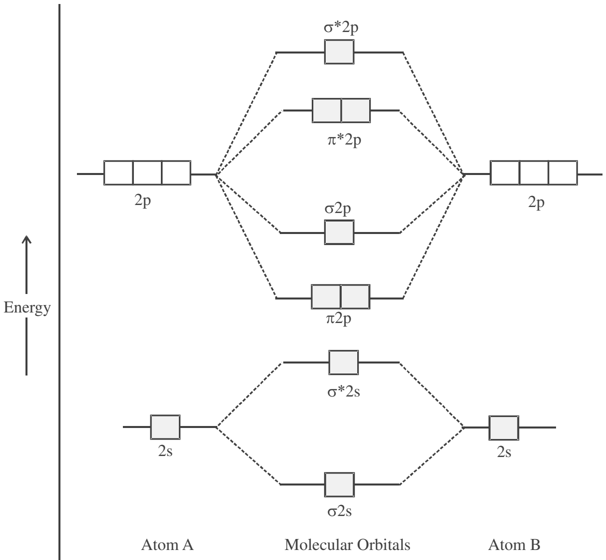
The following guidelines are helpful in describing molecular characteristics.

1. The valence electrons are distributed among he molecular orbitals in accordance with aufbau principle, Pauli's exclusion principle, and Hund's rule.

   Aufbau principle: Moleular orbitals are filled in the increasing order of energy.

   Pauli exclusion principle: No more than two electrons can occupy a single molecular orbital. The two electrons have opposite spins.

   Hund's rule: The degenerate orbitals are singly occupied by electrons with parallel spins followed by double occupancy.



Correlation diagram for Li_2 to H_2 and F_2

2. The number of bonds in a molecule is defined by a physical quantity, known as bond order. It is defined as one half of the net excess of bonding electrons, i.e.,

$$\text{Bondorder} = \frac{\text{Number of (bonding} - \text{antibonding) electrons}}{2}$$

3. The strength of a bond depends on the bond order of the molecule. The larger the bond order, the stronger the bond, the larger the dissociation energy of the molecule.

4. Addition of an electron in the bonding orbital or removal of an electron form the antibonding orbital increases bond order and hence increases stability of a molecule.

5. Removal of an electron form a bonding orbital or addition of an electron in the antibonding orbital decreases bond order and hence decreases stability of a molecule.

6. Paramagnetism in a substance is due to the presence of unpaired electrons in the molecules.

Solved Examples

1. An element (X) forms compounds of the formula XCl_3, X_2O_5 and Ca_3X_2 but does not form XCl_5. Which of the following is the element(X)?

(a) B (b) Al

(c) N (d) P

Sol.(c) 'N' can form NCl_3, N_2O_5 and Ca_3N_2 but can not form NCl_5. Due to absence of d – orbital's, 'N' can not expand its valency to 5.

2. Which of the following anions can not be formed by boron?

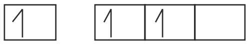
(a) BF_6^{3-} (b) BH_4^-

(c) $B(OH)_4^-$ (d) BO_2^-

Sol.(a) Any second period element can form maximum 4 bonds (covalent and co-ordinate). After formation of 3 covalent bonds, 'B' can form only one co-ordinate bond because it has only one vacant orbital.

2S 2P

B(I excitation)



3. Which of the following would result in the formation of strongest π- bond if the molecular axis is x – axis?

(a) $2p_x + 2p_x$ (b) $2p_y + 2p_y$

(c) $2p_y + 3d_{xy}$ (d) $2p_z + 4p_z$

Sol.(b) $2p_x + 2p_x$ will form σ – bond

$2p_y+2p_y$ and $2p_x+3d_{xy}$ will form π-bond but $2p\pi + 2p\pi$ bond is stronger than $2p\pi + 3d\pi$

4. Which of the following statement is wrong?

(a) d – orbital taking part in dsp^2 is $d_{X^2-Y^2}$

(b) d – orbital taking part in sp^3d is d_{XY}

(c) d – orbital taking part in sp^3d^2 are $d_{X^2-Y^2}$ and d_{Z^2}

(d) d – orbital taking part in sp^3d^3 are d_{XY}, d_{Z^2} and $d_{X^2-Y^2}$

Sol.(b) dsp^2 $(s + p_X + p_Y + d_{X^2-Y^2})$

sp^3d $(s + p_X + p_Y)$ $(p_Z + d_{Z^2})$

sp^3d^2 $(s + p_X + p_Y + d_{X^2-Y^2})$ $(p_Z + d_{Z^2})$

sp^3d^3 $(s + p_X + p_Y + d_{XY} + d_{X^2-Y^2})$ $(p_Z + d_{Z^2})$

5. Which of the following set is not correct?

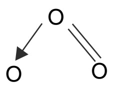
(a) N_2O, O_3, NH_4^+ all have co – ordinate bonds.

(b) H_2O, NO_2, ClO_2 all are 'V' shape molecules.

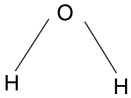
(c) I_3^-, ICl_2^-, NO_2^+ all are linear molecules.

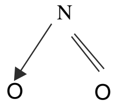
(d) SF_4, SiF_4, XeF_4 all are tetrahedral in shape.

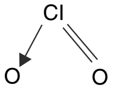
Sol.(d) $N \equiv N \rightarrow O$



$H_3N \rightarrow H^+$ (all have co– ordinate bond)







('V' shape)

I_3^-, ICl_2^-, NO_2^+ (all are linear)

SF_4 (See-saw shape) SiF_4 (Tetrahedral) XeF_4 (square planar shape)

6. The incorrect order of bond dissociation energy will be :

(a) H – H > Cl – Cl > Br – Br

(b) Si – Si > P – P > Cl – Cl

(c) C – C > N – N > O – O

(d) H – Cl > H – Br > H – I

Sol.(b) Bond length depends on size of atoms order of bond length is:-

Si – Si < P – P < Cl – Cl

$$\text{Bond energy} \propto \frac{1}{\text{Bond length}}$$

Hence, correct order of bond energy is:

Si – Si > P – P > Cl – Cl

7. The incorrect order of bond dissociation energy will be :

(a) $CO < CO_2 < CO_3^{2-}$ (C – O bond)

(b) $CN^- < NCN^{2-} < R\text{-}CO\text{-}NH_2$ (C – N bond)

(c) $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$ (Cl – O bond)

(d) $SO_2 < SO_4^{2-} < SO_3^{2-}$ (S – O bond)

Sol.(a)

CO	CO_2	CO_3^{2-}
(3)	(2)	(1.33)

CN^-	NCN^{2-}	$R\text{-}CO\text{-}NH_2$
(3)	(2)	(1.5)

ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
(1)	(1.5)	(1.67)	(1.75)

SO_2	SO_4^{2-}	SO_3^{2-}
(1.5)	(1.5)	(1.33)

In bracket bond order is given.

8. In which of the following change, adjacent bond angle increases?

(a) $BeF_2 + 2F^- \rightarrow BeF_4^{2-}$

(b) $SiF_4 + 2F^- \rightarrow SiF_6^{2-}$

(c) $BF_3 + F^- \rightarrow BF_4^-$

(d) $NH_3 + H^+ \rightarrow NH_4^+$

Sol.(d) $\underline{Be}F_2 + 2F^- \rightarrow \underline{Be}F_4^{2-}$
sp sp^3
(180°) (109° 28')

$\underline{Si}F_4 + 2F^- \rightarrow \underline{Si}F_6^{2-}$
sp^3 sp^3d^2
(109° 28') (90°)

$\underline{B}F_3 + F^- \rightarrow \underline{B}F_4^-$
sp^2 sp^3
(120°) (109° 28')

$\underline{N}H_3 + H^+ \rightarrow \underline{N}H_4^+$
sp^3 sp^3
(107°48') (109° 28')

9. In which of the following processes, the value of magnetic moment does not change?

(a) $N_2 \rightarrow N_2^{-2}$ (a) $B_2 \rightarrow B_2^{-2}$

(c) $O_2^+ \rightarrow O_2^-$ (d) $O_2^- \rightarrow O_2^{-2}$

Sol.(c) By using molecular orbital theory, we can calculate number of unpaired e^- in all these species.

$N_2 \rightarrow N_2^{-2}$ $B_2 \rightarrow B_2^{-2}$
(0) (2) (2) (0)

$O_2^+ \rightarrow O_2^-$ $O_2^- \rightarrow O_2^{-2}$
(1) (1) (1) (0)

10. Which of the following statement(s) is not true for the given species?

N_2, CO, CN^- and NO^+

(a) All species have linear shape

(b) All species have some dipole moments

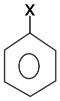
(c) All species are isoelectronic

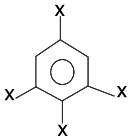
(d) All species have identical bond order and they are diamagnetic in nature.

Sol.(b) All diatomic species are linear.

Dipole moment of N_2 is zero but remaining species have some dipole moments.

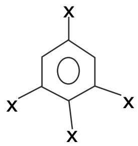
All species have 14 e^-, bond order is 3 and diamagnetic in nature.

11. Dipole moment of  is 1.5 D. Calculate

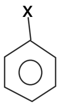
Dipole moment of 

(a) 1.5 D (b) 1 D

(c) 2.35 D (d) 3 D

Sol.(c) 

Three bond moments are equal in magnitude and they are 120° apart hence, their result is zero. Net dipole moment of this molecule equals to the

that of 

12. Which of the following pair of compounds are polar, planar and sp^2 hybridisation?

(a) H_2CO_3, SO_2 (b) $HClO_2$, H_2CO_3

(c) BFClBr, ClF_3 (d) SO_3, O_3

Sol.(a) H_2CO_3 and SO_2

(Both are polar, planar and have sp^2 hybridisation)

In $HClO_2$, hybridisation of Cl is sp^3

In ClF_3, hybridisation of Cl is sp^3d

SO_3 is non – polar

13. Back bonding in BF_3 does not affect:

(a) Planarity, Lewis acidic strength and bond angle
(b) Bond length, hybridization and bond strength
(c) Bond angle, planarity and geometry
(d) Lewis acidic strength, bond length and bond order (B-F)

Sol.(c) Due to back bonding in BF_3, it's bond length , bond energy, bond strength and lewis acidic strength changes but there is no change in bond angle, hybridization, geometry and planarity.

14. Which of the following molecule has $2p\pi$ - $3p\pi$ back bonding?

(a) OCl_2 (b) BF_3

(c) $:CCl_2$ (d) CCl_3^-

Sol.(c)

Molecule	Type of back bonding
OCl_2	$2p\pi - 3d\pi$
BF_3	$2p\pi$ - $2p\pi$
CCl_3^-	$2p\pi - 3d\pi$
$:CCl_2$	$2p\pi - 3p\pi$

In $:CCl_2$, vacant 2p-orbital of 'C' and paired 3p-orbital of 'Cl' form back bond.

15. In which of the following molecule $2C - 2e^-$ bond is absent?

(a) $BeCl_2$ in Vapor state (b) Al_2Cl_6

(c) BeH_2 in solid state (d) B_2H_6

Sol.(c) In BeH_2 all bonds are $3C$-$2e^-$.

16. In which of the following d – orbital's are not used by central atom in hybridization?

(a) PF_5 (s) (b) PCl_5 (s)

(c) PBr_5 (s) (d) XeF_6 (s)

Sol.(c) Solid form of PF_5 is $\underset{sp^3}{PF_4^+}\ \underset{sp^3d^2}{PF_6^-}$

Solid form of PCl_5 is $\underset{sp^3}{PCl_4^+}\ \underset{sp^3d^2}{PCl_6^-}$

Solid form of PBr_5 is $\underset{sp^3}{PBr_4^+}\ Br^-$

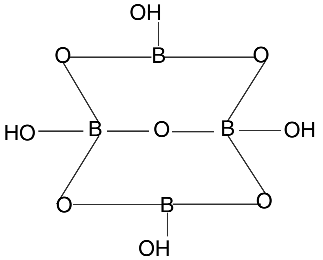
Solid form of XeF_6 is $\underset{sp^3d^2}{XeF_5^+}\ \underset{sp^3d^4}{XeF_7^-}$

17. In $(B_4O_5(OH)_4)^{2-}$ the number of boron atoms having on octet of electron is :

(a) 0 (b) 1

(c) 2 (d) 4

Sol.(c) Structure of $(B_4O_5(OH)_4)^{2-}$ is:-

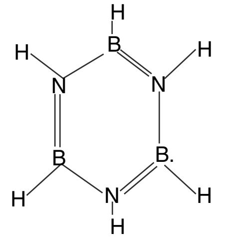


In this structure 2 Boron atoms have octet of electrons in their outermost shell.

18. Which of the following statement is not correct?

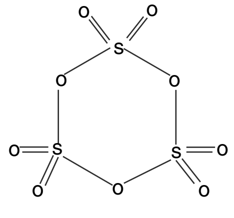
(a) The maximum number of atoms in one plane in $B_3N_3H_6$ are 12.
(b) There is no S – S bond in S_3O_9.
(c) Maximum number of identical bond angles in ClO_4^- are 4.
(d) Number of bridging oxygen in P_4O_{10} are 6.

Sol.(c)



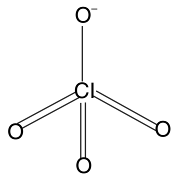
The complete structure is Planar hence, all 12 atoms are in same plane.

Structure of S_3O_9 is:-



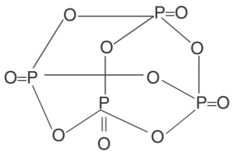
There is no S – S bond

Structure of ClO_4^- is:-



In this tetrahedral structure identical bond angles are 6.

Structure of P_4O_{10} is:-



In this structure 6, P – O – P linkage is present.

19. Which of the following compound produces only basic products on hydrolysis?

(a) Mg_3N_2 (b) NCl_3

(c) BBr_3 (d) PCl_5

Sol.(a) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

(Both are basic)

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

(One is basic and other is acidic)

$BBr_3 + 3H_2O \rightarrow H_3BO_3 + 3HBr$

(Both are acidic)

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

(Both are acidic)

20. Which of the following reactions is incorrect?

(a) $Pb(NO_3)_2 \xrightarrow{\Delta} PbO_2 + NO_2 + O_2$

(b) $2\ NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

(c) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

(d) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

Sol.(a) The correct reaction is:

$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$

21. Which of the following is not correctly matched?

(a) $NH_3 > SbH_3 > PH_3 > AsH_3$ (Melting point)

(b) $NH_3 > PH_3 > AsH_3 > SbH_3$ (Proton affinity)

(c) $CH_4 > SiH_4 > GeH_4 > SnH_4$ (Thermal stability)

(d) $H_2O > H_2Te > H_2Se > H_2S$ (Boiling point)

Sol.(a) The correct order of melting point is:

$NH_3 > SbH_3 > AsH_3 > PH_3$

The order depends on strength of intermolecular bonding. In solid state, intermolecular bonding in NH_3 is much stronger than in liquid state.

22. Which of the following substance has the highest melting point?

(a) NaCl (b) KCl

(c) MgO (d) BaO

Sol.(c) For ionic compounds, melting point

$\propto$ lattice energy (Uo)

$$Uo \propto \frac{/Z^+//Z^-/}{r}$$

Here, $/Z^+/$ and $/Z^-/$ are charge of cation and anion.

$r = r^+ + r^-$

r^+ = radius of cation

r^- = radius of anion

In these four compounds, MgO has highest lattice energy.

23. The dipole moment of LiH is 1.964×10^{-29} Cm and the inter atomic distance between Li and H in this molecule is 1.596 Å. What is the percent ionic character in LiH?

Sol. The dipole moment of 100% ionic molecule (Li^+H)

= (1 electronic charge) (inter atomic distance)

= $(1.602 \times 10^{-19} C)(1.596 \times 10^{-10} m)$

= 2.557×10^{-29} Cm

$$\text{Fractional ionic character} = \frac{\text{Experimental dipole moment}}{\text{Theoretical value of dipole moment}}$$

$$= \frac{1.94 \times 10^{-29}}{2.557 \times 10^{-29}} = 0.768$$

The bond in LiH is 76.8% ionic.

24. KF Combines with HF to form KHF_2. The Compound contains the species-

(a) K^+, F^- and H^+ (b) K^+, F^- and HF

(c) K^+ and $(HF_2)^-$ (d) $(KHF)^+$ and F^-

Sol.(c) $KHF_2 \rightarrow K^+ + HF_2^-$

25. Two elements X and Y have following electronic configuration:

$X : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

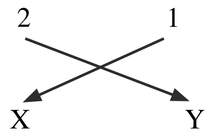
$Y : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

The expected compound formed by combination of X and Y Will be expressed as-

(a) XY_2 (b) X_5Y_2

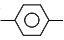
(c) X_2Y_5 (d) XY_5

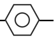
Sol.(a) Valency of element X is 2 (2 electrons in the outermost shell) while that of element Y is 1(1electron in the outermost shell). So the formula of the compound between X and Y is XY_2



26. Which of the following interaction lies in the range of 8-42 kJ/mol?

(a) F^-…..HF (b) Xe…..H_2O

(c) Cs^+…..OH^- (d) O_2N––OH…H_2O

Sol.(d) The interaction present in O_2N––OH…H_2O is intermolecular H-bond. It's bond energy lies between 8-42 kJ/mol.

The interaction in F^-…..HF is very strong H-bond. It's strength almost equals to the covalent bond.

The interaction in Cs^+…..OH^- is an ionic bond.

The interaction in Xe…..H_2O is dipole – induced dipole interaction which is weaker than H-bond.

27. Which of the following compound has highest lattice energy?

(a) AlF_3 (b) Na_2S

(c) Al_2O_3 (d) CaF_2

Sol.(c) Lattice energy (Uo) $\propto \frac{/Z^+//Z^-/}{r}$

Here, $/Z^+/$ and $/Z^-/$ are magnitude of charge of cation and anion respectively.

$r \approx r^+ + r^-$

Al_2O_3 has highest lattice energy among these four because it has highest value of $/Z^+/ /Z^-/$

28. What is the ΔH of the following reaction?

$Mg\ (g) + 2F\ (g) \longrightarrow Mg^{2+}\ (g) + 2F^-\ (g)$

If $\Delta_{eg}H$ of F = -328 kJ/mol

First ionisation energy of Mg = 737.7 kJ/mol

Second Ionisation energy of Mg = 1451 kJ/mol

(a) 1532.7 kJ/mol (b) 1860.7kJ/mol

(c) 2516.7kJ/mol (d) 1451kJ/mol

Sol.(a) Given that,

$F\ (g) + e^- \rightarrow F^-\ (g);\ \Delta H_1 = -328$ KJ/mol

$Mg\ (g) \rightarrow Mg^+\ (g) + e^-;\ \Delta H_2 = 737.7$ KJ/mol

$Mg^+(g) \rightarrow Mg^{+2}\ (g) + e^-;\ \Delta H_3 = 1451$ KJ/mol

$Mg\ (g) + 2F(g) \rightarrow Mg^{+2}\ (g) + 2F^-\ (g);\ \Delta H$

$\Delta H = \Delta H_2 + \Delta H_3 + 2\Delta H_1$

Or $= 737.7 + 1451 + 2\ (-328)$

Or $= 1532.7$ KJ/mol

29. Which of the following order is incorrect?

(a) Ionic character : $MCl < MCl_2 < MCl_3$

(b) Polarisibility : $F^- < Cl^- < Br^- < I^-$

(c) Polarising power : $Na^+ < Ca^{+2} < Mg^{+2} < Al^{+3}$

(d) Covalent character : LiF < LiCl < LiBr < LiI

Sol.(a) Ionic character $\propto \frac{1}{\text{Polarising power of cation}}$

As positive oxidation state increases or, size of cation decreases, polarising power of cation increases hence, the correct order of ionic character is: $MCl > MCl_2 > MCl_3$

30. Select wrong statement:

(a) A transition metal ion has more polarising power than S-block ions of comparable size and charge.

(b) Order of solubility in water is AgF > AgCl > AgBr > AgI

(c) LiCl is soluble in organic solvents

(d) The hydration of ions involves absorption of heat.

Sol.(d) Out of cations having comparable size and charge the one having

Noble gas configuration has less polarizing power.

LiCl is a covalent compound hence, it is soluble in organic solvents.

Order of solubility of heavy metal halides depends order on hydration energy.

(AgF > AgCl > AgBr > AgI)

The hydration of ions involves evolution of heat.

$M^+\ (g) + H_2O \longrightarrow M^+\ (aq);\ \Delta H = -Ve$

Exercise

LEVEL I

1. The phosphate of a metal has the formula M_3PO_4. The formula of its chloride would be:

(a) MCl (b) MCl_2

(c) MCl_3 (d) M_2Cl_3

2. Solid NaCl is a bad conductor of electricity because:

(a) In solid NaCl there are no ions

(b) Solid NaCl is covalent

(c) In solid NaCl there is no mobility of ions

(d) In solid NaCl there are no electrons

3. Knowing that $Na^+ > Mg^{2+}$ and $S^{2-} > Cl^-$ (Order of size), predict which compound will be more covalent?

(a) MgS (b) Na_2S

(c) $MgCl_2$ (d) NaCl

4. Which of the following compound possesses the largest lattice energy?

(a) LiF (b) NaCl

(c) KH (d) CsI

5. Select the incorrect statement:

(a) Lithium is least reactive but the strongest reducing agent among all the metals.

(b) Lithium hydrogen carbonate is not obtained in the solid form while all other alkali metals forms solid hydrogen carbonates.

(c) Lithium nitrate when heated gives lithium oxide whereas other alkali metal nitrates decompose to give the corresponding nitrite.

(d) Solubility of alkali metal hydroxides decreases down the group. It is due to decrement in hydration energy from Li^+ to Cs^+.

6. Which pair of element can form multiple bond with itself and oxygen?

(a) F, N (b) N, Cl

(c) N, P (d) N, C

7. Bonds present in N_2O_5 (nitrogen pentaoxide) are:

(a) Only ionic

(b) Only covalent

(c) Covalent and co-ordinate

(d) Covalent and ionic

8. The fluorine molecules is formed by:

(a) p-p orbital's (sideways overlap)

(b) p-p orbital's (end-to-end overlap)

(c) sp-sp orbital's

(d) s-s orbital's

9. Among given species identify the isostructural pairs:

(a) [NF_3 and BF_3]

(b) [BF_4^- and NH_4^+]

(c) [BCl_3 and $BrCl_3$]

(d) [NH_3 and NO_3^-]

10. The molecule exhibiting maximum number of non-bonding electron pairs (lp) around the central atom is:

(a) $XeOF_4$ (b) XeO_2F_2

(c) XeF_3^- (d) XeO_3

11. The shapes of XeF_4, XeF_5^- and $SnCl_2$ are:

(a) Octahedral, trigonalbipyramidal and bent

(b) Square pyramidal, pentagonal planar and linear

(c) Square planar, pentagonal planar and angular

(d) See-saw, T-shaped and linear

12. Which is not correctly matched?

(a) XeO_3 – Trigonalbipyramidal

(b) ClF_3 – bent T-shape

(c) $XeOF_4$ – Square pyramidal

(d) XeF_2 – Linear shape

13. The geometry of ammonia molecule can be best described as:

(a) Nitrogen at one vertex of a regular tetrahedron, the other three vertices being occupied by three hydrogens

(b) Nitrogen at the centre of the tetrahedron, three of the vertices being occupied by three hydrogens

(c) Nitrogen at the centre of an equilateral triangle, three corners being occupied by three hydrogens

(d) Nitrogen at the junction of a T, three open ends being occupied by three hydrogens

14. Which one of the following compounds has the smallest bond angle?

(a) OH_2 (b) SH_2

(c) NH_3 (d) SO_2

15. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order:

(a) $NH_2^- > NH_3 > NH_4^+$

(b) $NH_4^+ > NH_3 > NH_2^-$

(c) $NH_3 > NH_2^- > NH_4^+$

(d) $NH_3 > NH_4^+ > NH_2^-$

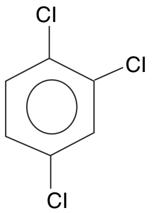
16. Which of the following molecules will have polar bonds but zero dipole moment?

(a) O_2 (b) $CHCl_3$

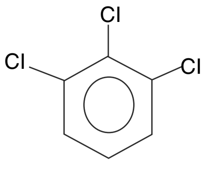
(c) CF_4 (d) None of these

17. Which has maximum dipole moment?

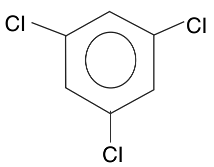
(a)



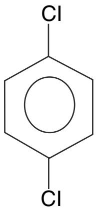
(b)



(c)



(d)



18. The hybridisation of central iodine atom in IF_5, I_3^- and I_3^+ are respectively:

(a) sp^3d^2, sp^3d, sp^3

(b) sp^3d, sp^3d, sp^3

(c) sp^3d^2, sp^3d^2, sp^3

(d) sp^3d, sp^3d^2, sp^3

19. Which of the following species used axial set of d-orbital's in hybridisation of central atom?

(a) PBr_4^+ (b) PCl_4^-

(c) ICl_4^- (d) None of these

20. Low melting point is expected for a solid:

(a) Ionic solid (b) Metallic solid

(c) Molecular solid (d) Covalent solid

21. Which molecule does not exist?

(a) OF_2 (b) OF_4

(c) SF_2 (d) SF_4

22. How many resonance forms can be written for the nitrate ion, (NO_3^-)?

(a) 1 (b) 2

(c) 3 (d) 4

23. When the substances Si, KCl, CH_3OH and C_2H_6 are arranged in order of increasing melting point, what is the correct order?

(a) Si, KCl, CH_3OH, C_2H_6

(b) CH_3OH, C_2H_6, Si, KCl

(c) KCl, Si, C_2H_6, CH_3OH

(d) C_2H_6, CH_3OH, KCl, Si

24. The H-O-H bond angles in H_3O^+ are approximately 107°. The orbitals used by oxygen in these bonds are best described as:

(a) p-orbitals

(b) sp-hybrid orbitals

(c) sp^2-hybrid orbitals

(d) sp^3-hybrid orbitals

25. Which of the following fact is directly explained by the statement oxygen is a smaller atom than sulphur?

(a) H_2O boils at a much higher temperature than H_2S

(b) H_2O undergoes intermolecular hydrogen bonding

(c) H_2O is liquid and H_2S is gas at room temperature

(d) S-H bond longer than O-H bond

26. Which of the following statement is correct about $I_3^+$and I_3^- molecular ions?

(a) Number of lone pairs at central atoms are same in both molecular ions

(b) Hybridisation of central atoms in both ions are same

(c) Both are polar species

(d) Both are planar species

27. Iodine molecule are held in the solid lattice by……………………..

(a) London forces

(b) Dipole-dipole interactions

(c) Covalent bonds

(d) Both are planar species

28. Species having maximum Cl-O bond order is:

(a) ClO_3^- (b) ClO_3

(c) ClO_2 (d) ClO_2^-

29. Which of the following species contains minimum number of atoms in XY Plane ?

(a) XeF_5^- (b) SF_6

(c) IF_7 (d) All

30. In which of the following molecular shape d_{Z^2}– orbital must not be involved in bonding?

(a) Pentagonal Planar
(b) Trigonal Planar
(c) Linear
(d) Square Planar

31. The correct statement regarding SO_2 molecule is:

(a) Two $p\pi$ - $d\pi$ bonds
(b) Molecule has 2 lone pair, 2 σ bonds and 2π bonds
(c) Two $p\pi$ - $p\pi$ bonds
(d) One $p\pi$ - $p\pi$ and one $p\pi$ -$d\pi$ bonds

32. The molecule ML_X is Planar with 7 pairs of electrons around M in the valence shell. The value of X is:

(a) 6 (b) 5

(c) 4 (d) 3

33. In which of the following pairs, both the species have the same hybridisation?

(I) SF_4, XeF_4 (II) I_3^-, XeF_2

(III) ClO_3^+, PO_4^{-3} (IV) ClO_3^-, PO_4^{3-}

(a) I, II (b) II, III

(c) II, IV (d) I, II, III

34. Which of the following possess two lone pair of electrons on the central atom and square planar shape:

(I) SF_4 (II) XeO_4

(III) XeF_4 (IV) ICl_4^-

(a) I , III (b) II , IV

(c) III , IV (d) All

35. Which of the following does not follow the octet rule?

(a) NaCl (b) $CaCl_2$

(c) ClF_3 (d) CCl_4

36. Which of the following does not have coordinate bonds?

(a) HNO_2 (b) O_3

(c) $NaBF_4$ (d) NH_4Cl

37. The bonds present in KHF_2 are:

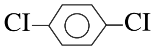
(a) Only ionic
(b) Covalent and coordinate
(c) Only covalent
(d) Covalent, ionic and H-bond

38. The correct order of dipole moment is:

(a) $CH_4 < NF_3 < NH_3 < H_2O$
(b) $NF_3 < CH_4 < NH_3 < H_2O$
(c) $NH_3 < NF_3 < CH_4 < H_2O$
(d) $H_2O < NH_3 < NF_3 < CH_4$

39. Among the following which is polar?

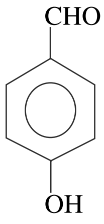
(a) CO_2 (b) SO_2

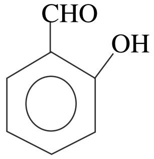
(c) $BeCl_2$ (d) 

40. In the reaction, $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$, the change in hybridisation is from:

(a) sp^3d to sp^3 and sp^3d^2
(b) sp^3d to sp^2 and sp^3
(c) sp^3d to sp^3d^2 and sp^3d^2
(d) sp^3d^2 to sp^3 and sp^3d

41. Out of the compounds shown below, the vapour pressure of II at a particular temperature is expected to be

I. p-hydroxybenzaldehyde ⇒ 

II. o-hydroxybenzaldehyde ⇒ 

(a) Higher than that of I
(b) Lower than that or I
(c) Same as that of I
(d) Can be higher or lower depending upon the size of vessel

42. Which of the following have been arranged in increasing bond order as well as bond dissociation energy?

(a) $O_2^{-2} < O_2^- < O_2^+ < O_2$
(b) $O_2^{-2} < O_2^- < O_2 < O_2^+$
(c) $O_2 < O_2^+ < O_2^{2-} < O_2^-$
(d) $O_2^+ > O_2^{2-} > O_2^- < O_2$

43. The statement true for azide ion (N_3^-) is:
(a) It has a non–linear structure
(b) It is called pseudo halogens
(c) The oxidation state of N in this anion is- 1
(d) It is isoelectronic with NO_2

44. The pair of strongest hydrogen bond is:
(a) SiH_4 and $SiCl_4$
(b) CH_3COOH and CH_3OCH_3
(c) CH_3COOH and CH_3COCH_3
(d) H_2O and H_2O_2

45. The strongest force among the following is:
(a) London force
(b) Ion-dipole interaction
(c) Dipole-induced dipole interaction
(d) Dipole-dipole interaction

LEVEL II

1. In which of the following species maximum atoms can lie in same plane?
(a) XeF_2O_2 (b) PCl_5
(c) AsH^+_4 (d) XeF_4

2. The correct order of Cl - O bond order is:
(a) $ClO_3^- < ClO_4^- < ClO_2^- < ClO^-$
(b) $ClO^- < ClO_4^- < ClO_3^- < ClO_2^-$
(c) $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$
(d) $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$

3. Resonance structures can be written for:
(a) O_3 (b) NH_3
(c) CH_4 (d) H_2O

4. The number of sp^2 – s sigma bonds in benzene are:
(a) 3 (b) 6
(c) 12 (d) None of these

5. Which is the following pair of species have identical shapes?
(a) NO_2^+ and NO_2^- (b) PCl_5 and BrF_5
(c) XeF_4 and ICl_4^- (d) $TeCl_4$ and XeO_4

6. The hybridisation of the central atom will change when:
(a) NH_3 combines with H^+
(b) H_3BO_3 combines with OH^-
(c) NH_3 forms NH^-_2
(d) H_2O combines with H^+

7. Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false:
(I) The order of repulsion between different pair of electrons is:
lp – lp > lp– bp > bp– bp
(II) In general, as the number of lone pair of electrons on central atom increases, value of bond angle from normal bond angle also increases
(III) The number of lone pair on O in H_2O is 2 while on N in NH_3 is 1
(IV) The structures of xenon fluorides and xenon oxofluorides could not be explained on the basis of VSEPR theory
(a) TTTF (b) TFTF
(c) TFTT (d) TFFF

8. Among the following species, the least angle around the central atom is in:
(a) O_3 (b) I_3^-
(c) NO_2^- (d) PH_3

9. BF_3 and NF_3 both are covalent compounds but NF_3 is polar whereas BF_3 is non–polar. This is because:
(a) Nitrogen atom is smaller than boron atom
(b) N – F bond is more polar than B – F bond
(c) NF_3 is pyramidal whereas BF_3 is planar triangular
(d) BF_3 is electron deficient whereas NF_3 is not

10. Which statement is incorrect?
(a) MP of H_2O, NH_3, HF are maximum in their respective group due to intermolecular H-bonding
(b) BP of CH_4 out of CH_4, SiH_4, GeH_4, and SnH_4 is least due to weak intermolecular force of attraction
(c) Acetic acid forms dimer by H-bonding
(d) NH_3 has lower BP than SbH_3

11. The molecular size of ICl and Br_2 is approximately same, but BP of ICl is about 40°C higher than of Br_2. It is because:
(a) ICl bond is stronger than Br-Br bond
(b) IE of iodine < IE of bromine
(c) ICl is polar while Br_2 is nonpolar
(d) I has larger size than Br

12. Number of S-S bond is $H_2S_nO_6$:

(a) n (b) (n-1)

(c) (n-2) (d) (n+1)

13. The nodal plane in the π-bond of ethane is located in:

(a) The molecular plane

(b) A plane parallel to the molecular plane

(c) A plane perpendicular to the molecular plane which bisects the carbon-carbon σ bond at right angle

(d) A plane perpendicular to the molecular plane which contain the carbon-carbon bond

14. Which set of compound in the following pair of ionic compound has the higher lattice energy?

(i) KCl or MgO

(ii) LiF or LiBr

(iii) Mg_3N_2 or NaCl

(a) KCl, LiBr, Mg_3N_2

(b) MgO, LiBr, Mg_3N_2

(c) MgO, LiF, NaCl

(d) MgO, LiF, Mg_3N_2

15. The bond having the highest bond energy is:

(a) C = C (b) C = S

(c) C = O (d) P = N

16. Which of the following overlaps is incorrect (assuming Z-axis is internuclear axis)?

(I) $2p_Y + 2p_Y \rightarrow \pi$- Bond formation

(II) $2p_X + 2p_X \rightarrow \sigma$- Bond formation

(III) $3d_{XY} + 3d_{XY} \rightarrow \pi$- Bond formation

(IV) $2s + 2p_Y \rightarrow \pi$ - Bond formation

(V) $3d_{XY} + 3d_{XY} \rightarrow \delta$- Bond formation

(VI) $2p_Z + 2p_Z \rightarrow \sigma$- Bond formation

(a) I, II, III (b) III, VI

(c) II, V (d) II, III, IV

17. In which of the following combination-hybridisation of central atom does not change?

(a) $H_2O + \underline{C}O_2$

(b) $H_3\underline{B}O_3 + OH^-$

(c) $BF_3 + \underline{N}H_3$

(d) None of these

18. Which species has the same shape as NH_3?

(a) SO_3^{2-} (b) CO_3^{2-}

(c) NO_3^- (d) SO_3

19. Which of the following is the correct order for increasing bond angle?

(a) $NH_3 < PH_3 < AsH_3 < SbH_3$

(b) $H_2O < OF_2 < Cl_2O$

(c) $H_3Te^+ < H_3Se^+ < H_3S^+ < H_3O^+$

(d) $BF_3 < BCl_3 < BBr_3 < BI_3$

20. SbF_5 reacts with XeF_4 and XeF_6 to form ionic compound $[XeF_3]^+[SbF_6]^-$ and $[XeF_5]^+$ $[SbF_6]^-$ then molecular shape of $[XeF_3]^+$ ion and $[XeF_5]^+$ ion respectively:

(a) Square pyramidal, T– shaped

(b) Bent – T – shape, square pyramidal

(c) See – Saw, square pyramidal

(d) square pyramidal, See–Saw

21. Melting point of calcium halides decreases in the order:

(a) $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$

(b) $CaI_2 > CaBr_2 > CaCl_2 > CaF_2$

(c) $CaBr_2 > CaI_2 > CaF_2 > CaCl_2$

(d) $CaCl_2 > CaBr_2 > CaI_2 > CaF_2$

22. Which of the following order is incorrect?

(a) NaCl> KCl > RbCl > LiCl (Order of melting point)

(b) LiCl > CsCl > RbCl > NaCl > KCl (Order of solubility in water)

(c) LiCl > NaCl > KCl > RbCl > CsCl (Order of lattice energy)

(d) NaF > MgF_2 > AlF_3 (Order of melting point)

23. Which of the following process is correct?

(a) $$Ca(NO_3) \xrightarrow{\Delta} CaO + 2NO_2\uparrow + \frac{1}{2}O_2\uparrow$$
$$\downarrow\Delta$$
$$Ca + \frac{1}{2}O_2\uparrow$$

(b) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$

(c) $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2\uparrow + H_2O$

(d) Both (b) and (c)

24. Choose the correct code of characteristics for the given order of hybrid orbitals of same atom, $sp < sp^2 < sp^3$

(I) Electronegativity

(II) Bond angle between same hybrid orbitals

(III) Size

(IV) Energy level

(a) (II), (III) and (IV)
(b) (III), (IV)
(c) (II) and (IV)
(d) (I), (II), (III) and (IV)

25. Select pair of compound in which both have different hybridisation but similar shape:

(a) BF_3, BrF_3 (b) ICl_2^-, $BeCl_2$
(c) BCl_3, PCl_3 (d) PCl_3, NCl_3

26. Assuming the bond direction to the z-axis, which of the overlapping of atomic orbitals of two atom (A) and (B) will result in bonding?

(i) s-orbital of A and p_x–orbital of B
(ii) s-orbital of A and p_z–orbital of B
(iii) p_y-orbital of A and p_z–orbital of B
(iv) s-orbital of both (A) and (B)

(a) I, and IV (b) I and II
(c) III and IV (d) II and IV

27. The number and type of bonds between two C-atoms in SrC_2 are:

(a) $1\sigma, 1\pi$ (b) $1\sigma, 2\pi$
(c) $1\sigma, 1.5\pi$ (d) 1σ

28. Which of the following is the decreasing order of their dipole moments?

(a) $NH_3 > BF_3 > NF_3$
(b) $NH_3 > NF_3 > BF_3$
(c) $BF_3 > NH_3 > NF_3$
(d) $NH_3 > BF_3 > NF_3$

29. The maximum number of 90° angles between bp-bp of electrons is observed in:

(a) sp^3d hybridisation
(b) dsp^3 hybridisation
(c) dsp^2 hybridisation
(d) sp^3d^2 hybridisation

30. The bond angles of SO_3, SO_2 and SO_3^{2-} are in the order:

(a) $SO_3 > SO_2 > SO_3^{2-}$
(b) $SO_3^{2-} > SO_3 > SO_2$
(c) $SO_2 > SO_3 > SO_3^{2-}$
(d) $SO_3 > SO_3^{2-} > SO_2$

31. In forming (i) $N_2 \rightarrow N_2^+$ and (ii) $O_2 \rightarrow O_2^+$; the electrons respectively are removed from:

(a) $(\pi_{2py}^*$ or $\pi_{2px}^*)$ or $(\pi_{2py}^*$ or $\pi_{2px}^*)$
(b) $(\pi_{2py}$ or $\pi_{2px})$ or $(\pi_{2py}$ or $\pi_{2px})$
(c) $(\sigma_{2py}$ or $\sigma_{2px})$ or $(\pi_{2py}^*$ or $\pi_{2px}^*)$
(d) $(\pi_{2py}^*$ or $\pi_{2px}^*)$ or $(\pi_{2py}$ or $\pi_{2px})$

32. The decreasing (O - O) bond length order in the following point?

(a) $O_2 > H_2O_2 > O_3$ (b) $H_2O_2 > O_3 > O_2$
(c) $O_3 > H_2O_2 > O_2$ (d) $O_3 > O_2 > H_2O_2$

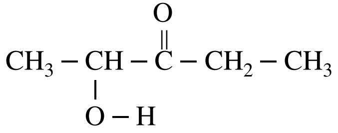
33. Which of the following substance has the highest melting point?

(a) BaO (b) MgO
(c) KCl (d) NaCl

34. Which of the following statement is correct?

(a) $FeCl_2$ is more covalent than $FeCl_3$
(b) $FeCl_3$ is more covalent than $FeCl_2$
(c) Both $FeCl_2$ and $FeCl_3$ are equally covalent
(d) $FeCl_2$ and $FeCl_3$ do not have any covalent character

35. Which of the following compound does not have hydrogen bonding?

(a) K_2HPO_4
(b) K_2HPO_3
(c) $NaHCO_3(s)$
(d) 
$CH_3 - \underset{\underset{O-H}{|}}{CH} - \overset{\overset{O}{||}}{C} - CH_2 - CH_3$

36. Which of the hydrogen halide forms salts like KHX_2 (where X is a halogen atom)?

(a) HF (b) HCl
(c) HI (d) HBr

37. Which of the following is an incorrect statement for ice:

(a) Less density than liquid water
(b) Each O atom is surrounded by four equidistance H-atoms
(c) Distance between two adjacent O-atoms is equal
(d) Open cage-like crystal structure.

38. The intermolecular interaction that is dependent on the inverse cube of distance between molecules is:

(a) Ion-ion interaction
(b) Ion-dipole interaction
(c) London force
(d) Hydrogen bond

39. Which of these is not true for metallic bond ?

(a) Metallic bond is non-directional in nature

(b) Metallic bonds are weaker than covalent bond.

(c) Energy required to vapourise a mole of Cu metal is high to the energy required to vapourise a mole of a covalent substance like diamond.

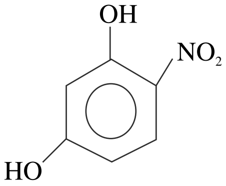
(d) The valency electrons in a metallic bond are mobile.

40. Which substance has the strongest London dispersion forces?

(a) SiH_4 (b) CH_4

(c) SnH_4 (d) GeH_4

41. The type of molecular forces of attraction present in the following compound is:



(a) Intermolecular H-bonding

(b) Intramolecular H-bonding

(c) van der Waals' force

(d) All of these

42. Which among the following attraction is strongest?

(a) HF ……… H_2O

(b) Na^+ ……… HCl

(c) H_2O ……… Cl_2

(d) Cl – Cl …… Cl – Cl

43. In which of the following species back- π bonding exists?

(a) NF_3 (b) NH_3

(c) BF_3 (d) BF^-_4

44. Which statement about hybridisation is correct?

(a) It involves the mixing of atomic orbitals of the atom at the time of their participation in bonding.

(b) sp^3d^3 hybridisation orbital point out towards the corners of regular hexagon.

(c) Hybrid orbitals form weaker bonds than pure atomic orbitals.

(d) For hybridisationto occur, the atom must have vacant orbitals in the valence shell.

45. Which of the following has highest melting point?

(a) SF_6 (b) NaCl

(c) SiC (d) Xe

LEVEL III

ONE OR MORE THAN ONE CORRECT

1. Which species have same bond order?

(a) CO_3^{-2} (b) NO_3^-

(c) NO_2^- (d) NO

2. In Which of the following molecule bonding is taking place in excited state?

(a) CH_4 (b) BF_3

(c) ICl_3 (d) PCl_3

3. Which is/are in linear shape?

(a) NO_2^+ (b) XeF_2

(c) I_3^- (d) I_3^+

4. The species which are paramagnetic is/are:

(a) NO (b) NO_2

(c) ClO_2 (d) N_2O_4

5. Which of the following statements are correct?

(a) O–hydroxybenzaldehyde is a liquid at room temperature due to intramolecular H–bonding.

(b) Order of boiling point is $H_2O > H_2Te > H_2Se > H_2S$

(c) Order of boiling point is $HF > HI > HBr > HCl$

(d) Order of boiling point is $SbH_3 > NH_3 > AsH_3 > PH_3$

6. The molecule that is/are having N – N bond:

(a) N_2O (b) N_2O_3

(c) N_2O_5 (d) N_2O_4

7. There is change in the type of hybridisation when:

(a) NH_3 combines with H^+

(b) AlH_3 combines with H^-

(c) NH_3 forms NH_2^-

(d) SiF_4 forms SiF_6^{2-}

8. Select correct statement(s) regarding σ and π-bonds:

(a) σ-bond lies on the line joining the nuclei of bonded atoms

(b) π-electron cloud lies on either side to the line joining the nuclei of bonded atoms

(c) ($2p\pi$-$3d\pi$) pi-bond is stronger than ($2p\pi$-$3p\pi$) pi-bond.

(d) σ-bond has primary effect to decide direction of covalent bond, while π-bond has no primary effect in direction of bond

9. In which of the following there is intermolecular hydrogen bonding?

(a) Water (b) Ethanol

(c) Acetic acid (d) H-F

10. Which of the following statements are correct about sulphur hexafluoride?

(a) All S-F bonds are equivalent

(b) SF_6 is a planar molecule

(c) Oxidation number of sulphur is the same as number of electrons of sulphur involved in bonding

(d) Sulphur has acquired the electronic structure of the gas argon

11. Correct order of decreasing boiling points is:

(a) $HF > HI > HBr > HCl$

(b) $H_2O > H_2Te > H_2Se > H_2S$

(c) $Br_2 > Cl_2 > F_2$

(d) $CH_4 > GeH_4 > SiH_4$

12. Which of the following species does/do not exist?

(a) OF_4 (b) NH_2^-

(c) NCl_5 (d) ICl_3^{2-}

13. Ionic compounds in general do not possess:

(a) high melting points and non-directional bonds

(b) high melting points and low-boiling points

(c) directional bond and low-boiling points

(d) high solubilities in polar and non-polar solvents

PASSAGE BASED QUESTIONS

Passage # 1 (Q. 14 and 15)

The distribution of electrons among various molecular orbital's is called the electronic configuration of the molecule which provides us the following very important information's about the molecule.

(a) **Stability of molecule:** The molecule is stable if number of bonding molecular orbital electrons (N_b) is greater than the number of anti bonding molecular orbital electrons (N_a) and vice – versa.

(b) **Bond order:** Bond order = $\frac{1}{2}$ (N_b - N_a)

A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.

(c) **Nature of the bond:** Bond order 1, 2, or 3 corresponds to single, double or triple bonds respectively.

(d) **Bond length:** Bond length decreases as bond order increases.

(e) **Magnetic nature:** Molecular orbital's in a molecule are double occupied, the substance is diamagnetic and if one or more molecular orbital's are singly occupied, it is paramagnetic.

14. Select correct statement(s):

(a) Among O_2^+, O_2 and O_2^- the stability decreases as $O_2^+ > O_2 > O_2^-$

(b) He_2 molecule does not exist as the effect of bonding and anti-bonding molecular orbital's cancel each other

(c) C_2, O_2^{2-} and Li_2 are diamagnetic

(d) In F_2 molecule, the energy of $\sigma\, 2p_z$ is more than π_{2px} and π_{2py}

15. N_2 has greater bond dissociation energy than N_2^+, where as O_2 has a lower bond dissociation energy than O_2^+ because :

(a) Bond order is reduced when O_2 is ionised to O_2^+ and bond order increased when N_2 is ionised to N_2^+

(b) Bond order is increased when O_2 is ionised to O_2^+ and bond order is decreased when N_2 is ionised to N_2^+

(c) Bond order is deceased when O_2 is ionised to O_2^+ and bond order is decreased when N_2 is ionised to N_2^+

(d) None of these.

Passage # 2 (Q. 16 and 17)

Molecular geometry is the general shape of a molecule as determined by the relative positions of the atomic nuclei. VSEPR model predicts the shape of the molecules and ions in which valence shell electron pairs are arranged about the atom as far away from one another as possible. Thus minimising electron pair repulsion gives information about the geometry of a molecule. Information about the geometry of a molecule can sometimes be obtained from an experimental quantity called dipole moment.

16. The dipole moment of a tri-atomic molecule AX_2 was found to be equal to the bond moment of A – X bond.

Which of the following information regarding geometry of the molecule can be drawn from the above observation?

(a) Molecule is linear

(b) Molecule is V shaped with $\angle X - A - X = 90°$

(c) Molecule is V shaped with $\angle X - A - X = 120°$

(d) Molecule geometry cannot be predicted with the given information.

17. Which of the following inter – halogen compounds is non–polar in nature?

(a) ClF_3
(b) BrF_5
(c) IF_7
(d) BrCl

Passage # 3 (Q. 18 and 19)

When hybridisation involving d-orbitals are considered then all five d-orbitals are not degenerate, rather $d_{x^2-y^2}$, d_{z^2} and d_{xy}, d_{yz}, d_{zx} form two different sets of orbitals and orbitals of appropriate set is involved in the hybridisation.

18. In sp^3d^2 hybridisation, which sets of d-orbitals is involved?

(a) $d_{x^2-y^2}, d_{z^2}$
(b) d_{z^2}, d_{xy}
(c) d_{xy}, d_{yz}
(d) $d_{x^2-y^2}, d_{xy}$

19. Molecule having trigonalbipyramidal geometry and sp^3d hybridisation, d-orbitals involved is:

(a) d_{xy}
(b) d_{yz}
(c) $d_{x^2-y^2}$
(d) d_{z^2}

INTEGER TYPE QUESTIONS

20. Consider y-axis as inter-nuclear axis, how many of following will lead to π bond formation?

(a) $p_y - p_y$
(b) $p_x - p_x$
(c) $p_z - p_z$
(d) $d_{xy} - d_{xy}$
(e) $d_{yz} - d_{yz}$
(f) $p_x - d_{xy}$
(g) $d_{xy} - p_z$
(h) $d_{xz} - d_{xz}$

21. How many of the following have $p\pi$ - $d\pi$ bonding?

(a) CO_3^{-2}
(b) NO_3^-
(c) SO_3^{-2}
(d) SO_4^{-2}
(e) PO_4^{-3}
(f) NO_2^-
(g) $S_2O_8^{-2}$
(h) R_3PO
(i) $S_2O_3^{-2}$
(j) ClO_4^-
(k) ClO_3^-
(l) SO_2

22. Find the number of species having fractional bond order?

$N_2^+, N_2^-, O_2, O_2^+, F_2, B_2, C_2^+, CN^-, NO^+$

23. P_4O_{10} has two different types of P – O bonds. Find the number of P – O bonds with shorter bond length.

24. In a P_4O_6 molecule, the total number of P-O-P bonds is :

25. Find the total number of polar molecules.

PF_3Cl_2, SF_4, PCl_5, PCl_3F_2, SF_6, XeF_2, NO_2^+, BF_2Cl, BF_3

26. How many of the following have hydrogen bonding?

NH_3, CH_4, H_2O, HI, HF, HCOOH, $B(OH)_3$, CH_3COOH, HCO_2^- ion

27. In which of the following all bond length are not equal?

PCl_5, SF_4, ClF_3, XeF_2, $[SF_5]^+$, $[ClF_4]^+$, $[XeF_3]^+$, O_3, P_4 (white)

COLUMN MATCHING TYPE QUESTIONS

28. Match the following :

Column I	Column II
(A) BF_3	(a) sp^3 hybridisation
(B) $(SiH_3)_3N$	(b) $p\pi - p\pi$ back bond
(C) B_2H_6	(c) $p\pi - d\pi$ back bond
(D) SiO_2	(d) 3c – 2e bond

29. Match the following:

Column I	Column II
(A) O_2 and NO^-	(a) Same magnetic property and bond order as that in N_2^+
(B) O_2^+ and NO	(b) Same bond order but not same magnetic property as that in O_2
(C) CO and CN^-	(c) Same magnetic property and bond order as that N_2^{2-}
(D) C_2 and CN^+	(d) Same magnetic property and bond order as that in NO^+

30. Match the following:

Column – I	Column - II
(A) $H_3P_3O_9$	(a) S-O-S bond is present
(B) $H_2S_2O_7$	(b) Dibasic acid
(C) $H_2S_4O_6$	(c) P-O-P bond is present
(D) $H_4P_2O_5$	(d) Central atom (S or P) in maximum oxidation state

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is:
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight

[IIT-2000]

2. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are:
(a) sp^2, sp^3, and sp^2 respectively
(b) sp, sp^2, and sp^3 respectively
(c) sp^2, sp, and sp^3 respectively
(d) sp^2, sp^3, and sp respectively

[IIT-2000]

3. The correct order of hybridisation of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is:
(a) dsp^2, sp^3d, sp^2 and sp^3
(b) sp^3, dsp^2, sp^3d and sp^2
(c) dsp^2, sp^2, sp^3, sp^3d
(d) dsp^2, sp^3, sp^2, sp^3d

[IIT-2001]

4. The common features among the species CN^-, CO and NO^+ are:
(a) Bond order three and isoelectronic
(b) Bond other three and weak field ligands
(c) Bond order two and π - acceptors
(d) Isoelectronic and weak field ligands

[IIT-2001]

5. Specify hybridisation of N and B atoms in a 1:1 complex of BF_3 and NH_3:
(a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
(b) N : Pyramidal, sp^3 ; B : Pyramidal, sp^3
(c) N : Pyramidal, sp^3 ; B : Planar, sp^3
(d) N : Pyramidal, sp^3 ; B : tetrahedral, sp^3

[IIT-2002]

6. The nodal plane in the π bond of ethene is located in:
(a) The molecular plane.
(b) A plane parallel to the molecular plane.
(c) A plane perpendicular to the molecular plane which bisects, the carbon-carbon σ bond at right angle.
(d) A plane perpendicular to the molecular plane which contains, the carbon-carbon bond.

[IIT-2002]

7. Which of the following molecular species has unpaired electrons?
(a) N_2 (b) F_2
(c) O_2^- (d) O_2^{2-}

[IIT-2002]

8. Which of the following are isoelectronic and isostructural ? NO_3^-, CO_3^{2-}, ClO_3^-, SO_3
(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

[IIT-2002]

9. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+?
(a) Paramagnetic and bond order < O_2
(b) Paramagnetic and bond order > O_2
(c) Diamagnetic and bond order < O_2
(d) Diamagnetic and bond order > O_2

[IIT-2003]

10. Which species has the maximum number of lone pair of electrons on the central atom?
(a) ClO_3^- (b) XeF_4
(c) SF_4 (d) I_3^-

[IIT-2005]

11. The percentage of p-character in the orbitals forming p-p bonds in P_4 is:
(a) 25 (b) 33
(c) 50 (d) 75

[IIT-2007]

12. Among the following, the paramagnetic compound is:
(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

[IIT-2007]

13. The species having bond order different from that in CO is:
(a) NO^- (b) NO^+
(c) CN^- (d) N_2

[IIT-2007]

14. The structure of XeO_3 is:

(a) Linear (b) Planar

(c) Pyramidal (d) T-shaped

[IIT-2007]

15. Statement-1: p-hdroxybenzoic acid has a lower boiling point then o-hdroxybenzoic acid.

Statement-2: o-hdroxybenzoic acid has intramolecular hydrogen bonding.

(a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True, Statement-2 is not a correct explanation for Statement-1.

(c) Statement-1 is True, Statement-2 is False.

(d) Statement-1 is False, Statement-2 is True.

[IIT-2007]

16. Statement-1: In water, orthoboric acid behaves as a weak monobasic acid.

Statement-2: In water, orthoboric acid acts as a proton donor.

(a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True, Statement-2 is Not a correct explanation for Statement-1.

(c) Statement-1 is True, Statement-2 is False.

(d) Statement-1 is False, Statement-2 is True.

[IIT-2007]

17. Statement-1: Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to inert pair effect.

(a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for statement-1.

(b) Statement-1 is True, Statement-2 is True, Statement-2 is Not a correct explanation for statement-1.

(c) Statement-1 is True, Statement-2 is False.

(d) Statement-1 is False, Statement-2 is True.

[IIT-2008]

18. The nitrogen oxide(s) that contain(s) N-N bond(s) is(are):

(a) N_2O (b) N_2O_3

(c) N_2O_4 (d) N_2O_5

[IIT-2009]

19. The bond energy (in kcal mol^{-1}) of a C-C single bond is approximately:

(a) 1 (b) 10

(c) 100 (d) 1000

[IIT-2010]

20. Assuming that hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is:

(a) 1 and diamagnetic

(b) 0 and diamagnetic

(c) 1 and paramagnetic

(d) 0 and paramagnetic

[IIT-2010]

21. The species having pyramidal shape is:

(a) SO_3 (b) BrF_3

(c) SiO_3^{2-} (d) OSF_2

[IIT-2010]

22. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are):

(a) sp and sp^3 (b) sp and sp^2

(c) Only sp^2 (d) sp^2 and sp^3

[IIT-2012]

23. The shape of XeO_2F_2 molecule is:

(a) Trigonalbipyramidal

(b) Square planar

(c) Tetrahedral

(d) See-saw

[IIT-2012]

24. Hybridisation of the underlined atom changes when,

(a) $\underline{Al}H_3$ changes to $\underline{Al}H_4^-$

(b) $H_2\underline{O}$ changes to $H_3\underline{O}^+$

(c) $\underline{N}H_3$ changes to $\underline{N}H_4^+$

(d) All of these

[AIEEE-2002]

25. The maximum number of 90° angles between bond pair- bond pair of electrons is observed in,

(a) dsp^3 hybridisation

(b) sp^3d hybridisation

(c) dsp^2 hybridisation

(d) sp^3d^2 hybridisation **[AIEEE-2003]**

26. Based on lattice energy and other considerations, which one of the following alkali metal chlorides is expected to have the highest melting point?

(a) RbCl (b) KCl

(c) NaCl (d) LiCl

[AIEEE-2004]

27. The number and types of bonds between two carbon atoms in calcium carbide are:

(a) One sigma, One pi
(b) One sigma, Two pi
(c) Two sigma, One pi
(d) Two sigma, Two pi

[AIEEE-2005]

28. In silicon dioxide:

(a) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.
(b) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.
(c) Silicon atom is bonded to two oxygen atoms.
(d) There are double bonds between silicon and oxygen atoms.

[AIEEE-2005]

29. The molecular shapes of SF_4, CF_4 and XeF_4 are:

(a) Different with 1, 0 and 2 lone pairs of electrons on the central atoms, respectively
(b) Different with 0, 1 and 2 lone pairs of electrons on the central atoms, respectively
(c) Different with 1, 1 and 1 lone pairs of electrons on the central atoms, respectively
(d) Different with 2, 0 and 1 lone pairs of electrons on the central atoms, respectively

[AIEEE-2005]

30. The number of hydrogen atom(s) attached to phosphorus atom hypophosphorus acid is:

(a) Zero (b) Two

(c) One (d) Three

[AIEEE-2005]

31. The correct order of the thermal stability of hydrogen halides (H-X) is:

(a) HI > HBr > HCl > HF
(b) HF > HCl > HBr > HI
(c) HCl < HF < HBr < HI
(d) Hl < HCl < HF < HBr

[AIEEE-2005]

32. The decreasing values of bond angles from NH_3(106°) to SbH_3 (101°) down group-15 of the periodic table is due to:

(a) Increasing bp-bp repulsion
(b) Increasing p-orbital character in sp^3
(c) Decreasing lp-bp repulsion
(d) Decreasing electronegativity

[AIEEE-2006]

33. In which the following ionisation processes, the bond order has increased and magnetic behaviour has changed?

(a) $C_2 \rightarrow C_2^+$ (b) $NO \rightarrow NO^+$

(c) $O_2 \rightarrow O_2^+$ (d) $N_2 \rightarrow N_2^+$

[AIEEE-2007]

34. The charge/size of a cation determines its polarising power. Which one of the following sequences represents the increasing order polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?

(a) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(b) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(c) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

[AIEEE-2007]

35. The bond dissociation energy of B–F in BF_3 is 646kJ mol^{-1} whereas that of C–F bond in CF_4 is 515kJ mol^{-1}. The correct for higher B-F bond dissociation energy as compared to that of C – F is:

(a) Smaller size of B-atom as compared to that of C-atom
(b) Stronger σ bond between B and F in BF_3 as compared to that between C and F is CF_4
(c) Significant $p\pi$–$p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
(d) Lower degree of $p\pi$–$p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

[AIEEE-2009]

36. The hybridisation of orbitals of N atom in NO_3^-, NO_2^+ and NH_4^+ are respectively:

(a) sp, sp^2, sp^3 (b) sp^2, sp, sp^3

(c) sp, sp^3, sp^2 (d) sp^2, sp^3, sp

[AIEEE-2011]

37. The molecule having smallest bond angle is:

(a) NCl_3 (b) $AsCl_3$

(c) $SbCl_3$ (d) PCl_3

[AIEEE-2011]

38. Boron cannot form which one of the following anions?

(a) BF_6^{3-} (b) BH_4^-

(c) $B(OH)_4^-$ (d) BO_2^-

[AIEEE-2011]

39. Among the following the maximum covalent character is shown by the compound:

(a) $FeCl_2$ (b) $SnCl_2$

(c) $AlCl_3$ (d) $MgCl_2$

[AIEEE-2011]

40. Ortho-nitrophenol is less soluble in water than p-and m-nitrophenols because:

(a) O-nitrophenol is more steam volatile than those or m-and p-isomers.

(b) O-nitrophenol shows intramolecular H-bonding

(c) O-nitrophenol shows intermolecular H-bonding

(d) Melting point of O-nitrophenol is lower than those of m-and p-isomers.

[AIEEE-2012]

41. In which of the following pairs the two species are not isostructural?

(a) $CO_3^{2-}$and NO^-_3

(b) PCl^+_4 and $SiCl_4$

(c) PF_5 and BrF_5

(d) AlF_6^{3-} and SF_6

[AIEEE-2012]

42. Which one of the following molecules is expected to exhibit diamagnetic behaviour?

(a)S_2 (b) C_2

(c) N_2 (d) O_2

[IIT-JEE Main-2013]

43. Which of the following exists as covalent crystals in the solid state?

(a) Phosphorus (b) Iodine

(c) Silicon (d) sulphur

[IIT-JEE Main-2013]

44. In which of the following pairs of molecules/ions, both the species are not likely to exist ?

(a) H_2^-, He_2^{2+} (b) H_2^+, He_2^{2-}

(c) H_2^-, He_2^{2-} (d) H_2^{2+}, He_2

[IIT-JEE Main-2013]

45. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of:

(a) $Li_2^- < Li_2 < Li_2^+$

(b) $Li_2 < Li_2^+ < Li_2^-$

(c) $Li_2^- < Li_2^+ < Li_2$

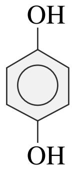
(d) $Li_2 < Li_2^- < Li_2^+$

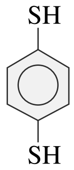
[IIT-JEE Main-2013]

46. For which of the following molecule significant $\mu \neq 0$?

(i)


(ii)


(iii)


(iv)


(a) (i) and (ii) (b) Only (iii)

(c) (iii) and (iv) (d) Only (i)

[IIT-JEE Main-2014]

47. The correct statement for the molecule, CsI_3, is:

(a) It contain Cs^+ and I_3^- ions

(b) It contains Cs^{3+} and I^- ions

(c) It contains Cs^+, I^- and lattice I_2 molecule

(d) It is a covalent molecule

[IIT-JEE Main-2014]

48. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is:

(a) ion-ion interaction

(b) ion-dipole interaction

(c) London force

(d) hydrogen bond

[JEE-Main 2015]

49. The species in which the N-atom is in a state of sp hybridisation is:

(a) NO_2^- (b) NO_3^-

(c) NO_2 (d) NO_2^+

[JEE-Main 2016]

Answer Key

LEVEL I

1. (a) 2. (c) 3. (a) 4. (a) 5. (d) 6. (d) 7. (c) 8. (b) 9. (b) 10. (c)
11. (c) 12. (a) 13. (b) 14. (b) 15. (b) 16. (c) 17. (b) 18. (a) 19. (c) 20. (c)
21. (b) 22. (c) 23. (d) 24. (d) 25. (d) 26. (d) 27. (a) 28. (b) 29. (b) 30. (c)
31. (d) 32. (b) 33. (c) 34. (c) 35. (c) 36. (a) 37. (d) 38. (a) 39. (b) 40. (a)
41. (a) 42. (b) 43. (b) 44. (d) 45. (b)

LEVEL II

1. (d) 2. (c) 3. (a) 4. (b) 5. (c) 6. (b) 7. (b) 8. (d) 9. (c) 10. (a)
11. (c) 12. (b) 13. (a) 14. (d) 15. (c) 16. (d) 17. (c) 18. (a) 19. (c) 20. (b)
21. (a) 22. (d) 23. (d) 24. (b) 25. (b) 26. (d) 27. (b) 28. (b) 29. (d) 30. (a)
31. (c) 32. (b) 33. (b) 34. (b) 35. (b) 36. (a) 37. (b) 38. (d) 39. (c) 40. (c)
41. (d) 42. (b) 43. (c) 44. (a) 45. (c)

LEVEL III

1. (a, b) 2. (a, b, c) 3. (a, b, c) 4. (a, b, c) 5. (b, c, d) 6. (a, b, d) 7. (b, d) 8. (a, b, c, d)
9. (a, b, c, d) 10. (a, c) 11. (a, b, c) 12. (a, c, d) 13. (b, c, d) 14. (a, b, c) 15. (b) 16. (c)
17. (c) 18. (a) 19. (d) 20. (5) 21. (9) 22. (4) 23. (4) 24. (6)
25. (3) 26. (6) 27. (5)
28. A → b; B → c; C → a,d; D → a,c
29. A → c; B → a; C → b;d; D → b,c
30. A →c,d; B → a,b,d; C → b; D → b,c

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (a) 2. (b) 3. (b) 4. (a) 5. (a) 6. (a) 7. (c) 8. (a) 9. (b) 10. (d)
11. (d) 12. (d) 13. (a) 14. (c) 15. (d) 16. (c) 17. (c) 18. (a, b, c) 19. (c) 20. (a)
21. (d) 22. (b) 23. (d) 24. (a) 25. (d) 26. (c) 27. (b) 28. (a) 29. (a) 30. (b)
31. (b) 32. (d) 33. (b) 34. (c) 35. (c) 36. (b) 37. (c) 38. (a) 39. (c) 40. (b)
41. (c) 42. (b, c) 43. (c) 44. (d) 45. (c) 46. (c) 47. (a) 48. (d) 49. (d)

Hints and Solutions

LEVEL I

1. **(a)** $\overset{+1}{M_3}PO_4$

Formula of chloride of M is MCl

2. **(c)** Due to presence of lettice, there is no free ions in NaCl hence, there is no mobility of ions.

3. **(a)** According to Fazan's rule,

smaller cation and larger anion leads more covalent character.

4. **(a)** Lattic energy $(U_0) \propto \frac{|Z^+|.|Z^-|}{r_0}$

$|Z^+|$ and $|Z^-|$ are magnitude of charge of cation and anion.

$r_0 \approx r^+ + r^-$

In LiF, both cation and anion are very small.

5. **(d)** Most reactive metal is Cs but Li is the strongest reducting agent among all the metals.

Only bicarbonates of Na^+, K^+, Rb^+ and Cs^+

exist in solid state.

$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2\uparrow + 1/2O_2\uparrow$

$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$

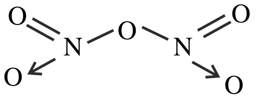
(K^+, Rb^+ or Cs^+)

Order of solubility in water :

$LiOH < NaOH < KOH < RbOH < CsOH$

6. **(d)** F can not form multiple bond. Cl and P can not form multiple bond with itself because $3p\pi - 3p\pi$ bond is not stable.

7. **(c)**



8. **(b)** In F_2 molecule,

$F \xrightarrow{\sigma} F$ (p – p end-to-end overlapping)

9. **(b)**

Species	Shape
NH_3, NF_3	Pyramidal
BF_3, BCl_3, NO_3^-	Trigonal planar
BF_4^-, NH_4^+	Tetrahedral
$BrCl_3$	‘T’-shape

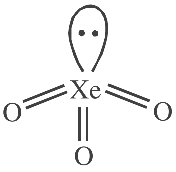
10. **(c)**

Species	lp on central atom
$XeOF_4$	1
XeO_2F_2	1
XeF_3^-	3
XeO_3	1

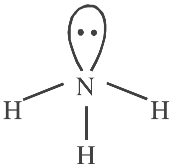
11. **(c)**

Species	Shape
XeF_4	Square planar
XeF_5^-	Pentagonal planar
$SnCl_2$	Angular or ‘v’-shape

12. **(a)** XeO_3 (Pyramidal shape)



13. **(b)**



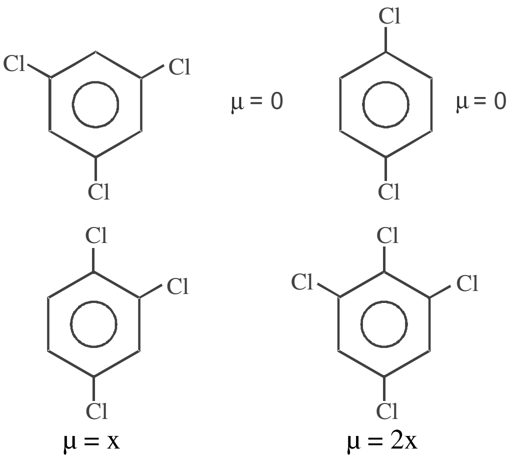
Geometry is tetrahedral, shape is pyramidal

14. **(b)** $\underset{(\approx 104.5^\circ)}{H_2O}\quad \underset{(\approx 92^\circ)}{H_2S}\quad \underset{(\approx 107^\circ.48')}{NH_3}\quad \underset{(\approx 109.5^\circ)}{SO_2}$

15. **(b)** $\underset{(\approx 109.5^\circ)}{NH_4^+} > \underset{(\approx 107^\circ 48')}{NH_3} > \underset{(<<109^\circ\cdot 5^\circ)}{NH_2^-}$

16. **(c)** If CF_4, all C–F bonds are polar but due to regular geometry it has zero dipole moment.

17. **(b)**



18. **(a)**

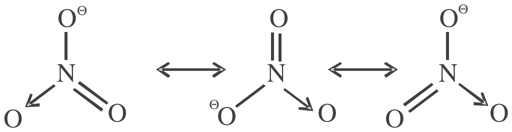
Species	lp + bp (σ)	Hybridization
IF_5	6	sp^3d^2
I^-_3	5	sp^3d
I_3^+	4	sp^3

19. **(c)** In ICl_4^-, hybridization of central atom is sp^3d^2. In sp^3d^2, axial d-orbitals $d_{x^2-y^2}$ and d_{z^2} participates.

20. **(c)** General order of melting point:
Covalent network solid > Ionic solid > Metallic solic > molecular solid.

21. **(b)** OF_4 does not exist becuase, due to absence of d-orbitals ‘O’ can form only 2 covalent bonds.

22. **(c)**



23. **(d)**

$$\underset{\text{(Molecular with van der Waal's force of attraction)}}{C_2H_6} < \underset{\text{(Molecular with H–bond)}}{CH_3OH} < \underset{\text{(Ionic)}}{KCl} < \underset{\text{(Covalent network)}}{Si}$$

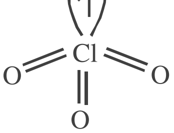
24. **(d)** Hybridisation of ‘O’ in H_3O^+ is sp^3.

25. **(d)** Bond length directly depends on size of atoms.

26. **(d)** $\underset{\substack{\text{'V'–shape}\\\text{(Planar)}}}{I_3^+}\quad \underset{\substack{\text{Linear}\\\text{(Planar)}}}{I_3^-}$

27. **(a)** In I_2 solid, I_2 molecules are attached by London forces (because I_2 is a non-polar molecule)

28. **(b)** In ClO_3, all Cl–O bonds are double bond.



29. **(b)**

Species	Shape
XeF_5^-	Pentagonal planar (6 atoms are in XY-plane)

SF_6.	Octahedral (5 atoms are in XY-plane)
IF_7.	Pentagonal bipyramidal (6 atoms are in XY plane)

30. **(c)**

Shape	**Possible hybridisation**
Pentagonal planar	sp^3d^3
Trigonal planar	sp^2
Linear	sp, sp^3d
Square planar	dsp^2, sp^3d^2

31. **(d)** In SO_2, $2p\pi–3p\pi$ and $2p\pi–3d\pi$ bonds are present.

32. **(b)** ML_5 must be pentagonal planar with 5 bond pair and 2 lone pair around M.

33. **(c)**

Species	**lp + bp (σ)**	**Hybridisation**
I_3^-, XeF_2, SF_4	5	sp^3d
X_eF_4	6	sp^3d^2
ClO_3^-, PO_4^{3-}	4	sp^3
ClO_3^+	3	sp^2

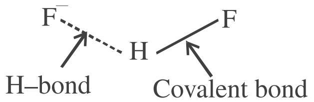
34. **(c)**

Species	**Shape**
SF_4	see-saw
XeO_4	Tetrahedral
XeF_4, ICl_4^-	Square planar

35. **(c)** In ClF_3, Cl has 10 electrons in its valence shell after sharing.

36. **(a)** H – O – N = O

37. **(d)** K^+ ionic HF_2^-



38. **(a)** Dipole moment of CH_4 is zero (it has regular geometry).

NF_3, NH_3 and H_2O have non-zero dipole moment becuase they have irregular geometry.

39. **(b)** SO_2 is polar because it has irragular geometry.

40. **(a)**

Species	**lp + bp(s)**	**Hybridisation**
PCl_5	5	sp^3d
PCl_4^+	4	sp^3
PCl_6^-	6	sp^3d^2

41. **(a)** Due to intramolecular H-bond, O-hydroxybenzaldehyde has weaker intermolecular bonding hence, it has higher vapour pressure than p-hydroxybenzaldehyde.

42. **(b)**

Species	**Bond order**
O_2^{-2}	1
O_2^-	1.5
O_2^+	2.5
O_2	2

43. **(b)** N_3^- has linear structure. It is called as pseudo halogen. Oxidation state of 'N' is –1/3. Number of electrons in N_3^- and NO_2 are 22 and 23 respectively.

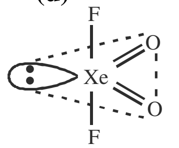
44. **(d)** Only H_2O and H_2O_2 can form H-bond.

45. **(b)** Order of strength of bond:

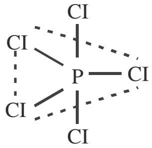
Ion-dipole > Dipole-dipole > Dipole-induced dipole > London force

LEVEL II

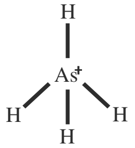
1. **(d)**



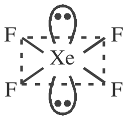
(4 atoms in same plane)



(4 atoms in same plane)

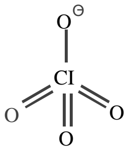


(3 atoms in same plane)

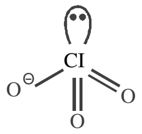


(5 atoms in same plane

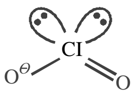
2. **(c)**



BO = 1.75



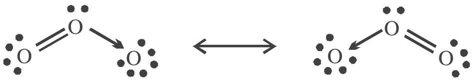
BO = 1.67



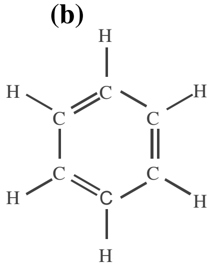
BO = 1.5

BO = 1

3. **(a)**



4. **(b)**



6, sp^2 – s sigma bonds are present

5. **(c)**

Species	**Shape**
NO_2^+	linear
NO_2^-	'V'– shape
PCl_5	Trigonal bipyramidalr
BrF_5	Square pyramidal
X_eF_4, ICl_4	Square planar
$TeCl_4$	See-saw
XeO_4	Tetrahedral

6. **(b)**

$$\underset{sp^3}{NH_3} + H^+ \longrightarrow \underset{sp^3}{NH_4^+}$$

$$\underset{\substack{\text{or}\\ \underset{sp^2}{\underline{B}}(OH)_3}}{H_3BO_3} + OH^- \longrightarrow [\underset{sp^3}{\underline{B}}(OH)_4]^-$$

$$\underset{sp^3}{\underline{N}}H_3 \longrightarrow \underset{sp^3}{\underline{N}}H_2^- + H^+$$

$$H_2\underset{sp^3}{\underline{O}} + H^+ \longrightarrow H_3\underset{sp^3}{\underline{O}}^+$$

7. **(b)**

order of repulsion is :

$\ell p - \ell p > \ell p - bp > bp - bp$

As number of ℓp on central atom increases, bond angle decreases.

The number of ℓp on O in H_2O is 2 while on N in NH_3 is 1. The structures of xenon fluorides and xenon oxofluorides could be explained on the basis of VSEPR theory.

8. **(d)**

Species	Bond angle
O_3	≈ 116°
I_3^-	180°
NO_2^-	< 120°
PH_3	≈ 93.8°

9. **(c)** NF_3 has irregular geometry while BF_3 has regular geometry.

10. **(a)** Order of melting point:

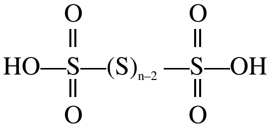
$H_2O > H_2Te > H_2Se > H_2S$

$NH_3 > BiH_3 > SbH_3 > AsH_3 > PH_3$

$HI > HF > HBr > HCl$

11. **(c)** ICl is polar and Br_2 is non-polar

12. **(b)**



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(S)_{n-2}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Total number of S-S bonds = (n – 1)

13. **(a)** Electron density of π-bond is present above and below of internuclear axis, not in the molecular plane.

14. **(d)** Order of lattice energy :

$MgO > KCl$

$LiF > LiBr$

$Mg_3N_2 > NaCl$

15. **(c)** Size of O < size of C

16. **(d)** $2p_x + 2p_x \longrightarrow \pi\text{-bond}$

$3d_{xy} + 3d_{xy} \longrightarrow \delta\text{-bond}$

$2s + 2p_y \longrightarrow \text{no bond}$

17. **(c)** $H_2O + \underset{sp}{\underline{C}}O_2 \rightarrow H_2CO_3 \text{ or } (HO)_2\,\underset{sp^2}{\underline{C}}O$

$H_3\,\underset{sp^2}{\underline{B}}O_3 + OH \rightarrow [\,\underset{sp^3}{\underline{B}}(OH)_4]^-$

$BF_3 + \underset{sp^3}{\underline{N}}H_3\,H_3 \rightarrow [H_3\,\underset{sp^3}{\underline{N}} \rightarrow BF_3]$

18. **(a)**

Species	Shape
SO_3^{2-}, NH_3	Pyramidal
SO_3, NO_3^-, CO_3^{2-}	Trigonal planer

19. **(c)** Correct order of bond angle:

$NH_3 > PH_3 > AsH_3 > SbH_3$

$Cl_2O > H_2O > OF_2$

$H_3O^+ > H_3S^+ > H_3Se^+ > H_3Te^+$

$BF_3 = BCl_3 = BBr_3 = BI_3$

20. **(b)**

Species	Shape
$[XeF_3]^+$	Bent T-shape
$[XeF_5]^+$	Squar pyramidal

21. **(a)** Order of melting point:

$CaF_2 > CaCl_2 > CaBr_2 > CaI_2$

22. **(d)** Correct order of melting point is,

$NaF < CaF_2 < AlF_3$ (depends on lattice energy)

23. **(d)**

$$CaO \xcancel{\xrightarrow{\Delta}} Ca + \frac{1}{2}O_2\uparrow$$

(Metal oxides have very high thermal stability)

24. **(b)** Order of electronegativity:

$sp > sp^2 > sp^3$

order of bond angle between same hybrid orbitals:

$sp > sp^2 > sp^3$

25. **(b)** Both ICl_2^- and $BeCl_2$ have linear shape but they have different hybridisation of central atom.

ICl_2^-	$BeCl_2$
sp^3d	sp

26. **(d)** $S + p_x \longrightarrow$ no bond

$p_y + p_z \longrightarrow$ no bond

27. **(b)** SrC_2 $(Sr^{+2} - {}^{-}C \equiv C^{-})$

28. **(b)** Due to regular geometry, BF_3 has zero dipole moment.

NH_3 has higher dipole moment than NF_3 because in NH_3 lp moment supports dipole moment while in NF_3 lp moment opposes dipole moment.

29. **(d)** In sp^3d^2 hybridisation (octahedral geometry), 12, 90° angles are observed between bp - bp of electrons.

30. **(a)** Order of bond angle:

SO_3	>	SO_2	>	SO_3^{2-}
(120°)		(≈ 109.5°)		(< 109.5°)

31. **(c)** $N_2 \longrightarrow N_2^+$

$1e^-$ is removed from σ_{2p_x} or σ_{2p_y} or σ_{2p_z}

$O_2 \longrightarrow O_2^+$

$1e^-$ is removed from $\pi^*_{2p_x}$ or $\pi^*_{2p_y}$ or $\pi^*_{2p_z}$

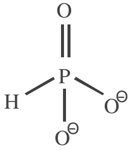
32. **(b)** Order of bond length:

	H_2O_2	>	O_3	>	O_2
(Bond order =	1		1.5		2)

33. **(b)** MgO has high lattice energy

34. **(b)** Fe^{+3} has greater polarising power than Fe^{+2}.

35. **(b)** K_2HPO_3 $(2K^+ HPO_3^{-2})$



36. **(a)** HF forms KHF_2 because HF can form H-bond.

37. **(b)** 'O' forms covalent bond with 2 H-atoms and H-bond with 2 H-atoms.

38. **(d)** $E \propto \frac{1}{r^3}$ (This relation is valid for dipole-dipole interaction)

H-bond is a type dipole - dipole interaction

39. **(c)** Cu is a metallic substance.

For metallic substance heat of vapourisation is lower than for covalent network substance like diamond.

40. **(c)** Strength of London dispersion forces depends on molecular mass.

41. **(d)** In this compound, intermolecular H-bond, intramolecular H-bond and van der Waal's force, all are present.

42. **(b)** Ion-dipole interaction is stronger than H-bond.

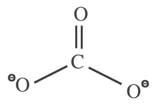
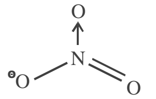
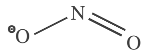
43. **(c)** In BF_3, $p\pi - p\pi$ back bonding is present.

44. **(a)** Hybridization involves the mixing of atomic orbitals of the atom at the time of their participation in bonding.

45. **(c)** Covalent network substance (SiC) has high melting point.

LEVEL III

1. **(a, b)**

Species	Structure	Bond order
CO_3^{-2}		1.33
NO_3^-		1.33
NO_2^-		1.5
NO		1.5

2. **(a, b, c)**

In CH_4,

C (I excitation) 2s $\boxed{\uparrow}$ 2p $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$

In BF_3,

B (I excitation) 2s $\boxed{\uparrow}$ 2p $\boxed{\uparrow\,|\,\uparrow\,|\;\;}$

In ICl_3,

I (I excitation)

5s $\boxed{\uparrow\downarrow}$ 5p $\boxed{\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow}$ 5d $\boxed{\uparrow\,|\;\;|\;\;|\;\;|\;\;}$

In PCl_3,

P (Ground state) 3s $\boxed{\uparrow\downarrow}$ 3p $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$

3. **(a, b, c)**

Species	Molecular shape
NO_2^+	Linear
XeF_2	Linear
I_3^-	Linear
I_3^+	'V'-shape

4. **(a, b, c)**

NO, NO_2 and ClO_2 are odd e^- molecules.

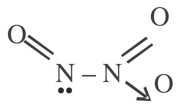
5. **(b, c, d)**

Cause of a particular physical state of a molecular compound is strength of intermolecular bonding not intramolecular bonding

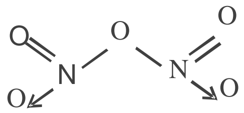
6. **(a, b, d)**

N_2O $\quad \ddot{N} \equiv N \rightarrow \underset{\cdot\cdot}{\ddot{O}}:$

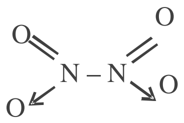
N_2O_3



N_2O_5



N_2O_4



7. **(b, d)**

$\underset{sp^3}{\underline{N}H_3} + H^+ \rightarrow \underset{sp^3}{\underline{N}H_4^+}$

$\underset{sp^2}{\underline{Al}H_3} + H^- \rightarrow \underset{sp^3}{\underline{Al}H_4^-}$

$\underset{sp^3}{\underline{N}H_3} \rightarrow \underset{sp^3}{\underline{N}H_2^-} + H^+$

$\underset{sp^3}{\underline{Si}F_4} + 2F^- \rightarrow \underset{sp^3d^2}{\underline{Si}F_6^{-2}}$

8. **(a, b, c, d)**

e^- density of σ-bond lies on the internuclear axis. e^- density of π-bond lies on the either side of internuclear axis. Direction of a covalent bond is decided by σ-bond.

Order of strength of π-bond :

$2p_\pi - 2p_\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi$

9. **(a, b, c, d)**

In all these compounds H-atom is attached with highly electronegative atom.

10. **(a, c)**

SF_6 has octahedral geometry (Non-planar)

In SF_6, 'S' has $12e^-$ in outermost shell after sharing hence, it does not acquire e^- configuration of Ar gas.

11. **(a, b, c)**

The correct order of boiling point is:

$CH_4 < SiH_4 < GeH_4$

12. **(a, c, d)**

'O' can form only 2 covalent bonds hence, OF_4 does not exist.

'N' can form only 3 covalent bonds hence,

NCl_5 does not exist.

In octahedral geometry 3lp are not possible hence ICl_3^{2-} does not exist.

13. **(b, c, d)**

Ionic compounds have high melting point, boiling point, solubility in polar solvents and have non-directional bonds.

14. **(a, b, c)**

Order of stability :

$O_2^+ > O_2 > O_2^-$

Bond order = 2.5 2 1.5

He_2 does not exist because bonding and antibonding electrons are equal.

In C_2, O_2^{2-} and Li_2, all molecular orbitals are paired hence, they are diamagnetic.

In F_2, the energy of σ_{2p_z} is less than π_{2px} and π_{2py}.

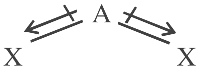
15. **(b)** $\underset{\text{Bond order=3}}{N_2} \rightarrow \underset{\text{Bond order=2.5}}{N_2^+}$

$\underset{\text{Bond order=2}}{O_2} \rightarrow \underset{\text{Bond order=2.5}}{O_2^+}$

16. **(c)** Let the bond moment of A–X bond = x

The dipole moment of AX_2 =

$\sqrt{x^2 + x^2 + 2x^2(\cos 120°)} = x$



17. **(c)** Dipole moment of IF_7 is zero hence, IF_7 is non-polar.

18. **(a)** In sp^3d^2 hybridisation, $d_{x^2-y^2}$ and d_{z^2} are involved.

19. **(d)** In sp^3d hybridisation d_{z^2} is involved.

20.

$p_y - p_y \longrightarrow$ σ-bond

$p_x - p_x \longrightarrow$ π-bond

$p_z - p_z \longrightarrow$ π-bond

$d_{xy} - d_{xy} \longrightarrow$ π-bond

$d_{yz} - d_{yz} \longrightarrow$ π-bond

$p_x - d_{xy} \longrightarrow$ π-bond

$d_{xy} - d_{xz} \longrightarrow$ δ-bond

$d_{xy} - p_z \longrightarrow$ no-bond

21.

$CO_3^{-2}, NO_3^-, NO_2^- \rightarrow p\pi - p\pi$

$SO_3^{-2}, SO_4^{-2}, PO_4^{-3}, S_2O_8^{-2}, R_3PO, S_2O_3^{-2}, ClO_4^-, ClO_3^-, SO_2 \rightarrow p\pi - d\pi$

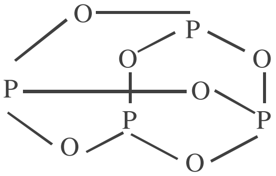
22.

Species	**Bond order**
N_2^+	2.5
N_2^-	2.5
O_2	2
O_2^+	2.5
F_2	1
B_2	1
C_2^+	1.5
CN^-	3
NO^+	3

23. In P_4O_{10},

4, P = O	(Shorter bonds)
12, P – O	(Longer bonds)

24. 6, P – O – P bonds are present.



25.

Molecules	**Nature**
PF_3Cl_2	Polar
SF_4	Polar
PCl_5	Non-polar
PCl_3F_2	Non-polar
SF_6	Non-polar
XeF_2	Non-polar
NO_2^+	Non-polar
BF_2Cl	Polar
BF_3	Non-polar

26. NH_3, H_2O, HF, HCOOH, $B(OH)_3$ and CH_3COOH have hydrogen bonding.

27. PCl_5, SF_4, ClF_3, $[ClF_4]^+$, $[XeF_3]^+$ → all bond lengths are not equal

XeF_2, $[SF_5]^+$, O_3, P_4 → all bond lengths are equal

28. [A → (b); B → (c) ; C → (a),(d) ; D → (a), (c)]

29. [A → (c); B → (a) ; C → (b),(d) ; D → (b), (c)]

30. [A → (c, d); B → (a, b, d) ; C → (b) ; D → (b), (c)]

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **(a)** Order of boiling point is:

$H_2O > H_2Te > H_2Se > H_2S$

2. **(b)**

	ℓp + bp (σ)	**Hybridisation**
NO_2^+	2	sp
NO_3^-	3	sp^2
NH_4^+	4	sp^3

3. **(b)**

	ℓp + bp (σ)	**Hybridisation**
NH_3	4	sp^3
PCl_5	5	sp^3d
BCl_3	3	sp^2

In $[PtCl_4]^{2-}$, hybridisation of Pt is dsp^2.

4. **(a)** They all have 14 e^- and bond order 3.

5. **(a)** $H_3N \longrightarrow BF_3$

Or

$H_3\underset{sp^3}{\overset{\oplus}{N}} - \underset{sp^3}{\overset{\ominus}{B}}F_3$

6. **(a)** Electron density of π-bond is present above or below of the molecular plane.

7. **(c)** O_2^- is an odd e^- species. It has 1 unpaired e^-.

8. **(a)** Both NO_3^- and CO_3^{2-} have 32 e^- and they have trigonal planar shape.

9. **(b)**

	Bond order	**Magnetic character**
O_2	2	paramagnetic
O_2^+	2.5	paramagnetic

10. **(d)**

	Number of lp on central atom
ClO_3^-	1
XeF_4	2
SF_4	1
I_3^-	3

11. **(d)** Hybridisation of P in P_4 is sp^3.

12. **(d)** Anion of KO_2 is O_2^- (superoxide). O_2^- is an odd e^- species.

13. **(a)**

	Bond order
CO	3
NO^-	2
NO^+	3
CN^-	3
N_2	3

14. **(c)** In XeO_3, Xe has 1 *l*p and 3 bp (σ).

Hence, its shape is pyramidal.

15. **(d)** p-hydroxybenzoic acid has intermolecular H-bond while O-hydroxybenzoic acid has intramolecular H-bond. Due to intermolecular H-bond, intermolecular bond becomes weaker hence, p-isomer has greater boiling point than O-isomer.

16. **(c)** In water, orthoboric acid behaves as OH^- acceptor

$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$

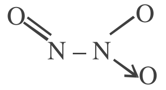
Or

$B(OH)_3$

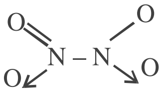
17. **(c)** For heavier members of group 14, due to inert pair effect, lower oxidation state is more stable.

18. **(a, b, c)**

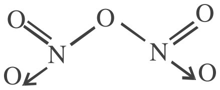
$N = N \rightarrow O$ (N_2O)



(N_2O_3)



(N_2O_4)

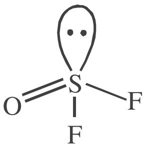


(N_2O_5)

19. **(c)** Bond energy of C–C bond ≈ 100 kCal mol^{-1}.

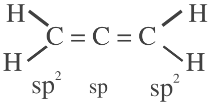
20. **(a)** If Hund's rule is not followed then Bond order of B_2 is 1 and it is diamagnetic

21. **(d)**

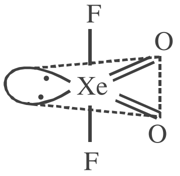


(Pyramidal shape)

22. **(b)**



23. **(d)**



(see-saw shape)

24. **(a)** $AlH_3 \longrightarrow AlH_4^-$

sp^2 sp^3

$H_2O \longrightarrow H_3O^+$

sp^3 sp^3

$NH_3 \longrightarrow NH_4^+$

sp^3 sp^3

25. **(d)** After sp^3d^2 hybridisation, geometry is octahedral. In octahedral geometry.

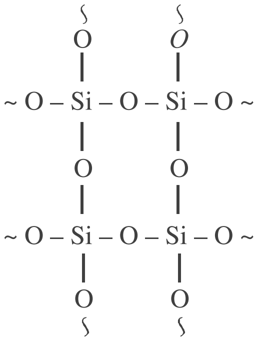
12, 90° angles are present.

26. **(c)** Order of melting point :

$NaCl > KCl > RbCl > LiCl$

27. **(b)** CaC_2 (Ca^{+2} $^{\ominus}C \equiv C^{\ominus}$)

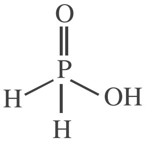
28. **(a)**



29. **(a)**

Molecule	*l*p on central atom	Shape
SF_4	1	see-saw
CF_4	0	Tetrahedral
XeF_4	2	Square planar

30. **(b)** Hypophosphorus acid (H_3PO_2)



31. **(b)** As bond length increases, bond breaking becomes easier.

32. **(d)** Order of bond angles :

$NH_3 > PH_3 > AsH_3 > SbH_3$

33. **(b)** NO $\longrightarrow$ NO^+

Bond order : 2.5 3

Magnetic character : paramagnetic Diamagnetic

34. **(c)** Order of polarizing power :

$K^+ < Ca^{+2} < Mg^{+2} < Be^{+2}$,

Polarising power $\propto \frac{1}{\text{size of ion}}$

35. **(c)** Due to pπ–pπ back bonding, B – F bond has partial π-character hence, its bond energy becomes more than expected.

36. **(b)**

	*l*p + bp(σ)	Hybridisation
NO_3^-	3	sp^2
NO_2^+	2	sp
NH_4^+	4	sp^3

37. **(c)** Order of bond angle:

$NCl_3 > PCl_3 > AsCl_3 > SbCl_3$ (Order depends on electronegativity of central atom)

38. **(a)** Due to absence of d-orbitals, 'B' can maximum form 4 bonds (3 covalent and 1 co-ordinate bond)

39. **(c)** Covalent character ∝ polarising power of cation

∝ charge density of cation

40. **(b)** Due to intramolecular H-bond, O-nitrophenol is less soluble in water.

41. **(c)**

Species	**Molecular shape**
CO_3^{2-}, NO_3^-	Plane triangle
PCl_4^+, $SiCl_4$	Tetrahedral
PF_5	Trigonal bipyramidal
BrF_5	Square pyramidal
AlF_6^{3-}, SF_6	Octahedral

42. **(b, c)** In C_2 and N_2, all molecular orbitals are paired.

43. **(c)** Phosphorus (P_4), Iodine (I_2) and sulphur (S_8) are molecular solids while silicon (Si) is covalent network crystal.

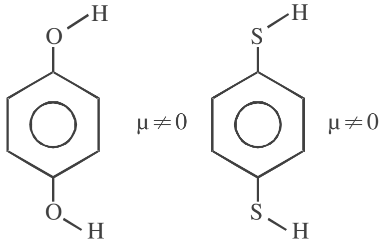
44. **(d)** H_2^{2+} has no electron and bond order of He_2 is zero.

45. **(c)**

	Molecular orbital electronic arrangement	**Bond order**
Li_2	$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2$	(4–2)/2 = 1
Li_2^+	$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^1$	(3–2)/2 = 0.5
Li_2^-	$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma^*{}_{2s}^1$	(4–3)/2 = 0.5

Both Li_2^+ and Li_2^- have similar bond order but Li_2^- has more number of antibonding e^- than Li_2^+ hence, Li_2^+, is more stable than Li_2^-.

46. **(c)**



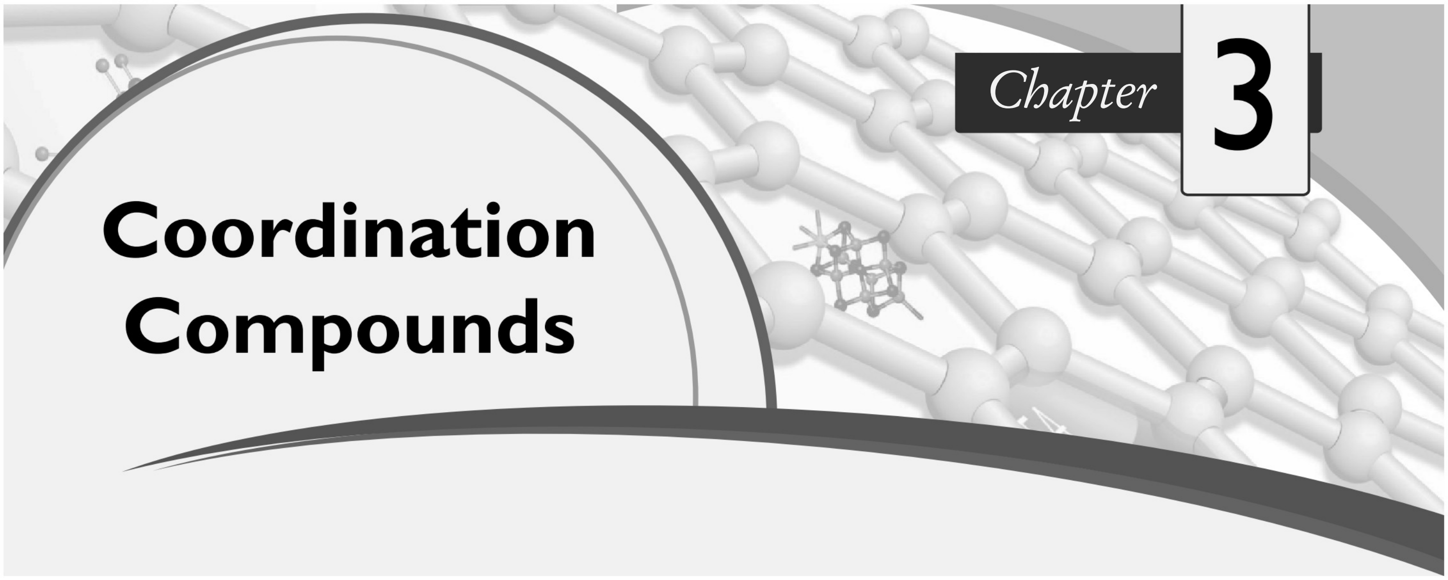
47. **(a)** $CsI_3 \longrightarrow Cs^+ + I_3^-$

48. **(d)** For dipole-dipole interaction (or, H-bond).

$$E \propto \frac{1}{r^3}$$

49. **(d)**

Species	**Hybridization**
NO_2^-	sp^2
NO_3^-	sp^2
NO_2	sp^2
NO_2^+	sp



Chapter 3

Coordination Compounds

Key Concepts

A metal atom or ion may combine with neutral molecules or anions to form a new identifiable species called a complex or coordination compound. For example, $[Co(NH_3)_6]^{3+}$ is a complex species which can be identified as a whole. The groups that surround the metal ion in a coordination compounds are called ligands. The total number of the ligands bound around a metal ion is called the coordination number of the metal ion. Ligands have been classified depending upon the number of donor atoms it has. A few examples are given below :-

Mono or Unidentate Ligand: Examples are F^-, Cl^-, Br^-, H_2O, NH_3, CN^- and NO_2^- etc.

Bidentate: Examples are ethylenediamine (en), glycinate ion (gly) etc.

Tridadentate: Examples are diethylenetriamine and 2, 2', 2”- tripyridine etc.

Tetradentate: Examples are triethylenetetrammine and ethylenebis (salicyladimine) ion.

Pentadentate: Examples is ethylenediaminetriacetate ion.

Hexadentate: Example is ethylenediamine tetracetate ion.

NOMENCLATURE OF COORDINATION COMPOUNDS

The International Union of Pure and Applied Chemistry (IUPAC) have suggested the following basic rules for naming a coordination compound.

1. The positive ion is named first followed by the negative ion.
2. When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is written first, then the coordinated group are listed in the order: negative ligands, neutral ligands, positive ligands (and alphabetically according to the first sysmbol within each group). While writing the name of a complex, the ligands are quote in alphabetical order regardless of their charges followed by the metal.
   - (a) The name of negative ligands end in '–o', e.g. fluoro (F^-), chloro (Cl^-), hydrido (H^-), thio (S^{2-}), nitro (NO_2^-) and so on.
   - (b) Neutral groups have no special endings, e.g. ammine (NH_3), aqua (H_2O), carbonyl (CO) and nitrosyl, (NO).
   - (c) Positive groups en '-ium', e.g. hydrazinium ($H_2NNH_3^+$).
3. Where there are several ligands of the same kind, we normally use the prefixes di, tri, tetra, penta and hexa to show the number of ligands of that type. For ligands already containing such number, the prefixes bis, tris and tetrakis are used to indicate the numbers of ligands. In such a case, ligand is written within the brackets immediately after the prefix.
4. The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the name without any interventing blanks, e.g. cobalt (II) and cobalt (III)

5. Complex positive ions and neutral molecules have no special ending but complex negative ions end in '-ate'.
6. If the complex contains two or more metal atoms, the bridging ligands are indicated by the prefix μ,
7. Sometimes a ligand may be attached though different atoms. For example M—NO_2 is called a nitro and M—ONO is called nitrito; M—SCN is called thicoyanato and M—NCS isothiocyanto.
8. Water or solvent of crystallization are indicated after the name of the complex, Arabic numerals are used to indicate the number of such molecules.

   A few example of naming the complex compounds are given in the following:

$[Co(NH_3)_6]Cl_3.$	Hexaamminecobalt (III) chloride
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechlorcoblat (III) ion
$[CoSO_4(NH_3)_4]NO_3.$	Tetraamminesulphatocobalt (III) nitrate
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt (III)
$Na_2[ZnCl_4]$	Sodium tetrachlorozincate (III)
$K_3[Fe(CN)_5(NO)]$	Potassium pentacyanonitrosylferrate (II)
$Fe(C_5H_5)_2.$	Bis(cyclopentadienyl) iron (II)

EXPLANATION OF FORMATION OF COORDINATION COMPOUNDS

On of the earliest theories to explain the formation of coordination compounds has given by Alfred Werner. According to him, each element exhibits two types of valencies. There is primary valency (which corresponds to the oxidation state of the central metal) and secondary valency (which represents the coordination number of the central metal). The primary valency is satisfied by anions whereas the secondary valency is satisfied by either negative ion or neutral molecules. The primary valencies are shown by dotted lines while secondary valencies by solid lines. The secondary valencies are always directed towards fixed positions in space giving a definite geometry to the complex.

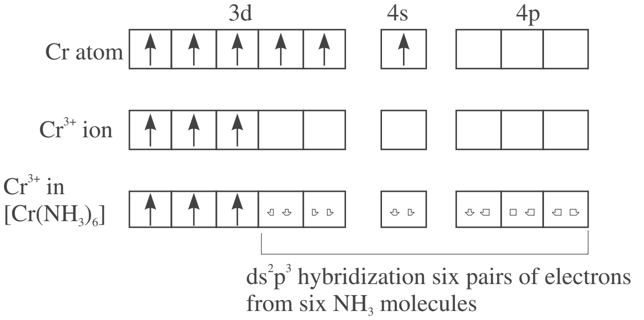
Modern theories to explain the formation of complex compounds are valence-bond theory area, crystal field theory. The salient features of the valence bond theory are as follows:-

1. The central metal looses a requisite number of electrons to form the ion. The number of electrons lost is the valency of the resulting cation.
2. The cation makes available a number of orbitals equal to its coordination number, for the formation of covalent bonds with the ligands.
3. The cation orbitals hybridize to form a new set of equivalent hybrid orbitals with definite directional characteristics.
4. The nonbonding metal electrons occupy the inner d orbitals and do not participate in the hybridization.
5. Each ligand contains a lone pair of electrons. A covalent bond is formed by the overlap of vacant hybrid metallic orbitals and a filled orbital of the ligand.

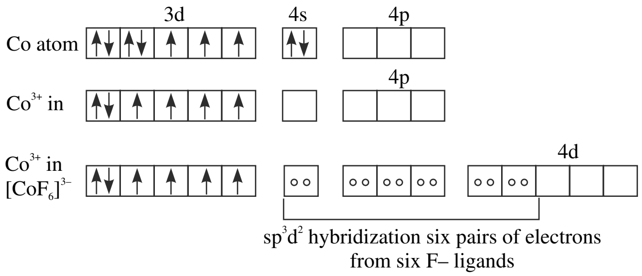
   The above rules are illustrated with the following typical examples.

$[Cr(NH_3)_6]^{3+}$

The outer electronic configuration of Cr is $(3d)^5$ $(4s)^1$. Chromium in the above complex is in +3 oxidation state, hence, Cr(III) has the configuration of $(3d)^3$. There are six ligands, so six empty orbitals of chromium are required. These include two 3d orbitals, one 4s orbital and three 4p orbitals. These orbitals hybridize to give d^2sp^3 hybrid orbitals directed towards the corners of an octahedron. The find configuration of the complex will contain three unpaired electrons in three 3d orbitals of chromium. Hence, the complex will be paramagnetic. The above description is diagrametically represented as follows:

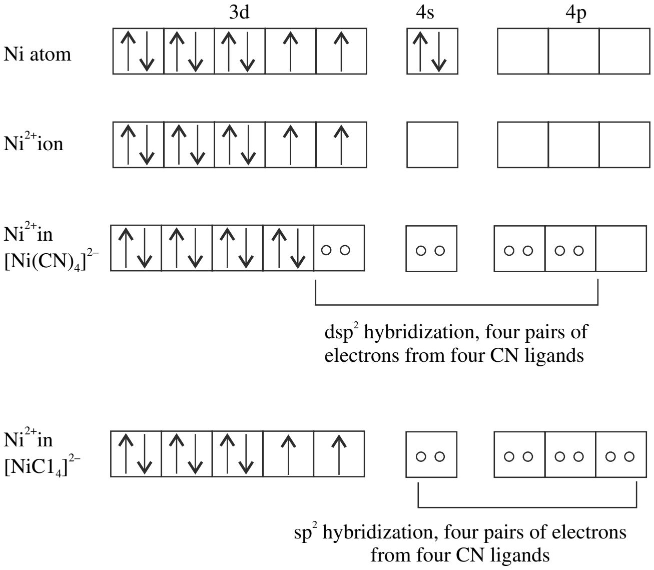


$[CoF_6]^{3-}$



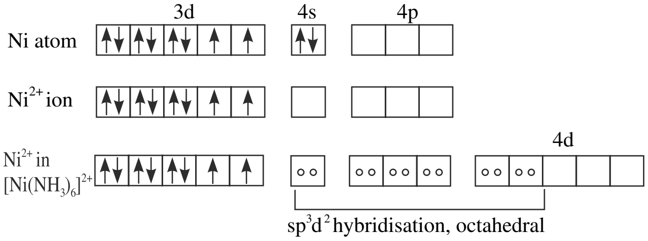
The complex $[CoF_6]^{3-}$ is octahedral and is strongly paramagnetic.

$[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$



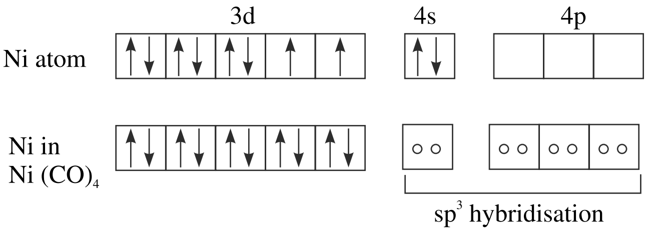
$[Ni(CN)_4]^{2-}$ is a square planar (dsp^2 hybridisation) and diamagnetic (no unpaired electrons) while $[NiCl_4]^{2-}$ is tetrahedron (sp^3 hybridisation) and paramagnetic (two unpaired electrons). The CN^- ligand is strong and it forces the two unpaired electrons to pair up.

$[Ni(NH_3)_6]^{2+}$



$[Ni(NH_3)_6]^{2+}$ has an octahedral structure and is paramagnetic (two unpaired electrons).

$Ni(CO)_4$



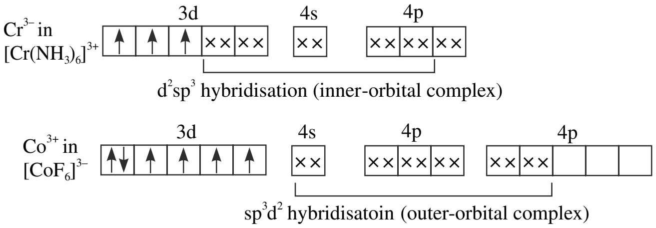
$Ni(CO)_4$ has a tetrahedral structure and is diamagnetic (no unpaired electrons).

INNER AND OUTER ORBITAL OCTAHEDRAL COMPLEXES

In the inner orbital octahedral complexes d^2sp^3 hybridisation in the central metal occurs while in the outer orbital complexes sp^3d^2 hybridisation is involved.

The inner orbital complexes involve lesser number or unpaired electrons and thus these are known as low-spin complexes. On the other hand, the outer orbital complexes involve comparatively larger number of unpaired electrons and thus are known as high-spin complexes.

Example $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridisation while $[CoF_6]^{3-}$ involves sp^3d^2 hybridisation.



For octahedral complexes,

$d^0 - d^3 \xrightarrow{\text{SFL/WFL}} d^2sp^3$ (Inner-orbital complexes)

$d^4 - d^7 \xrightarrow{\text{SFL}}$ (Pairing occurs) d^2Sp^3 (inner orbital/low spin complex)

$\xrightarrow{\text{WFL}} Sp^3d^2$ (outer orbital/high spin complex)

$d^8 - d^{10} \xrightarrow{\text{SFL/WFL}} Sp^3d^2$ (Outer-orbital complexes)

Exceptions of above rule are :-

$\underset{d^2sp^3}{[Co(OX)_3]^{-3}}$, $\underset{d^2sp^3}{[Co(H_2O)_6]^{+3}}$, $\underset{d^2sp^3}{[NiF_6]^{-2}}$, $\underset{sp^3d^2}{[Mn(NH_3)_6]^{+2}}$, $\underset{sp^3d^2}{[Fe(NH_3)_6]^{+2}}$

Isomerism in coordination compounds

Coordination compounds exhibit various types of isomerism. A brief description of these are as follows:-

Ionization Isomerism

The isomers involving the exchange of ligand in the coordination sphere and the anion present outside the coordination sphere are known as ionization isomers. For example, $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)Br$.

Linkage Isomerism

The isomers involving the attachment of different donor atom of a ligand to the metal in the coordination sphere are known as linkage isomers. For example $[Co(NH_3)_5(NO_2)]CI_2$ and $[Co(NH_3)_5(ONO)]CI_2$

Coordination Isomerism

The isomers involving the exchange of ligands between the complex catoin and complex anion of a complex compound are known as coordinate isomers. For example, $[Cr(NH_3)_6]^{3+}[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}[Cr(CN)_6]^{3-}$.

HYDRATE/SOLVATE ISOMERISM

The isomers involving the exchange of H_2O molecules are known as hydrate isomers.

For example : $[Co(H_2O)_6]Cl_3$ and $[Co(H_2O)_5]Cl_2.H_2O$

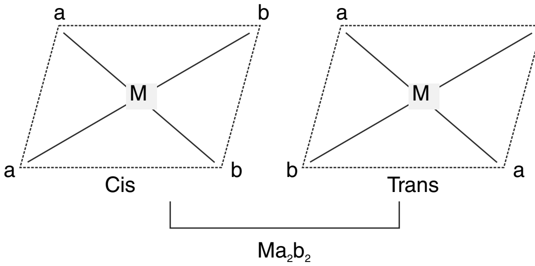
GEOMETRICAL ISOMERISM

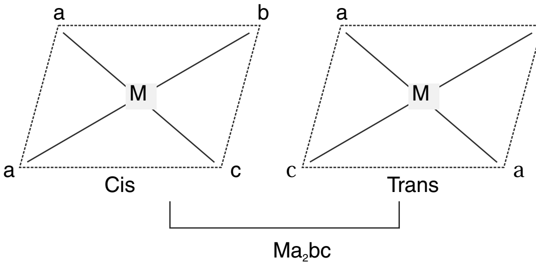
The isomers involving the different geometrical arrangement of ligands around the central metal atom are known as geometrical isomers. The two identical ligands occupying he adjacent position is known as cis isomer while those occupying the opposite by the lower case alphabets (such as a, b, c,…) and bidentate by the upper case alphabets (such as AA and AB), the geometrical isomerism in complex compounds are as follows. AA is symmetrical and AB is unsymmetrical bidentate ligand.

Geometrical isomerism in square planar complexes

The complexes $[Ma_4]$ and $[Ma_3b]$ do not exhibit geometrical isomerism.

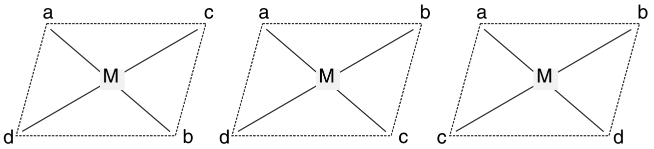
The complexes $[Ma_2b_2]$ and $[Ma_2bc]$ exhibit cis-trans isomerism.



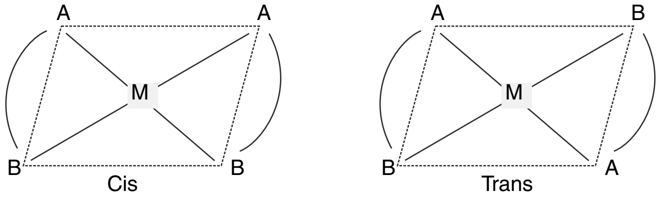


The complex [Mabcd] exists in three isomeric forms

The have different pairs of ligands at the trans positions.



The complex $[M(AB)_2]$ also exists in cis-and trans-forms.



Geometrical isomerism in Octahedral Complexes

In an octahedral complex, if the two similar ligands occupy positions at the two ends of the twelve edges of the octahedron, the complex is the cis isomer.

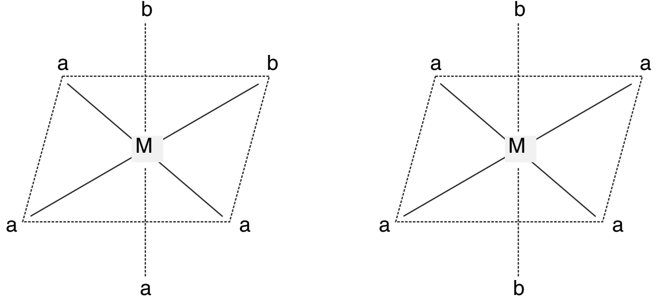
If the two similar ligands occupy positions at the end of a straight line passing through the centre of the octahedron (which is occupied by the central atom M), the complex is the trans isomer.

A brief account of geometrical isomers of a few complex compound is given below.

The complexes $[Ma_6]$, $[Ma_5b]$ and $[M(AA)_3]$ do not show geometrical isomerism.

The complexes $[Ma_4b_2]$, $[Ma_3b_3]$ and $[Ma_4bc]$ exhibit two isomers each.

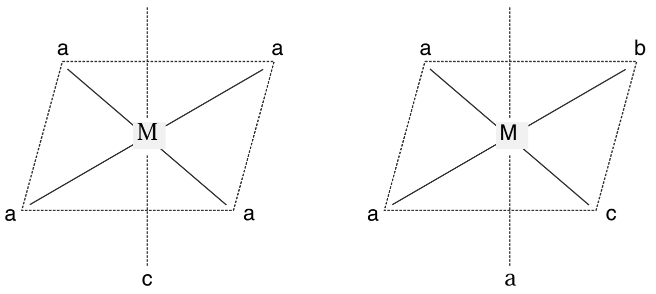
$[Ma_4b_2]$



Cis-isomer Trans-isomer

In cis-form, the two 'b' ligands have cis positions to each other. In trans-form, the two 'b' ligands have trans positions to each other.

$[Ma_4bc]$

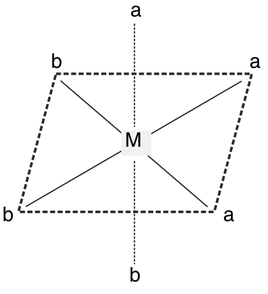


Cis-isomer Trans-isomer

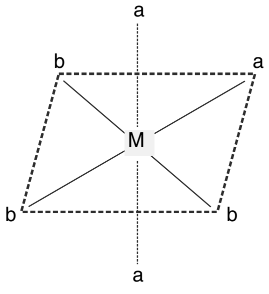
$[Ma_3b_3]$

In cis-form, the three ligands 'a' occupy positions at the corners of a triangular face and the three 'b' ligands occupy positions at the corners of the opposite face. This isomer is also known as facial (abbreviation-face) isomer

The trans-form is known as meri-donal (abbreviation-mer) isomer.

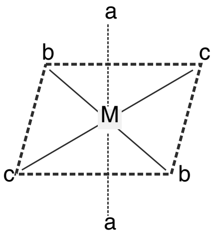


face-isomer

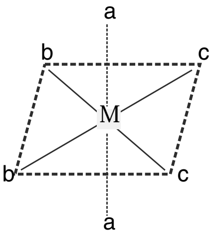


mer-isomer

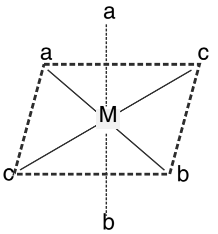
The complex $[Ma_2b_2c_2]$ exists in five geometrical isomers, (three are five ways of distributing pairs of ligands in trans positons), one of which also has its enantionmer, thus there exists a total of six isomers.



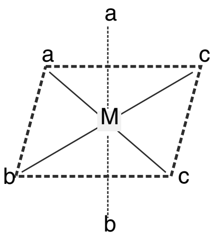
Trans positions, aa; bb; cc



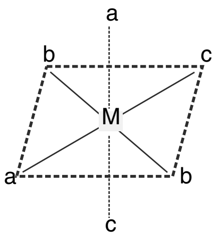
aa; bc; bc



ab; ab; cc



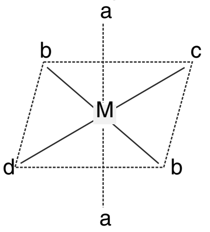
(enantiomer)
ab; ac; bc

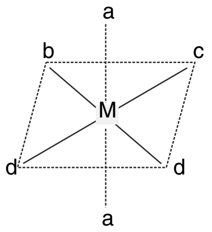


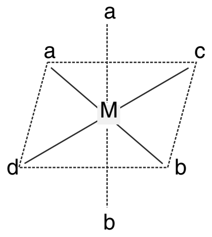
ac; bb; ac

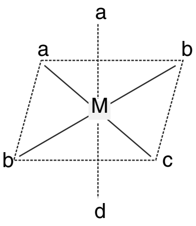
Co-ordination compounds having no plane of symmetry or centre of symmetry exists in two optically active configuration which are related to each other through the mirror image of each other and are not super-imposable on each other.

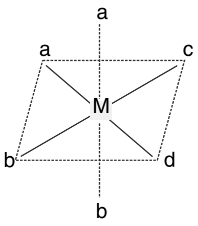
The complex $[Ma_2b_2cd]$ exhibits six geometrical isomers there are six ways of distributing pairs of ligands in trans positions, two of which have enantiomers, thus making a total of eight isomers.



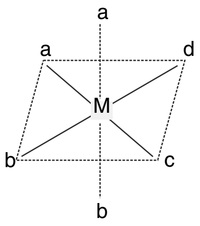








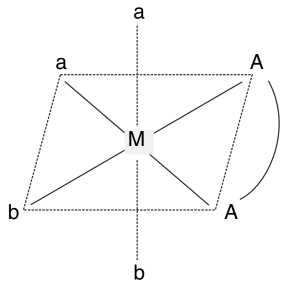
(and its enantiomer)



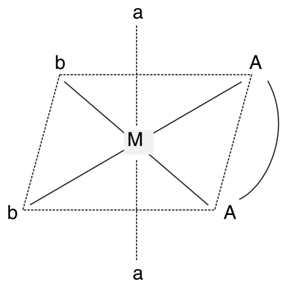
(and its enantiomer)

The complex [Mabcdef] exhibit fifteen isomers (= $^6C_2$ = 6!/(4! 2!)) all of them have their enantiomers, making a total of 30 isomers.

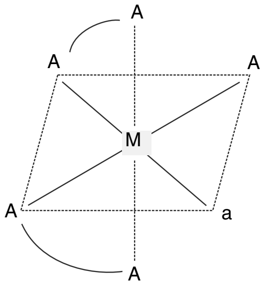
The complexes $[M(AA)a_2b_2]$, $[M(AA)_2a_2]$ and $[M(AA)_2ab]$, where AA is a symmetrical bidentate, exists in two forms, namely, cis and trans forms, of which cis form has its enantiomer.



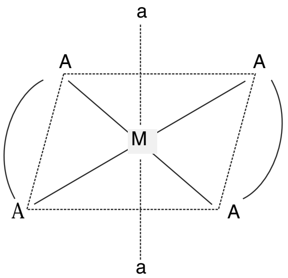
Cis-form
(and its enantiomer)



(Trans-form)



Cis-form
(and its enantiomer)



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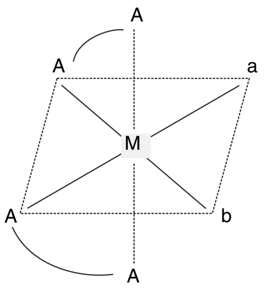
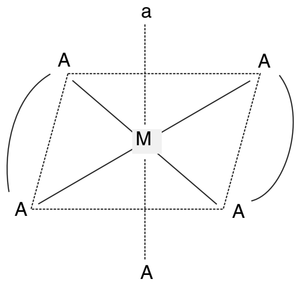
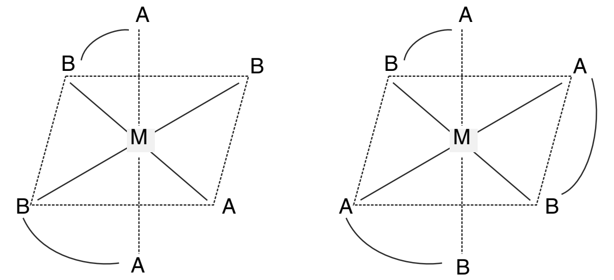


Cis-form
(and its enantiomer)



(Trans-form)

The complex $[M(AB)_3]$, where AB is unsymmetrical bidentate ligand in which A and B are two different donor atoms, exists in cis-and trans-forms. Each of the two also has its enantiomer.

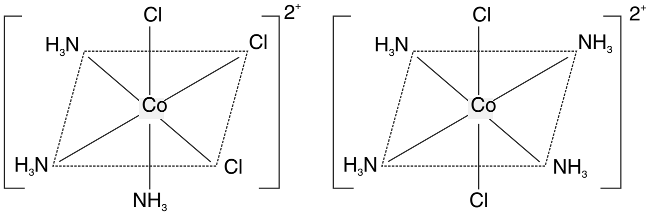


Cis-form (and its enantiomer)

Trans-form (and its enantiomer)

Example of Geometrical isomers in octahedral complexes

The cis isomers involve the two identical ligands on any of the twelve edges of the octahrdron and trans isomers involve the ligands on either end of a straight line passing through the metal.

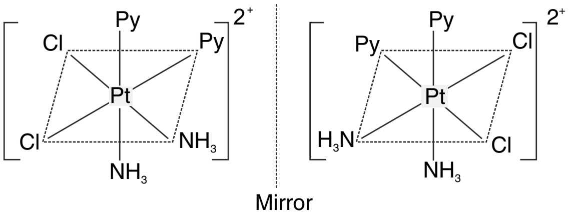


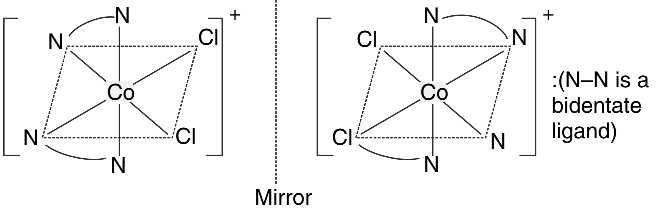
Cis-isomer

trans-isomer

Optical Isomers

A complex having no plane of symmetry or centre of inversion exists in two optically active isomers. Such a complex is said to be asymmetric. The two isomers are mirror image of each other and the are not superimposable on each other. The two have identical physical and chemical properties but differ in their action on the polarized light. Examples are





Tetrahedral Complex			
Case	Geometrical isomerism	Optical isomerism	Total number of steroisomers
Mabcd	×	✓	2
$M(AB)_2$	×	✓	2
Square Planer Complex			
Ma_2b_2	✓	×	2
Ma_2bc	✓	×	2
Mabcd	✓	×	3
$M(AB)_2$	✓	×	2
M(AB) cd	✓	×	2
Octohedral Complex			
Ma_4b_2	✓	×	2
Ma_4bc	✓	×	2
Ma_3b_3	✓	×	2
$Ma_2b_2c_2$	✓	✓	6
Ma_2b_2cd	✓	✓	8
Ma_2bc de	✓	✓	15
Mab cd ef	✓	✓	30
$M(AA)_3$	×	✓	2
$M(AA)_2b_2$	✓	✓	3
$M(AA)_2bc$	✓	✓	3
$M(AA)b_3c$	✓	×	2
$M(AA)b_2c_2$	✓	✓	4
$M(AA)b_2cd$	✓	✓	6
M (AA)bcde	✓	✓	12
$M(AB)_3$	✓	✓	4
$M(AB)_2c_2$	✓	✓	8
$M(AB)_2cd$	✓	✓	11
$M(AB)c_3d$	✓	✓	4
$M(AB)c_2d_2$	✓	✓	6
$M(AB)c_2de$	✓	✓	12
M(AB)cdef	✓	✓	24

Stability of coordination compounds

The stability of a complex compound depends on the nature of the metal and that of the ligand. In general, the higher the oxidation state of the metal, the more stable the complex. The cyano complexes are far more stable than those formed by halide ions.

The increasing order of the influence of ligands on the electronic configuration of central metal atom or ion (known as spectrochemical series) is:-

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < Ox < O^{2-} < H_2O < NH_3 < NO_2^- < CN^- < CO$$

Thus, halogens are said to be weak ligands while NO_2^-, CN^- are said to be strong ligands.

Thus stability of complexes also decreases with increases in the ionic size of the central metallic ion having the same charge number. For example, the stability of complexes formed from the same ligands increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+}, that is the order of stability is

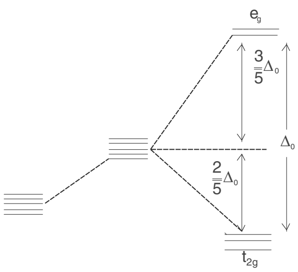
$$\underset{91\text{ pm}}{Mn^{2+}} < \underset{83\text{ pm}}{Fe^{2+}} < \underset{82\text{ pm}}{Co^{2+}} < \underset{78\text{pm}}{Ni^{2+}} < \underset{91\text{ pm}}{Cu^{2+}} > \underset{74\text{pm}}{Zn^{2+}}$$

This sequence is known as Iriving-Willam order of stability of complexes of M^{2+} ions.

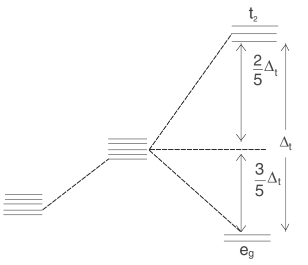
CRYSTAL FIELDS SPLITTING IN THE COMPLEXES

The ligands in a complex compound causes the splitting of d orbitals into two categories, namely, (d_{xy}, d_{xz}, d_{yz}) and (d_{z^2}, $d_{z^2-y^2}$) respectively.

In the octahedron environment, d_{xy}, d_{xz} and d_{yz} (known as t_{2g} orbitals) have lower energy than in $d_{x^2-y^2}$ and d_{x^2} (known as e_g orbitals). In the tetrahedron environment, the reverse is observed, that is e_g have lower energy than t_{2g}.



Octahedron arrangement of ligands



Tetrahedral arrangement of ligands

The difference in energy levels is represented at Δ_0 and is set equal to 10 D. This energy difference is known as crystal field splitting energy. The extent of splitting depends upon the influence power of the ligands. For a strong ligand, the splitting is large whereas for a weak ligand, the splitting is small. As mentioned earlier, the influence power of ligands arranged in increasing order is known as spectrochemical series.

Since for a strong ligand, splitting is large, they form low-spin complexes as the electrons occupy first t_2g level followed by e_g. depending upon the 3d electrons of metal ion. If the ligand is weak, splitting is small, all the five d-orbitals are singly occupied followed by double occupancy and the complex formed is the high-spin complex.

COLOUR

Many ionic and covalent compounds of transition elements are coloured. When light passes through a material, it absorbs some of the wavelengths due to electronic excitation. If absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complimentary colour to the light absorbed. The material looks coloured corresponding to the transmitted light.

In transition elements, the electronic excitation is due to d-d electronic excitation. In an isolated metal ions, d-orbitals are degenerate. This degeneracy is lost when the ligands approach the metal ion. The energy of some of d-orbitals is lowered while of the remaining orbitals the energy is raised. Electrons occupy the orbitals of lower energy and ca be excited to higher ones with the absorption of wavelength which lies in the visible region.

In some complexes, cause of colour is charge transfer spectra. It is of three types :-

(a) $L \rightarrow M$ charge transfer. For example:
MnO_4^-, MnO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, etc.

(b) $M \rightarrow L$ charge transfer. For example: $[Fe(C_5H_5)_2]$, $[Fe(CO)_5]$, etc.

(c) $M \rightarrow M$ charge transfer. For example:
$Fe_4[Fe(CN)_6]_3$, etc.

Solved Examples

1. Select the incorrect statement:

(a) Hydrazine can act as bidentate ligand.
(b) Oxalate is a chelating ligand.
(c) All bidentate ligands are chelating ligands.
(d) Number of chelate rings = (denticity – 1)

Sol.(a) Hydrazine ($H_2N - NH_2$) is a monodentate ligand. All bidentate ligands are chelating ligands, oxalate is a bidentate ligand.

2. Aqueous solution of Mohr's salt gives a positive test for:

(a) Ferrous ions only
(b) Sulphate ions only
(c) Ammonium and sulphate ions only
(d) Ferrous, ammonium and sulphate ions

Sol.(d) Mohr's salt ($FeSO_4.(NH_4)_2SO_4.\ 6H_2O$) is a double salt. Aqueous solution of a double salt gives a positive test of all constituent ions.

3. Chelating ligands among following are :

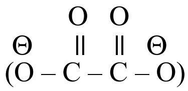
(i) dien (ii) $C_2O_4^{2-}$
(iii) gly (iv) py
(v) dipy

(a) i, ii, iv, v (b) i, ii, iii, v
(c) i, ii, iii, iv (d) i, iii, iv, v

Sol.(b) All polydentate ligands are chelating ligands

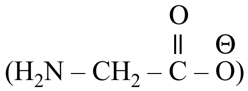
dien
$(H_2NCH_2CH_2NHCH_2CH_2NH_2)$

$C_2O_4^{2-}$



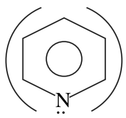
$$(\overset{\ominus}{O}-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O})$$

gly

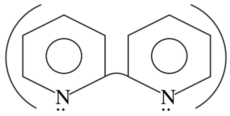


$$(H_2N-CH_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O})$$

py



dipy



4. On the basis of sidgwick EAN rule, which of the following statement is not correct?

(a) $[Mn(CO)_6]$ can act as reducing agent.
(b) $[V(CO)_6]$ can act as oxidising agent.
(c) $[Fe(CO)_5]$ can act as both oxidising agent and reducing agent.
(d) $[Mn(CO)_5]$ show dimerisation to gain stability.

Sol. (c) $[Mn(CO)_6]$

EAN of Mn = 25 – 0 + 12 = 37

To gain stability it has to loose an e^- hence, it can act as reducing agent.

$[V(CO)_6]$

EAN of V = 23 – 0 + 12 = 35

To gain stability it has to gain an e– hence, it can act as oxidising agent.

$[Fe(CO)_5]$

EAN of Fe = 26 – 0 + 10 = 36

It follows EAN rule. It does not behave as oxidising agent and reducing agent.

$[Mn(CO)_5]$ can dimerise $[Mn_2(CO)_{10}]$ to gain stability.

5. The IUPAC name for the complex, $[Co(NH_3)_2Cl(ONO)(Py)_2]NO_3$ is:

(a) Diamminechlorido dipyridinenitrito–N–cobaltate (III) nitrate
(b) Diammine chloridonitrito–O–bipyridine cobalt (III) nitrate
(c) Diamminechloridonitrito–O–dipyridine cobalt (III) nitrate
(d) Chloridodiamminenitrito–O– bis (pyridine) cobalt (III) nitrate

Sol.(c) Correct IUPAC name is:

Diamminechloridonitrito–O–dipyridinecobalt (III) nitrate.

6. Which of the following pairs of name and formula of complexes is not correct?

(a) Tetraamminecopper (II) sulphate $[Cu(NH_3)_4]SO_4$
(b) Diamminesilver (I) chloride $[Ag(NH_3)_2]Cl$
(c) Potassium hexacyanidoferrate (III) $K_4[Fe(CN)_6]$
(d) Potassium amminepentachloridoplatinate (IV) $K[Pt(NH_3)Cl_5]$

Sol.(c) The correct formula of Potassium hexacyanido ferrate (III) is $K_3[Fe(CN)_6]$

7. Different hydrated isomer of $CrCl_3.6H_2O$ can not be differentiated by:

(a) Conductivity measurements
(b) Precipitation by $AgNO_3$
(c) Dipole moment
(d) Magnetic moment

Sol.(d) Hydrated isomers of $CrCl_3.\ 6H_2O$ are :

(i) $[Cr(H_2O)_6]\ Cl_3$
(ii) $[Cr(H_2O)_5Cl]\ Cl_2.\ H_2O$
(iii) $[Cr(H_2O)_4Cl_2]\ Cl.\ 2H_2O$

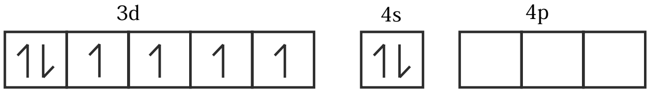
They all have different conductivity, dipole moment and precipitation by $AgNO_3$. The all have similar magnetic moment because in all complexes, ligands are weak field. Cr^{+3} has 3 unpaired e^-.

8. $[Fe(CO)_5]$ and $[Ni(CO)_4]$ do not show similarity in:

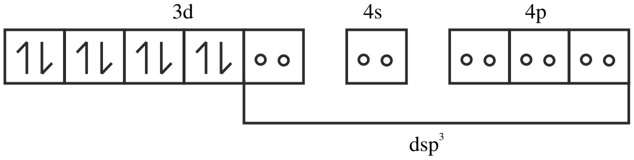
(a) participation of d-orbital in hybridization.
(b) polarity and magnetic nature.
(c) presence of synergic bonding.
(d) shifting of ns electron into (n–1) d subshell.

Sol.(a) Hybridization of Fe in $[Fe(CO)_5]$ is dsp^3 while hybridization of Ni in $[Ni(CO)_4]$ is sp^3.

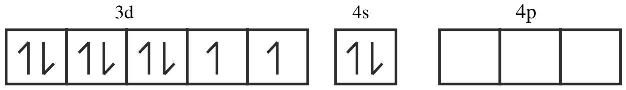
$[Fe(CO)_5]$



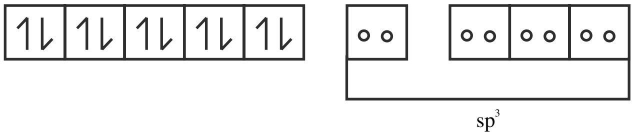
CO is strong field ligand hence pairing occurs.



$[Ni(CO)_4]$
Ni = [Ar] $4s^2\ 3d^8$



After pairing



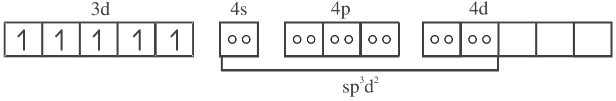
Hence, in $[Ni(CO)_4]$, there is no participation of d-orbital in hybridization.

9. In the following complex ions order of paramagnetism is :

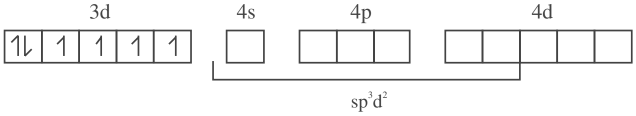
P: $[FeF_6]^{3-}$ Q: $[CoF_6]^{3-}$
R: $[V(H_2O)_6]^{3+}$ S: $[Ti(H_2O)_6]^{3+}$

(a) P > Q > R > S
(b) Q > P > R > S
(c) P = Q = R = S
(d) P > R > Q > S

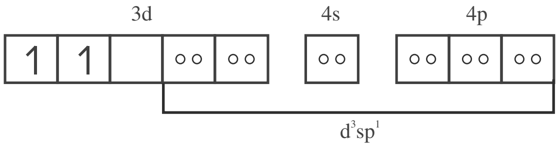
Sol.(a) $[F_eF_6]^{3-}$
Fe^{+3} = [Ar] $4s°.3d^5$



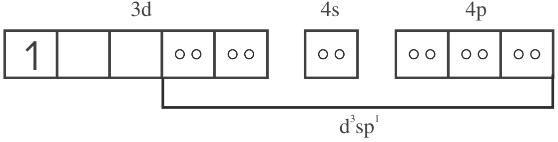
Number of unpaired e^- = 5
$[CoF_6]^{3-}$
Co^{+3} = [Ar] 4s° $3d^6$



Number of unpaired e^- = 4
$[V(H_2O)_6]^{3+}$
V^{+3} = [Ar] 4s° $3d^2$



Number of unpaired e^- = 2
$[Ti(H_2O)_6]^{3+}$
Ti^{+3} = [Ar] 4s° $3d^1$



Number of unpaired e^- = 1

10. Select the correct match:

Complex	**d-orbitals having highest energy**
(a) $[Ni(CN)_4]^{2-}$	d_{xy}, d_{z^2}
(b) $[NiCl_4]^{2-}$	$d_{x^2-y^2}$, d_{z^2}
(c) $[Cr(en)_3]Cl_3$.	$d_{x^2-y^2}$, d_{z^2}
(d) $[PtCl_4]^{-2.}$	d_{xy}, d_{yz}, d_{xz}

Sol.(c)

Complex	**Hybridization**	**d-orbitals having highest energy**
$[Ni(CN)_4]^{2-}$	dsp^2	$d_{x^2-y^2}$
$[NiCl_4]^{2-}$	sp^3	d_{xy}, d_{yz}, d_{xz}
$[Cr(en)_3]Cl_3$	d^2sp^3	$d_{x^2-y^2}$, d_{z^2}
$[PtCl_4]^{2-}$	dsp^2	$d_{x^2-y^2}$

11. For which one of the following ion the colour is not due to a d-d transition?

(a) CrO_4^{2-}	(lemon yellow)
(b) $[Cu(NH_3)_4]^{2+}$	deep blue
(c) $[Fe(H_2O)_6]SO_4$	green
(d) $[Ti(H_2O)_6]^{3+}$	purple

Sol.(a) Cause of colour in chromate ion (CrO_4^{2-}) is ligand to metal charge transfer. In all other complexes, unpaired e^- is present and cause of colour is d-d transition.

12. The complex exhibits lowest energy absorption band is:

(a) $[NiCl_4]^{2-}$
(b) $[Ni(CO)_4]$
(c) $[Ni(CN)_4]^{2-}$
(d) $[Ni(H_2O)_6]^{2+}$

Sol.[a] Order of CFSE (Δ) is:

$$\underset{\text{(Tetrahedral)}}{\Delta_t} < \underset{\text{(Octahedral)}}{\Delta_0} < \underset{\text{(Square planar)}}{\Delta_{sp}}$$

Absorb energy = Δ

$[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have tetrahedral geometry. So, they have low absorption energy. Cl^- is a weaker ligand than CO hence, $[NiCl_4]^{2-}$ exhibits lower energy absorption band.

13. Which of the following can show both geometrical and optical isomerism?

(a) $[Co(Ox)_3]^{-3}$

(b) $[Fe(NH_3)_4 Cl_2]^+$

(c) $[Fe(NH_3) (H_2O) (Py) (Br) (Cl) (OH)]$

(d) $[Co(NH_3)_3(NO_2)_3]$

Sol.(c)

(a)	$[Co(Ox)_3]^{-3}$	M $(aa)_3$ complex does not show geometrical isomerism
(b)	$[Fe(NH_3)_4Cl_2]^+$	Ma_4b_2 complex does not show optical isomerism.
(c)	$[Fe(NH_3) (H_2O) (Py) (Br) (Cl) (OH)]$	Mabcdef complex can show both geometrical and optical
(d)	$[Co(NH_3)_3 (NO_2)_3]$	Ma_3b_3 complex does not show optical isomerism.

14. Which of the following is not correct?

(a) $FeCl_3 + KCNS \longrightarrow$ Red colour

(b) $KI + PbCl_2 \longrightarrow$ Yellow ppt.

(c) NH_4Cl + Nesseler's reagent $\longrightarrow$ Blue colour

(d) $DMG + Ni^{2+} + NH_4OH \longrightarrow$ Scarlet red ppt.

Sol.(c) $FeCl_3 + KCNS \longrightarrow \underset{\text{Red colour}}{Fe(CNS)\,Cl_2}$

$KI + PbCl_2 \longrightarrow \underset{\text{Yellow}}{PbI_2} \downarrow$

$NH_4Cl + K_2HgI_4 + OH^- \longrightarrow \underset{\text{Reddish-brown}}{NH_2\text{–}HgO\text{–}HgI}$

$DMG + Ni^{2+} + NH_4OH \longrightarrow \underset{\text{Scarlet red}}{[Ni(DMG)_2]}$

15. Which of the following names are not correct? Point out the mistakes.

(a) $[Cu(H_2O)\ (NH_3)]\ Br_2$; Amminoaquodibromocopper (I)

(b) $Na_3[Al(C_2O_4)_3]$; Trisodium trioxalatoaluminate (III)

(c) $Na_2[Ni(EDTA)]$; Sodium ethylenediaminetetraacetato nickelate (II)

(d) $[Co(NH_3)_5ONO]\ SO_4$; Pentaamminenitrocobalt (III) sulphate

Sol. (a) Ammine aqua copper (II) bromide

(b) Sodium trioxalato aluminate (III)

(c) It is correct

(d) Pentammine nitrito cobalt (III) sulphate

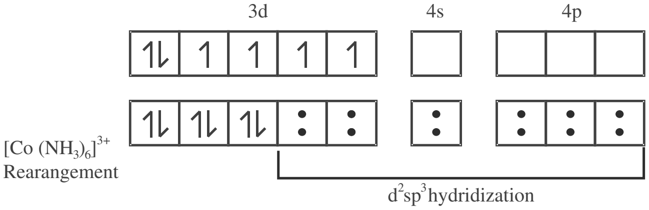
16. Find out the hybridization, geometry and magnetic moment of the complexes :

(a) $[Co(NH_3)_6]^{3+}$

(b) $[Cr(CN)_6]^{3-}$

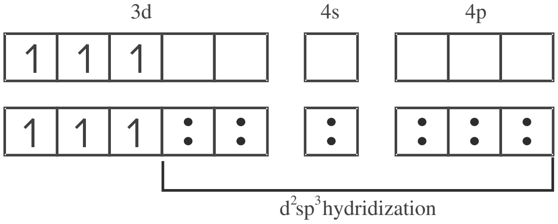
Sol.(a) The oxidation state of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is + 3

The electronic configuration of Co^{3+} ion is :



Octahedral, zero magnetic moment

(b) The oxidation state of chromium in the complex is +3. The electronic configuration



Octahedral, Magnetic moment = $\sqrt{15}$ = 3.87 BM

17. From the stability constants (hypothetical values), given below, predict which one is the strongest ligand?

(a) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ K $= 4.5 \times 10^{11}$

(b) $Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$ K $= 2.0 \times 10^{27}$

(c) $Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}$ K $= 3.0 \times 10^{15}$.

(d) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$ K $= 9.5 \times 10^{8}$

Sol.(b) Greater the value of stability constant, stronger is the ligand.

18. Each of the compounds $Pt(NH_3)_6Cl_4$, $Cr(NH_3)_6Cl_3$, $Co(NH_3)_4Cl_3$ and K_2PtCl_6 were dissolved in water to make its 0.001 M solution. The correct order of their increasing conductivity in solution is-

(a) $K_2PtCl_6 < Co(NH_3)_4Cl_3 < Cr(NH_3)_6Cl_3 < Pt(NH_3)_6Cl_4$

(b) $Cr(NH_3)_6Cl_3 < Co(NH_3)_4Cl_3 < K_2PtCl_6 < Pt(NH_3)_6Cl_4$

(c) $Co(NH_3)_4Cl_3 < K_2PtCl_6 < Cr(NH_3)_6Cl_3 < Pt(NH_3)_6Cl_4$

(d) $Pt(NH_3)_6Cl_4 < Co(NH_3)_4Cl_3 < Cr(NH_3)_6Cl_3 < K_2PtCl_6$

Sol.(c) In aqueous solution (0.001 M), the complexes will dissociate to give the ions :

$Pt(NH_3)_6Cl_4 \rightleftharpoons [Pt(NH_3)_6]^{4+} + 4Cl^-$; 5 ion.

$Cr(NH_3)_6Cl_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 3Cl^-$; 4 ions.

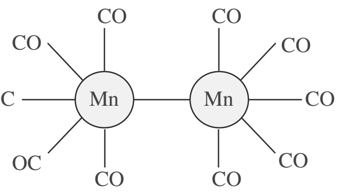
$Co(NH_3)_4Cl_3 \rightleftharpoons [Co(NH_3)_4Cl_2]^{+} + Cl^-$; 2 ions

$K_2PtCl_6 \rightleftharpoons [PtCl_6]^{2-} + 2K^+$; 3 ions.

19. The EAN of each Mn (Z = 25) in its carbonyl is 36. What is the structure of the carbonyl with molecular formula : $Mn_2(CO)_{10}$?

Sol. Electrons from each Mn = 25
Electrons from five CO ligands = 2 × 5 = 10
Electrons from (Mn — Mn) bond = 1
Thus EAN = 25 + 10 + 1 = 36

Thus is the complex five CO (ligands) are coordinated to each Mn atom and sixth coordination number is attained by other Mn atom of (Mn–Mn) bond. Thus it can have structure :



20. Identify the complexes which are expected to be coloured and explain.

(a) $Ti(NO_3)_4$
(b) $[Cu(NCCH_3)_4]^+BF_4^-$
(c) $[Cr(NH_3)_6]^{3+}\ 3Cl^-$
(d) $K_3[VF_6]$

Sol.(c & d) (c) and (d) are coloured because Cr^{3+} in $[Cr(NH_3)_6]^{3+}$ and V^{3+} in $[VF_6]^{3-}$ has unpaired electron in d subshell.

Exercise

LEVEL I

1. Incorrect statement for addition compound is:

(a) Simple salts do not lose their identify in double salt.
(b) Complex compounds retain their identity in aqueous solution.
(c) Simple salts lose their identity in complex compound.
(d) Double salts retain their identity in aqueous solution.

2. Neutral and symmetrical bidentate ligand is:

(a) Oxalate (b) dien
(c) gly (d) dipyridyl

3. Which of the following pair contains only ambidenate ligand?

(a) $^-CN, NH_3$ (b) NO_2^-, SCN^-
(c) H_2O, en (d) en, dien

4. EDTA is a:

(a) Polydenate ligand
(b) Chelating ligand
(c) Flexidenate ligand
(d) All of these

5. Chelating ligand is:

(a) thiocyanate (b) cyanide
(c) Oxalate (d) Ammonia

6. Which can't form chelates?

(a) Didentate ligand
(b) Ambidentate ligand
(c) Tetradentate lignad
(d) Flexidenate ligand

7. An example for a double salt is:

(a) Cuprammonium sulphate
(b) Mohr's salt
(c) Potassium ferricyanide
(d) Cobalthexammine chloride

8. Which of the following complexes are heteroleptic?

(a) $[Cr(NH_3)_6]^{3+}$ (b) $[Fe(NH_3)_4Cl_2]^+$
(c) $[Mn(CN)_6]^{4-}$ (d) $[Co(NH_3)_6]^{+2}$

9. Which of the following can not act as ligand?

(a) $H_2N—CH_2—COO^-$
(b) $H_2N–NH_2$
(c) $[H_3N—CH_2—CH_2—NH_3]^{2+}$
(d) $H_2N—\overset{\circ}{N}H_3$

10. The oxidizing agent is:

(a) $Fe(CO)_5$. (b) $Mn(CO)_5$
(c) $Mn_2(CO)_{10}$. (d) $Fe_2(CO)_9$

11. Which follows EAN Rule?

(a) $[Pd(NH_3)_6]Cl_4$. (b) $[Cr(NH_3)_5Cl]\ SO_4$

(c) $Na_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$

12. In sodium nitroprusside the oxidation number, coordination number and effective atomic number of iron are respectively:

(a) +3, 6, 35. (b) +3, 6, 36

(c) +2, 3, 36. (d) +2, 6, 36

13. EAN of metal carbonyl $M(CO)_x$ is 36 if atomic number of metal M is 26, what is the value of x?

(a) 4 (b) 8

(c) 5 (d) 6

14. The IUPAC name of $[Pt(NH_3)_3(Br)(NO_2)(Cl)]Cl$ is:

(a) Triamminechlorobromonitroplatinum (IV) chloride

(b) Triamminebromochloronitroplatinum (IV) chloride

(c) Triamminechlorobromoplatinum (IV) chloride

(d) Triamminechloronitrobromoplatinum (IV) chloride

15. Formula of potassium dicyanodioxalato nickelate (II) is:

(a) $K_4[Ni(CN)(OX)_2]$

(b) $K_3[Ni(CN)_2(OX)]$

(c) $K_4[Ni(CN)_2(OX)_2]$

(d) $K_2[Ni(CN)_2(OX)_2]$

16. Select the correct IUPAC name of $[Co(NH_3)_6][Co(ONO)_6]$:

(a) Hexaamminecobalt (II) hexanitrito–O cobalt (II)

(b) Hexaamminecobalt (III) hexanitrito–N cobaltate (III)

(c) Hexaamminecobalt (II) hexanitrito–O cobaltate (II)

(d) Hexaamminecobalt (III) hexanitrito–O cobaltate (III)

17. When 1 mol $CrCl_3.6H_2O$ is treated with excess of $AgNO_3$, 2 mol of AgCl are obtained. The formula of the complex:

(a) $[CrCl_3(H_2O)_3].3H_2O$

(b) $[CrCl_2(H_2O)_4].2H_2O$

(c) $[CrCl(H_2O)_5]Cl_2.H_2O$

(d) $[Cr(H_2O)_6]Cl_3$

18. Which of the following shows maximum conductance?

(a) $[Co(NH_3)_6]Cl_3$

(b) $[Co(NH_3)_3Cl_3]$

(c) $[Co(NH_3)_4Cl_2]Cl$

(d) $[Co(NH_3)_5Cl]Cl_2$

19. Which of the following ligand act as WFL for octahedral complex of Co^{+3} ion?

(a) F^- (b) H_2O

(c) $C_2O_4^{-2}$ (d) All of these

20. $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_4]^{-4}$ are not differ in:

(a) Oxidation state and co-ordination number

(b) Hybridisation state and geometry

(c) Magnetic behavior

(d) None of these

21. Inner orbital complex which is paramagnetic in nature?

(a) $[Ni(CN)_5]^{-3}$

(b) $[Fe(CN)_6]^{-4}$

(c) $[Fe(H_2O)_5(NO)]SO_4$

(d) $[Fe(CN)_6]^{-3}$

22. The complex ion $[Fe(CN)_6]^{4-}$ contains:

(a) total of 36 electrons on Fe^{2+} cation

(b) sp^3d^2 hybrid orbitals with octahedral structure

(c) Twelve coordinate bonds

(d) six sigma bonds

23. $[NiCl_4]^{-2}$ and $[Ni(CN)_4]^{-2}$ show similarity in:

(a) Geometry

(b) Magnetic nature

(c) Hybridisation of state of Ni

(d) Primary valency of Ni

24. VBT can not explain the geometry of:

(a) $[Cr(NH_3)_6]^{+3}$. (b) $[Co(NH_3)_6]^{+3}$

(c) $[Cu(NH_3)_4]^{+2}$. (d) $[Zn(NH_3)_4]^{+2}$

25. Incorrect order of splitting energy is:

(a) $[NiF_6]^{-4} < [NiF_6]^{-2}$

(b) $[Fe(H_2O)_6]^{+3} < [Ru(H_2O)_6]^{+3}$

(c) $[Co(NH_3)_6]^{+3} < [Co(en)_3]^{+3}$

(d) $[Ni(CN)_4]^{-2} < [Ni(CN)_6]^{-4}$

26. A complex has magnetic moment 1.73 BM. Which of the following configuration of metal ion is not possible?

(a) d^7, octahedral, lowspin

(b) d^5, octahedral, lowspin

(c) d^8, square planar

(d) d^9, tetrahedral

27. In which of the following complex ion, the metal ion will have $t_{2g}^6 e_g^0$ configuration according to CFT?

(a) $[FeF_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(H_2O)_6]^{+2}$

28. The Δ_0 (CFSE) for $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The splitting energy for $[CoCl_4]^{2-}$ will be:

(a) 18000 cm^{-1} (b) 16000 cm^{-1}

(c) 8000 cm^{-1} (d) 2000 cm^{-1}

29. Which of the following is correct order of stability?

(a) $[NiCl_4]^{-2} < [PdCl_4]^{-2} < [PtCl_4]^{-2}$

(b) $[Co(H_2O)_6]^{+3} < [Co(NH_3)_6]^{+3} < [Co(CN)_6]^{-3}$

(c) $[Co(H_2O)_6]^{+3} < [Rh(H_2O)_6]^{+3} < [Ir(H_2O)_6]^{+3}$

(d) All of these

30. The colour of a compound may be due to :

(a) polarisation

(b) d-d transition

(c) charge transfer spectra

(d) All of these

31. Which is coloured but not due to d-d transition?

(a) $Cr_2O_7^{2-}$ (b) $KMnO_4$

(c) AgBr (d) All of these

32. The colour of light absorbed by an aqueous solution of $CuSO_4$ is:

(a) orange-red (b) blue-green

(c) yellow (d) violet

33. Which of the following isomerism is not present in complex $[Co(NH_3)_4(SCN)_2]$ Br?

(a) Geometrical isomerism

(b) Linkage isomerism

(c) Ionisation isomerism

(d) Optical isomerism

34. Which is correct statement?

(a) $[Co(en)_3][Cr(CN)_6]$ will display coordination isomerism

(b) $[Mn(CO)_5(SCN)]$ will display linkage isomerism

(c) $[Co(NH_3)_5(NO_2)]SO_4$ will display ionization isomerism

(d) All are correct

35. How many isomers exist for $[Co(NH_3)_4Cl_2]^+$ and $[Co(en)_2Cl_2]^+$ complex ions, respectively?

(a) 2 and 2. (b) 2 and 3

(c) 3 and 2. (d) 3 and 3

36. The type of isomerism present in pentaamminenitro chromium (III) ion is:

(a) Optical (b) Linkage

(c) Ionization (d) Polymerisation

37. Na_2S forms violet colour complex when reacts with:

(a) Brown ring complex

(b) Sodium nitroprussible

(c) $K_4[Fe(CN)_6]$

(d) Hypo solution

38. The incorrect statement is:

(a) Fe^{+2} salt gives blue colloidal solution with $K_3[Fe(CN)_6]$

(b) $FeCl_3$ gives red colour with K SCN

(c) Cu^{+2} salt gives blue colloidal solution with $K_4[Fe(CN)_6]$

(d) Light blue solution of $CuSO_4$ turn into dark blue in presence of ammonia.

39. Select correct statement regarding $[Ni(DMG)_2]$ complex compound:

(a) It acts as oxidizing agent because Ni^{2+} cation is having EAN 35.

(b) It is extra stabilized by hydrogen bonding

(c) It's IUPAC name is Bis (dimethylglyoximato) nickelate (II)

(d) It's ligand contains two different donar sites

40. Sodium thiosulphate is used in photography to

(a) Reduce AgBr to metallic Ag

(b) Convert metallic Ag to Ag salt

(c) Remove undecomposed AgBr as a soluble silver thiosulphate complex

(d) Remove unreduced silver

LEVEL II

1. A six coordinate complex of formula $CrCl_3.6H_2O$ has green colour. A 0.1 M solution of the complex when treated with excess of $AgNO_3$ gave 28.7 g of white precipitate. The formula of the complex would be:

(a) $[Cr(H_2O)_6)]Cl_3$

(b) $[CrCl(H_2O)_5]Cl_2.H_2O$

(c) $[CrCl_2(H_2O)_4]Cl.2H_2O$

(d) $[Cr(H_2O)_3Cl_3]$

2. Which is not true about metal carbonyls?
(a) Here CO acts as a Lewis base as well as Lewis acid
(b) Here metal acts as Lewis base as well as Lewis acid
(c) Here dπ-pπ back bonding takes place
(d) Here pπ-pπ back bonding takes place

3. Which of the following pair the EAN of central metal atom is not same?
(a) $[Fe(CN)_6]^{3-}$ and $[Fe(NH_3)_6]^{3+}$
(b) $[Cr(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$
(c) $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$
(d) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$

4. The IUPAC name for $K_2[Cr(CN)_2O_2(O_2)NH_3]$ is:
(a) Potassium amminedicyanotetraoxo chromium (III)
(b) Potassium amminedicyanodioxygendioxo chromate (IV)
(c) Potassium amminedicyanosuperoxoperoxo chromate (III)
(d) Potassium amminedicyanodioxoperoxo chromate (VI)

5. The magnetic moment of $[NiX_4]^{2-}$ ion is found to be zero. Then the ion is:
(X = monodentate anionic ligand)
(a) sp^3 hydridised (b) spd^2 hydridised
(c) dsp^2 hydridised (d) d^2sp hydridised

6. The magnetic moment of a complex ion is 2.83 *BM*. The complex ion is :
(a) $[V(H_2O)_6]^{3+}$ (b) $[Cr(H_2O)_6]^{3+}$
(c) $[Cu(CN)_4]^{2-}$ (d) $[MnCl_4]^{2-}$

7. What is the magnetic moment (spin only) and hybridisation of the brown ring complex $[Fe(H_2O)_5NO]SO_4$?
(a) $\sqrt{3}$ BM, $sp^3\,d^2$. (b) $\sqrt{3}$ BM, $d^2\,sp^3$
(c) $\sqrt{15}$ BM, $sp^3\,d^2$. (d) $\sqrt{15}$ BM, d^2sp^3

8. Select the correct code about complex $[Cr(NO_2)(NH_3)_5]\,[ZnCl_4]$:
(I) IUPAC name of compound is pentaammine-nitrito-N-chromium (III) tetrachlorozincate (II)
(II) It shows geometrical isomerism
(III) It shows linkage isomerism
(IV) It shows coordination isomerism
(a) III, IV (b) I, III and IV
(c) II, III and IV (d) I, II, III and IV

9. Cis-trans isomerism is exhibited by:
(a) $[PtCl(NH_3)_3]^{3+}$ (b) $[Pt(NH_3)_4]^{2+}$
(c) $[PtCl_4]^{2-}$ (d) $[PtCl_2(NH_3)_2]$

10. Which one of the following platinum complexes is used in cancer chemotherapy?
(a) cis-$[PtCl_2(NH_3)_2]$
(b) trans-$[PtCl_2(NH_3)]$
(c) $[Pt(NH_3)_4]^{2+}$
(d) $[Pt(Cl_4)]^{2-}$

11. The cyanide complex of silver formed in the silver extraction in Mac-Arthur's Forrest cyanide process is:
(a) $[Ag(CN)_2]^{-}$ (b) $K_2[Ag(CN)_3]$
(c) $[Ag(CN)_4]^{2-}$ (d) $Na_3[Ag(CN)_4]$

12. Mixture X of 0.02 mole of $[Co(NH_3)_5SO_4]$ Br and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 litre of solution:

1 litre of mixture X + excess of $AgNO_3 \rightarrow$ Y

1 litre of mixture X + excess of $BaCl_2 \rightarrow$ Z

Number of moles of Y and Z respectively are:
(a) 0.01, 0.02. (b) 0.02, 0.01
(c) 0.01, 0.01. (d) 0.02, 0.02

13. In $Na_2[Fe(CN)_5NO]$, sodium nitroprusside:
(a) oxidation state of Fe is +2
(b) this has NO^+ as ligand
(c) both are correct
(d) none is correct

14. Complexes formed in the following methods are:
(I) Mond's process for purification of nickel
(II) Removal of unreacted AgBr from photographic plate
(III) Removal of lead poisoning from the body

	I	**II**	**III**
(a)	$Ni(CO)_4$.	$[Ag(CN)_2]^-$	$[Pb(EDTA)]^{2-}$
(b)	$Ni(CO)_4$.	$[Ag(S_2O_3)_2]^{3-}$	$[Pb(EDTA)]^{2-}$
(c)	$Ni(CO)_6$.	$[Ag(S_2O_3)_2]^{3-}$	$[Pb(EDTA)]^{4-}$
(d)	$Ni(CO)_6$.	$[Ag(S_2O_3)_2]^-$	$[Pb(EDTA)]^{2-}$

15. $NaCl + AgNO_3 \rightarrow \underset{\text{(white)}}{A}\downarrow + B$

$A + NH_{3(\text{solution})} \rightarrow \underset{\text{(Soluble Complex)}}{C}$

$CuSO_4 + NH_{3(\text{solution})} \rightarrow \underset{\text{(Soluble Complex)}}{D}$

Select correct statements.

(a) IUPAC name of complex D is Tetraammine cuprate (II) sulphate

(b) Complex C is $[Ag(NH_3)_4]^+$

(c) By adding HNO_3, complex C further converts into AgCl

(d) In complex D, hybridization of Cu^{2+} is sp^3

16. Set of d-orbitals which is used by central metal during formation of MnO_4^-?

(a) $d_{x^2-y^2}$, d_{z^2}, d_{xy}

(b) d_{xy}, d_{yz}, d_{xz}

(c) $d_{x^2-y^2}$, d_{xy}, d_{xz}

(d) $d_{x^2-y^2}$, d_{z^2}, d_{xz}

17. A $[M(H_2O)_6]^{2+}$ complex typically absorbs at around 600 nm. It is allowed to react with ammonia to form a new complex $[M(NH_3)_6]^{2+}$ that should have absorption at:

(a) 800 nm (b) 580 nm

(c) 620 nm (d) 320 nm

18. MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state, it is due to:

(a) Oxygen gives colour to it

(b) Charge transfer when Mn (+7) gives its electron to oxygen and oxidise to Mn (+8) temporarily

(c) Charge transfer when oxygen gives its electron to Mn (+7) changing in Mn (+6)

(d) None is correct explanation

19. Which of the following statement is not true for the reaction given below ?

$[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$

(a) It is a ligand substitution reaction

(b) NH_3 is a relatively strong field ligand while H_2O is a weak field ligand

(c) During the reaction, there is a change in colour from light blue to dark blue

(d) $[Cu(NH_3)_4]^{2+}$, has a tetrahedral structure and is paramagnetic

20. Select the correct IUPAC name for $[Cr(C_6H_6)(CO)_3]$:

(a) (η^6-benzene) tricarbonyl chromate (0)

(b) Tricarbonyl (η^6-benzene) chromate (0)

(c) Tricarbonyl (η^6-benzene) chromium (0)

(d) (η^6-benzene) tricarbonylchromium (0)

21. Ligand with two or more points of attachment to single metal atoms are called:

(a) Modnodentate ligand (b) Chelating ligand

(c) Ambidentate ligand (d) None of these

22. Number of water molecules acting as ligands in

$CuSO_4.5H_2O$, $ZnSO_4.5H_2O$, $FeSO_4.7H_2O$ respectively are

(a) 5,5,7. (b) 4,5,4

(c) 4,4,6. (d) 4,4,7

23. Coordination number of Cr is six. A complex with $C_2O_4^2$, en and superoxide $O_2^\ominus$ will be in the ratio to make complex $[Cr(C_2O_4)_x(en)_y(O_2)_z]^\ominus$

	x	*y*	*z*
(a)	1.	1.	1
(b)	1.	1.	2
(c)	1.	2.	2
(d)	2.	1.	1

24. Which of the following is most likely structure of $CrCl_3.6H_2O$ if $\frac{1}{3}$ of total chlorine of the compound is precipitated by adding $AgNO_3$ to its aqueous solution?

(a) $[Cr(H_2O)_6]Cl_3$

(b) $[Cr(H_2O)_3Cl_3].3H_2O$

(c) $[CrCl_2(H_2O)_4]Cl.2H_2O$

(d) $[CrCl.(H_2O)_5]Cl_2.H_2O$

25. Which of the following pair contains complex salt and double salt respectively?

(a) $FeSO_4,K_4[Fe(CN)_6]$

(b) $[Cu(NH_3)_4]SO_4$, $FeSO_4.7H_2O$

(c) $[Cu(NH_3)_4]SO_4$, $K_2SO_4Al_2(SO_4)_3.24H_2O$

(d) $MgSO_4.7H_2O$, $CuSO_4 .5H_2O$

26. Give EAN value of Mg in $[Mg(EDTA)]^{2-}$:

(a) 16 (b) 20

(c) 22 (d) 18

27. The type of isomerism present in pentaammine nitro chromium (III) perchlorate is

(a) Optical (b) Linkage

(c) Hydrate (d) Polymerisation

28. The following complexes are given

(A) trans-$[Co(NH_3)_4I_2]^\ominus$

(B) cis-$[Co(NH_3)_2(en)_2]^{3-}$

(C) trans-$[Co(NH_3)_2(en)_2]^{3+}$

(D) $[NiI_4]^{2-}$

(E) $[TiF_6]^{2-}$

(F) $[CoF_6]^{3-}$

Choose the correct code.

(a) D, E are coloured; F is colourless

(b) B is optically active; A, C are optically inactive

(c) A, B are optically active; C optically inactive

(d) D is coloured; E, F are colourless

29. One mole of complex compound $Cr(NH_3)_5Cl_3$ give 3 moles of ions on dissolution in water. One mole of the same, complex reacts with two moles of $AgNO_3$ to yield two moles of $AgCl_{(s)}$. The complex is

(a) $[Cr(NH_3)_4Cl]Cl_2.NH_3$

(b) $[Cr(NH_3)_4Cl_2]Cl.NH_3$

(c) $[Cr(NH_3)_5Cl]Cl_2$

(d) $[Cr(NH_3)_3Cl_3].2NH_3$

30. In which of the following pairs both the complexes show optical isomerism ?

(a) cis-$[Cr(C_2O_4)_2Cl_2]^{3-}$, cis-$[Co(NH_3)_4Cl_2]$

(b) $[Co(en)_3]Cl_3$, cis-$[Co(en)_2Cl_2]Cl$

(c) $[Co(NO_3)_3(NH_3)_3]$, cis-$[Pt(en)_2Cl_2]$

(d) $[PtCl(en)Cl]$, $[NiCl_2Br_2]^{2-}$

31. The correct order of magnetic moment (spin values in BM) is

(Atomic number Mn = 25, Fe = 26, Co = 27)

(I) $[MnBr_4]^{2-}$

(II) $[Fe(CN)_6]^{4-}$

(III) $[CoBr_4]^{2-}$

(a) II > III > I (b) I > II > III

(c) II > I > III (d) I > III > II

32. Which of the following compound is not coloured?

(a) $Na_2[CuCl_4]$ (b) $Na_2[CdCl_4]$

(c) $K_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$

33. In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field] will be maximum?

(a) $[Co(CN)_6]^{3-}$ (b) $[CoF_6]^{3-}$

(c) $[Co(NO_2)_6]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$

34. The increasing order of the crystal field splitting power of some common ligands is

(a) $NH_3 < NO_2^{\Theta} < CN^{\Theta} < H_2O$

(b) $H_2O < NO_2^{\Theta} < CN^{\Theta} < NH_3$

(c) $H_2O < NH_3 < NO_2^{\Theta} < CN^{\Theta}$

(d) $H_2O < NH_3 < CN^{\Theta} < NO_2^{\Theta}$

35. Which of the following complex is inner orbital as well as low spin complex?

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Cu(CN)_4]^{3-}$ (d) $[Ni(NH_3)_6]^{2+}$

36. Which of the following is incorrect about Wilkinson's catalyst?

(a) It is a diamagnetic complex.

(b) It is a non-ionic complex.

(c) It is tetrahedral complex.

(d) It is very effective for selective hydrogenation of organic molecule at room temperature and pressure.

37. $[Cr(H_2O)_6]Cl_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 BM. The correct distribution of 3d electron in the chromium of the complex is:

(a) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$

(b) $(3d_{x^2-y^2})^1, 3d^1_{z^2}, 3d^1_{xz}$

(c) $3d^1_{xz}, (3d_{x^2-y^2})^1, 3d^1_{yz}$

(d) $3d^1_{xz}, 3d^1_{yz}, 3d^1_{xz}$

38. What will be the correct order of absorption of wavelength of light in the visible region, for the complex, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$?

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

39. An ion M^{2+}, form the complexes

$[M(H_2O)_6]^{2+}$, $[M(en)_3]^{2+}$ and $[M\ Br_6]^{4-}$. Colour of these complexes may be:

(a) Green, blue & Red (b) Blue, Red & Green

(c) Green, Red & Blue (d) Red, Blue & Green

40. Cu^{2+} ions will be reduced to Cu^+ ions by the addition of an aqueous solution of:

(a) KI (b) KCl

(c) KSCN (d) (a) and (c) both

LEVEL III

ONE OR MORE THAN ONE TYPE QUESTIONS

1. Complex compound $[Co(SCN)_2(NH_3)_4]Cl$ exhibits:
   - (a) Ionization isomerism
   - (b) Geometrical isomerism
   - (c) Optical isomerism
   - (d) Linkage isomerism

2. Find out correct IUPAC name of complex compound.
   - (a) Pentaaminecyanidocyanidochromium (II) hexanitrito-N-irridate (III)
   - (b) Triamminetricyanidochromium (III) hexanitrito-N-irridate (III)
   - (c) Hexanitrito-N-irridium (III) pentaamminecyanidochromate (II)
   - (d) Pentaamminecyanidchromium (III) hexanitrito-N-irridate (III)

3. Complex ions $[NiCl_6]^{4-}$, $[Ni(CN)_6]^{4-}$ similar in their given properties:
   - (a) oxidation state, geometry
   - (b) co-ordination number, EAN
   - (c) magnetic moment, geometry
   - (d) stability, colour

4. Which of the following compound has/have effective atomic number equal to the atomic number of noble gas?
   - (a) $K[Co(CO)_4]$ (b) $K_2[Fe(CO)_4]$
   - (c) $[Co(NH_3)_6]Cl_2$. (d) $[CoCl_3(H_2O)_3]$

5. A d-block element forms octahedral complex but its magnetic moment remains same either in strong field or in weak field ligand. Which of the following is/are correct?
   - (a) Element always forms colourless compound.
   - (b) Number of electrons in t_{2g} orbitals are higher than in e_g orbitals.
   - (c) It can have either d^3 or d^8 configuration.
   - (d) It can have either d^7 or d^8 configuration.

6. Which of the following statement (s) is/are false?
   - (a) In $[PtCl_2(NH_3)_4]^{2+}$ complex ion, the cis-form is optically active, while trans-form is optically inactive.
   - (b) In $[Fe(C_2O_4)_3]^{2+}$, geometrical isomerism does not exist, while optical isomerism exists.
   - (c) In $[Mabcd]^{n\pm}$ tetrahedral complexes, optical isomerism cannot be observed.
   - (d) In $[Mabcd]^{n\pm}$ square planar complexes, optical isomerism can be observed.

7. The d-orbitals involved in sp^3d^2 or d^2sp^3 hybridisation of the central metal ion are:
   - (a) $d_{x^2-y^2}$ (b) d_{xy}
   - (c) d_{yz} (d) d_{z^2}

8. Which of the following pairs of name and formula of complexes, is correct?
   - (a) Tetramminecopper (II) sulphate ………… $[Cu(NH_3)_4]SO_4$
   - (b) Diamminesliver (I) chloride …………….. $[Ag(NH_3)_2]Cl$
   - (c) Potassium hexacyanidoferrate (III) ………………….. $K_4[Fe(CN)_6]$
   - (d) Potassium amminepentachloridoplatinate (IV) ……………… $K[Pt(NH_3)Cl_5]$

9. Which of the following is/are correctly matched?
   - (a) $[Ni(CO)_4]Cl_2$-dsp^2 and diamagnetic.
   - (b) $[Ni(en)_3]$ $(NO_2)_2$- sp^3d^2 and two unpaired electrons.
   - (c) $[V(NH_3)_6]Cl_3$-sp^3d^2 and two unpaired electrons.
   - (d) $[Mn(NO^+)_3(CO)]$-sp^3 and diamagnetic.

10. Consider the following statements:

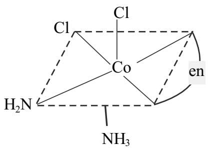
    S_1: Generally square planar complexes show geometrical isomerism but do not exhibit optical isomerism because they do not posses plane of symmetry.

    S_2: $\Delta_t = \frac{4}{9}\Delta_0$

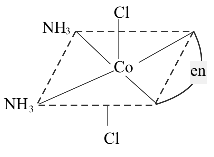
    S_3: In octahedral complexes each electron entering the t_{2g} orbitals stabilizes the complex ion by $0.4\ \Delta_0$ and each electrons the e_g orbital destabilizes the complex by an amount of $0.6\ \Delta_0$.

    Select the correct statement from the codes given below.
    - (a) S_1 and S_3 are correct
    - (b) S_2 and S_3 are correct
    - (c) S_1 is incorrect
    - (d) S_2 and S_3 are incorrect

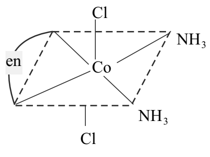
11. Three arrangements are shown for the complex $[Co(en)(NH_3)_2Cl_2]^+$. Pick up the wrong statement.



(I)



(II)



(III)

(a) I and II are geometrical isomers
(b) II and III are optical isomers
(c) I and III are optical isomers
(d) II and III are geometrical isomers

12. Consider the following complexies $[V(CO)_6]^-$, $[Cr(CO)_6]$ and $[Mn(CO)_6]^+$. Then incorrect statement (s) about metal carbonyls is/are.
(a) 'C–O' bond is strongest in the cation and weakest in the anion
(b) 'C–O' bond order is less in the cation than in anion.
(c) 'C–O' bond longer in the cation than in anionic or neutral carbonyl.
(d) 'M–C' bond order is higher in the cation than in anionic or neural carbonyl.

BASED ON PASSAGE TYPE QUESTIONS

Passage # 1 (Q. 13 and 14)

An isomer of the complex $CoBrCl_2(en)_2(H_2O)$, on reaction with concentrated H_2SO_4 (dehydrating agent), suffers no loss in weight and on reaction with $AgNO_3$ solution it gives only white precipitate, which is soluble in NH_3 solution.

13. The correct formula of the complex is:
(a) $[CoBr(H_2O)(en)_2]Cl_2$
(b) $[CoCl(en)_2(H_2O)]BrCl$
(c) $[CoBrCl(en)_2]Cl. H_2O$
(d) $[CoCl_2(en)_2]Br. H_2O$

14. The incorrect statement about complex is:
(a) It can show geometrical isomerism
(b) cis isomer is optically active
(c) Trans isomer is optically active
(d) It can exhibit solvate isomerism

Passage #2: (Q. 15 and 16)

According to CFT, attraction between the central metal ion and ligands in a complex is purely electrostatic. The transition metal which forms the central atom cation in the complex is regarded as positive ion. It is surrounding by negative ligands or neutral molecules which have a lone pair of electrons, if the ligand is a neutral molecule such as NH_3, the negative end of the dipole in the molecule is directed towards the metal cation. The electrons on the central metal ion are under repulsive forces from those on the ligands. Thus the electrons occupy the d-orbitals remain away from the direction of approach of ligands.

15. Correct relationship between pairing energy (P) and C.F.S.E (Δ_o) in complex ion $[Ir(H_2O)_6]^{3+}$ is:
(a) $\Delta_o < P$ (b) $\Delta_o > P$
(c) $\Delta_o = P$ (d) cannot comment

16. The crystal field-spliting order for Cr^{3+} cation in octahedral field for ligands CH_3COO^-, NH_3,H_2O CN^- is:
(a) $CH_3COO^- < H_2O < NH_3 < CN^-$
(b) $CH_3COO^- < NH_3 < H_2O < CN^-$
(c) $H_2O < CH_3COO^- NH_3 < CN^-$
(d) $NH_3 < CH_3COO^- < H_2O < CN^-$

Passage #3: (Q. 17 and 18)

Double salts are addition compounds which lose their identity in aqueous solution whereas complexes which are also addition compounds do not lose their identify in aqueous solution. The coordination compounds show isomerism and find applications in photography, qualitative analysis, metallurgy, water purification and in the treatment of various diseases.

17. Which of the following statements is incorrect?
(a) Alum is a double salt.
(b) EDTA salt of calcium is used in the treatment of lead poisoning.
(c) Effective atomic number of the metals in complexes $[Ni(CO)_4]$ and $[Fe(CN)_6]^{4-}$ is same.
(d) Chloridotris-(triphenylphosphine) rhodium (I) is effective heterogenous catalyst for hydrogenation of alkenes.

18. Which of the following statements is true for the complex $[Co(NH_3)_4Br_2]$ NO_2?
(a) It shows ionisation, linkage and geometrical isomerism.
(b) It does not show optical isomerism because its cis and trans forms each have at least one plane of symmetry.
(c) Its ionisation isomers cannot be differentiated by silver nitrate solution.
(d) (a) and (b) both.

INTEGER TYPE QUESTIONS

19. Brown colour of the complex $[Fe(H_2O)_5(NO)]SO_4$ is due to charge transfer spectrum which causes momentary change in oxidation state. Find out oxidation state of Fe in this complex.

20. Sum of denticity of following ligands are

Glycinate ion, Oxalate ion, o-phenathroline, 2,2'-bipyridyl, diethylenetriamine, ethylenediamine

21. Find the sum of number of geometrical isomers for following complexes.

(1) $[CoCl_2Br_2]^{2-}$ (2) $[Rh(en)_3]^{3+}$

(3) $[Cr(en)_2Br_2]^+$ (4) $[Pt(en)Cl_2]$

(5) $[Co(NH_3)_3(NO_2)_3]$

22. In the complex $Fe(CO)_x$, the value of x is:

23. Count the number of ions which can form both low spin and high spin complexes when co-ordination number 6

Co^{+3}, Ni^{+2}, Cr^{+3}, Fe^{+2}, Fe^{+3}, Cu^{+2}, Ti^{+3}, Co^{+2}

24. The number of unpaired electrons present in $[NiF_6]^{2-}$ is …………………

MATCH THE COLUMN TYPE QUESTIONS

25.

Column I	Column II
(A) $[MnCl_4]^{2-}$	(P) sp^3 hybridisation
(B) $[Ni(CN)_4]^{-2}$	(Q) Diamagnetic
(C) $[Ni(CO)_4]$	(R) Paramagnetic
(D) $[Cu(NH_3)_4]^{2+}$	(S) dsp^2 hybridisation

26.

Column I (Pair of complex compounds)	Column II (Property which is different in given pair)
(A) $[Ni(CO)_4]$ and $K_2[Ni(CN)_4]$	(P) Magnetic moment
(B) $[Cu(NH_3)_4]SO_4$ and $K_3[Cu(CN)_4]$	(Q) Oxidaton no. of central metal
(C) $K_2[NiCl_4]$ and $K_4[Ni(CN)_4]$	(R) Geometry
(D) $K_2[NiCl_4]$ and $K_2[PtCl_4]$	(S) EAN of central metal

27.

Column I (Molar conductance at infinite dilution)	Column II (Complex compound)
(A) 229	(P) $[Pt(NH_3)_5Cl]Cl_3$
(B) 0	(Q) $[Pt(NH_3)_2Cl_4]$
(C) 404	(R) $[Pt(NH_3)_4Cl_2]Cl_2$
(D) 523	(S) $[Pt(NH_3)_6]Cl_4$

28.

Column I (Coordination compounds)	Column II (Type of isomerism)
(A) $[Co(NH_3)_4Cl_2]$	(P) Optical isomerism
(B) cis-$[Co(en)_2Cl_2]$	(Q) Ionization isomerism
(C) $[Co(en)_2(NO_2)Cl]SCN$	(R) Coordination isomerism
(D) $[Co(NH_3)_6][Cr(CN)_6]$	(S) Geometrical isomerism

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. The compound having tetrahedral geometry is

(a) $[Ni(CN)_4]^{2-}$ (b) $[Pd(CN)_4]^{2-}$

(c) $[Pd(Cl)_4]^{2-}$ (d) $[Ni(Cl)_4]^{2-}$

[IIT-2004]

2. Spin only magnetic moment of the compound $Hg[Co(SCN)_4]$ is

(a) $\sqrt{3}$ (b) $\sqrt{15}$

(c) $\sqrt{24}$ (d) $\sqrt{8}$

[IIT-2004]

3. Which kind of isomerism is shown by $Co(NH_3)_4Br_2Cl$?

(a) Geometrical and ionisation

(b) Optical and ionisation

(c) Geometrical and optical

(d) Geometrical only

[IIT-2005]

4. If the bond length of CO bond in carbon monoxide is 1.128 Å, then what is the value of CO bond length in $Fe(CO)_5$?

(a) 1.15 Å (b) 1.128 Å

(c) 1.72 Å (d) 1.118 Å

[IIT-2006]

5. Among the following metal carbonyls, the C—O bond order is lowest in

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$

(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

[IIT-2007]

6. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes respectively, are

(a) sp^3, sp^3.   (b) sp^3, dsp^2
(c) dsp^2, sp^3.   (d) dsp^2, dsp^2

[IIT-2008]

7. Among the following, the coloured compounds is

(a) $CuCl$ (b) $K_3[Cu(CN)_4]$
(c) CuF_2 (d) $[Cu(CH_3CN)_4]BF_4$

[IIT-2008]

8. The IUPAC name of $[Ni(NH_3)_4]\ [NiCl_4]$ is

(a) Tetrachloronickel (II) - tetraamminenickel (II)
(b) Tetraamminenickel (II) - tetrachloronickel (II)
(c) Tetraamminenickel (II) - tetrachloronickelate (II)
(d) Tetrachloronickel (II) - tetraammnenickelate (0)

[IIT-2008]

9. **Statement I:** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
Statement II: The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true ; Statement II is false.
(d) Statement I is false; Statement II is true.

[IIT-2008]

10. The complex showing a spin only magnetic moment of 2.82 BM is

(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2-}$
(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)_4]^{2-}$

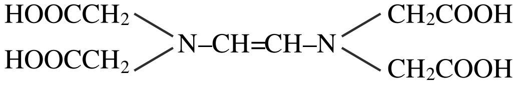
[IIT-2010]

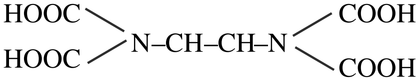
11. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is

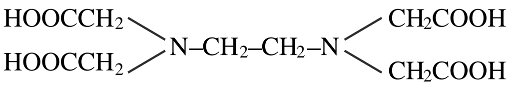
(a) 0   (b) 2.84
(c) 4.90   (d) 5.92

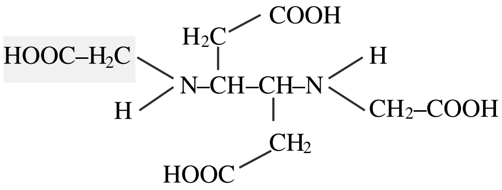
[IIT-2010]

12. The correct structure of ethylenediaminetetraacetic acid (EDTA) is

(a) 

(b) 

(c) 

(d) 

[IIT-2010]

13. The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is

(a) $[Cr(H_2O)_4(O_2N)]Cl_2$
(b) $[Cr(H_2O)_4\ Cl_2]\ (NO_2)$
(c) $[Cr(H_2O)_4\ Cl(ONO)]Cl$
(d) $[Cr(H_2O)_4\ Cl_2(NO_2)].\ H_2O$

[IIT-2010]

14. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are

(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral

[IIT-2011]

15. Among the following complexes (K to P)

$K_3[Fe(CN)_6]$ (K), $[Co(NH_3)_6]Cl_3$(L),
$Na_3[Co(ox)_3]$ (M), $[Ni(H_2O)_6]Cl_2$(N),
$K_2[Pt(CN)_4]$ (O), $[Zn(H_2O)_6](NO_3)_2$(P)

The diamagnetic complexes are

(a) K, L, M, N   (b) K, M, O, P
(c) L, M, O, P   (d) L, M, N, O

[IIT-2011]

16. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behavior (paramagnetic/diamagnetic) the coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states respectively, are

(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

[IIT-2012]

17. As per IUPAC nomenclature, the name of the complex $[Co\ (H_2O)_4\ (NH_3)_2]\ Cl_3$ is

(a) tetraaquadiaminecobalt (III) chloride
(b) tetraaquadiamminecobalt (III) choride

(c) diaminetetraquacobalt (III) chloride

(d) diamminetetraaquacobalt (III) chloride

[IIT-2012]

18. Consider the following complex ions, P, Q and R.

$P = [FeF_6]^{3-}$, $Q = [V(H_2O)_6]^{2+}$ and
$R = [Fe(H_2O)_6]^{2+}$.

The correct order of the complex ions, according to their spin-only magnetic moment values (in BM) is

(a) R < Q < P (b) Q < R < P

(c) R < P < Q (d) Q < P < R

[JEE-Advanced-2013]

19. Match each coordination compound in Column I with an appropriate pair of characteristics from Column II and select and correct answer using the codes given below the Columns

(en = $H_2NCH_2CH_2NH_2$; atomic numbers :
Ti = 22; Cr = 24; Co = 27; Pt = 78)

	Column I	**Column II**
(A)	$[Cr(NH_3)_4Cl_2]Cl$	(a) Paramagnetic and exhibits ionisation isomerism
(B)	$[Ti(H_2O)_5Cl](NO_3)_2$	(b) Diamagnetic and exhibits cis-trans isomerism
(C)	$[Pt(en)(NH_3)Cl]NO_3$	(c) Paramagnetic and cis-trans isomerism
(D)	$[Co(NH_3)_4(NO_3)_2]NO_3$	(d) Diamagnetic and exhibits ionisation isomerism

Codes:

	A	**B**	**C**	**D**		**A**	**B**	**C**	**D**
(a)	d	b	c	a	(b)	c	a	d	b
(c)	b	a	c	d	(d)	a	c	d	b

[JEE-Advanced-2014]

20. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is:

(a) pentaammine nitro-N-cobalt (II) chloride

(b) pentaammine nitro-N-cobalt (III) chloride

(c) nitrito-N-pentaammineocobalt (III) chloride

(d) nitrito-N-pentaammineocobalt (II) chloride

[AIEEE-2006]

21. In $Fe(CO)_5$, the Fe–C bond possesses-

(a) ionic character (b) σ-character only

(c) π-character (d) both σ and π character

[AIEEE-2006]

22. How many EDTA (ethylenediaminetetraacetate ion) molecules are required to make an octahedral complex with a Ca^{2+} ion?

(a) One (b) Two

(c) Six (d) Three

[AIEEE-2006]

23. The "spin only" magnetic moment [in units of Bohr magneton] of Ni^{2+} in aqueous solution would be. (At. No. Ni = 28)-

(a) 0 (b) 1.73

(c) 2.84 (d) 4.90

[AIEEE-2006]

24. The only of the 'spin only' magnetic moment for one of the following configuration is 2.84 BM. The correct one is:

(a) d^4 (in strong ligand field)

(b) d^4 (in weak ligand field)

(c) d^3 (in weak as well as in strong field)

(d) d^5 (in strong ligand field)

[AIEEE-2006]

25. Which one of the following has a square planar geometry–

(Co = 27, Ni = 28, Fe = 26, Pt = 78)-

(a) $[CoCl_4]^{2-}$ (b) $[FeCl_4]^{2-}$

(c) $[NiCl_4]^{2-}$ (d) $[PtCl_4]^{2-}$

[AIEEE-2007]

26. The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively–

(a) 6 and +2 (b) 4 and +2

(c) 4 and +3 (d) 6 and +3

[AIEEE-2008]

27. In which of the following octahedral magnitude of Δ_0 be the highest?

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$

(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

28. Which of the following has an optical isomer?

(a) $[Co(en)(NH_3)_2]^{2+}$ (b) $[Co(H_2O)_4(en)]^{3+}$

(c) $[Co(en)_2(NH_3)_2]^{3+}$ (d) $[Co(NH_3)_3Cl]^{+}$

[AIEEE-2009]

29. Which of the following pairs represents linkage isomers?

(a) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

(b) $[Co(NH_3)_5(NO_3)]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(c) $[Pt\,Cl_2\,(NH_3)_4]\,Br_2$ and $[Pt\,Br_2\,(NH_3)_4]\,Cl_2$
(d) $[Cu(NH_3)_4]\,[(PtCl_4)]$ and $[Pt(NH_3)_4]\,[CuCl_4]$

[AIEEE-2009]

30. Among the ligands NH_3, en, CN^- and CO the correct order the their increasing field strength, is-

(a) $NH_3 < en < CN^- < CO$
(b) $CN^- < NH_3 < CO < en$
(c) $en < CN^- < NH_3 < CO$
(d) $CO < NH_3 < en < CN^-$

[AIEEE-2011]

31. Which one of the following complex ions has geometrical isomers?

(a) $[Ni(NH_3)_5Br]^+$
(b) $[Co(NH_3)_2\,(en)_2]^{3+}$
(c) $[Cr(NH_3)_4(en)]^{3+}$
(d) $[Co(en)_3]^{3+}$ (en = ethylenediamine)

[AIEEE-2011]

32. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide?

(a) $[Cr(en)_2Br_2]$ Br (b) $[Cr(en)_2Br_2]$ Br
(c) $[Cr(en)\,Br_2]$ Br (d) $[Cr(en)_3]Br_3$

[AIEEE-2012]

33. The d-electron configuration of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and and d^7 respectively. Which one of the following will exhibit the lowest paramagnetic behavior?
(At number Cr = 24, Mn = 25, Fe = 26, Co = 27)

(a) $[Cr(H_2O)_6]^{2+}$ (b) $[Co(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{2+}$

[AIEEE Online-2012]

34. The correct order of ligands in the spectrochemical series is:

(a) $NCS^- > CN^- > Cl^- >$ en
(b) $CN^- >$ en $> NCS^- > Cl^-$
(c) $Cl^- >$ en $> CN^- > NCS^-$
(d) en $> CN^- > Cl^- > NCS^-$

[AIEEE Online-2012]

35. Square-planar geometry is shown by:

(a) $[NiCl_4]^{2-}$ (b) CrO_4^{2-}
(c) MnO_4^- (d) $[PtCl_2(NH_3)_2]$

[AIEEE Online-2012]

36. Which of the following complex ions will exhibit optical isomerism? (en = 1.2 diamine ethane)

(a) $[Co(en)_2Cl_2]^+$
(b) $[Zn(en)_2]^{2+}$
(c) $[Co(NH_3)_2Cl_2]^+$
(d) $[Cr(NH_3)_2Cl_2]^+$

[AIEEE Online-2012]

37. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$

(a) Linkage isomerism
(b) Coordination isomerism
(c) Ionisation isomerism
(d) Solvate isomerism

[AIEEE Online-2013]

38. Which of the following is diamagnetic?

(a) $[Fe(CN)_6]^{3-}$ (b) $[Co(OX)_3]^{3-}$
(c) $[FeF_6]^{3-}$ (d) $[Co(F_6)]^{3-}$

[AIEEE Online-2013]

39. In which of the following octahedral complex species the magnitude of Δ_0 will be maximum ?

(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Co(C_2O_4)_3]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

[JEE-Main Online-2013]

40. The correct statement about the magnetic properties of $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ is:

(Z = 26)

(a) both are paramagnetic
(b) both are diamagnetic
(c) $[Fe(CN)_6]^{3-}$ is diamagnetic, $[FeF_6]^{3-}$ is paramagnetic
(d) $[Fe(CN)_6]^{3-}$ is paramagnetic, $[FeF_6]^{3-}$ is diamagnetic

[JEE-Main Online-2014]

41. An octahedral complex of Co^{3+} is diamagnetic. The hybridisation involved in the formation of the complex is:

(a) $sp^3\,d^2$ (b) dsp^2
(c) d^2sp^3 (d) dsp^3d

[JEE-Main Online-2014]

42. Which of the following name formula combinations is not correct?

Formula	**Name**
(a) $K_2[Pt(CN)_4]$	Potassium tetracyanoplatinate (II)
(b) $[Mn(CN)_5]^{2-}$	Pentacyanomagnate (II) ion
(c) $K[Cr(NH_3)_2Cl_4]$	Potassium diammine tetrachlorochromate (III)
(d) $[Co(NH_3)_4(H_2O)I]SO_4$	Tetraammine aquaiodo cobalt (III) sulphate

[JEE-Main Online-2014]

43. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of this complex, the species which acts as the Lewis acid is-

(a) $[Co(NH)_6]^{3+}$ (b) Cl^-

(c) Co^{3+} (d) NH_3

[JEE-Main Online-2014]

44. Which one of the following complexes will most likely absorb visible light?

(At number Sc = 21, Ti = 22, V = 23, Zn = 30)

(a) $[Sc(H_2O)_6]^{3+}$ (b) $[Ti(NH_3)_6]^{4+}$

(c) $[V(NH_3)_6]^{3+}$ (d) $[Zn(NH_3)_6]^{2+}$

[JEE-Main Online-2014]

45. An octahedral complex with molecular composition $M.5NH_3$. $ClSO_4$ has two isomers, A and B. The solution of A gives a white precipitate with $AgNO_3$ solution and the solution of B gives white precipitate with $BaCl_2$ solution. The type of isomerism exhibited by the complex is:

(a) Linkage isomerism

(b) Ionisation isomerism

(c) Coordinate isomerism

(d) Geometrical isomerism

[JEE-Main Online-2014]

46. Nickel (Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex $[NiL_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively.

(a) sp^3, two (b) dsp^2, zero

(c) dsp^2, one (d) sp^3, zero

[JEE-Main Online-2014]

47. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is

(a) $L_4 < L_3 < L_2 < L_1$. (b) $L_1 < L_3 < L_2 < L_4$

(c) $L_3 < L_2 < L_4 < L_1$. (d) $L_1 < L_2 < L_4 < L_3$

[JEE-Main-2014]

48. Which molecule /ion among the following cannot act as a ligand in complex compounds

(a) CH_4. (b) CN^-

(c) Br^- (d) CO

[JEE-Main Online-2015]

49. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbits?

(a) $[FeF_6]^{3-}$ (b) $[Mn(CN)_6]^{4-}$

(c) $[CoF_6]^{3-}$ (d) $[Co(NH_3)_6]^{2+}$

[JEE-Main Online-2015]

50. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction

(a) $[CoCl_6]^{3-}$ (b) $[Co(H_2O)_6]^{2+}$

(c) $[CoCl_6]^{4-}$ (d) $[CoCl_4]^{2-}$

[JEE-Main Online-2015]

51. The colour of $KMnO_4$ is due to

(a) M → L charge transfer transition

(b) d → d transition

(c) L → M charge transfer transition

(d) $\sigma \rightarrow \sigma^*$ transition

[JEE-Main-2015]

52. The equation which is balanced and represents the correct product (s) is

(a) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$

(b) $[CoCl(NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$

(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{Excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$

(d) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$

[JEE-Main-2015]

53. The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH))]^+$ is (py = pyridine).

(a) 2 (b) 3

(c) 4 (d) 6

[JEE-Main-2015]

54. The pair having the same magnetic moment is [at number Cr = 24, Mn = 25, Fe = 26 and Co = 27]

(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$

(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$

(c) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$

(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

[JEE-Main-2016]

55. Which one of the following complexes shows optical isomerism?

(a) cis $[Co(en)_2Cl_2]Cl$

(b) trans $[Co(en)_2Cl_2]Cl$

(c) $[Co(NH_3)_4Cl_2]Cl$

(d) $[Co(NH_3)_3Cl_3]$

[JEE-Main-2016]

Answer Key

LEVEL I

1. (d) 2. (d) 3. (b) 4. (d) 5. (c) 6. (b) 7. (b) 8. (b) 9. (c) 10. (b)
11. (c) 12. (d) 13. (c) 14. (b) 15. (c) 16. (d) 17. (c) 18. (a) 19. (a) 20. (c)
21. (d) 22. (a) 23. (d) 24. (c) 25. (d) 26. (c) 27. (c) 28. (c) 29. (d) 30. (d)
31. (b) 32. (a) 33. (d) 34. (d) 35. (b) 36. (b) 37. (b) 38. (c) 39. (b) 40. (c)

LEVEL II

1. (b) 2. (d) 3. (d) 4. (d) 5. (c) 6. (a) 7. (c) 8. (b) 9. (d) 10. (a)
11. (a) 12. (c) 13. (c) 14. (b) 15. (c) 16. (b) 17. (b) 18. (c) 19. (d) 20. (d)
21. (b) 22. (c) 23. (b) 24. (c) 25. (c) 26. (c) 27. (b) 28. (b) 29. (c) 30. (b)
31. (d) 32. (b) 33. (a) 34. (c) 35. (b) 36. (c) 37. (d) 38. (c) 39. (b) 40. (d)

LEVEL III

1. (a,b,d) 2. (a,d) 3. (a,b,c) 4. (a,b,d) 5. (b,c) 6. (a,c,d) 7. (a.d) 8. (a,b,d)
9. (a,b,d) 10. (b,c) 11. (b,c,d) 12. (b,c,d) 13. (a) 14. (c) 15. (b) 16. (a)
17. (d) 18. (d) 19. (1) 20. (13) 21. (4) 22. (5) 23. (4) 24. (0)
25. A → P, R; B → Q, S; C → P, Q; D → R, S
26. A → Q, R, S ; B → P, Q, R; S; C → P, R; D → P, R, S
27. A → R, B → Q; C → P, D → S
28. P → 4; Q → 1; R → 1, 2, 4; S → 3

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (d) 2. (b) 3. (a) 4. (a) 5. (d) 6. (b) 7. (c) 8. (c) 9. (a) 10. (b)
11. (a) 12. (c) 13. (b) 14. (b) 15. (c) 16. (c) 17. (d) 18. (b) 19. (b) 20. (b)
21. (d) 22. (a) 23. (c) 24. (a) 25. (d) 26. (d) 27. (a) 28. (c) 29. (a) 30. (a)
31. (b) 32. (a) 33. (b) 34. (b) 35. (d) 36. (a) 37. (a) 38. (b) 39. (b) 40. (a)
41. (c) 42. (b) 43. (c) 44. (c) 45. (b) 46. (b) 47. (b) 48. (a) 49. (a) 50. (d)
51. (c) 52. (b) 53. (b) 54. (a) 55. (a)

Hints and Solutions

LEVEL I

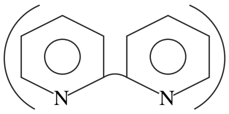
1. **(d)** Double salts completely ionise in aqueous solution.

2. **(d)** Oxalate is an anionic bidentate ligand.

gly is an unsymmetrical and anionic ligand.

dien is a trtidentate ligand.

dipyridyl



is a neutral and symmetrical bidentate ligand.

3. **(b)** NO_2^- and SCN^- are ambidentate ligands.

4. **(d)** EDTA is a polydentate ligand hence, it is also a chelating ligand. $EDTA^{-3}$ is a pentadentate while $EDTA^{-4}$ is a hexadentate ligand hence, it is a flexidentate ligand.

5. **(c)** Oxalate is a bidentate ligand hence, it is a chelating ligand.

6. **(b)** Ambidentate ligands are monodentate ligands.

7. **(b)** Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$) is a double salt.

8. **(b)** $[Fe(NH_3)_4Cl_2]^+$ is a heteroleptic complex because it has more than one type of ligands.

9. **(c)** In the structure, $[H_3N–CH_2–CH_2–NH_3]^{2+}$, no atom has any lone pair.

10. **(b)** EAN of Mn in $Mn(CO)_5$ is 35. To gain stability, it will gain an e^- hence, it will behave as oxidizing agent.

11. **(c)**

Complex	EAN of central metal
$[Pd(NH_3)_6]Cl_4$	46 – 4 + 12 = 54
$[Cr(NH_3)_5Cl]SO_4$	24 – 3 + 12 = 33
$Na_4[Fe(CN)_6]$	26 – 2 + 12 = 36
$K_3[Fe(CN)_6]$	26 – 3 + 12 = 35

12. **(d)** Sodium nitroprusside is

$Na_2[\overset{+2}{Fe}(CN)_5\overset{+1}{NO}]$

EAN of Fe = 26 – 2 + 12 = 36

13. **(c)** 36 = 26 – 0 + 2x

x = 5

$[M(CO)_5]$

14. **(b)** $[\overset{+4}{Pt}(\overset{a}{NH_3})_3(\overset{b}{Br})(\overset{n}{NO_2})(\overset{c}{Cl})]C\ell$

Triamminebromochloronitroplatinum (IV) chloride

15. **(c)** Potassium dicyanodioxalatonickelate (II)

$K_4[Ni(CN)_2(OX)_2]$

16. **(d)** $[\overset{+3}{Co}(NH_3)_6][\overset{+3}{Co}(ONO)_6]$

Hexaamminecoblat (III) Hexanitrito-O-cobaltate (III)

17. **(c)** $\underset{1mol}{CrCl_3 . 6H_2O} + \underset{excess}{Ag\,NO_3} \rightarrow \underset{2mol}{AgCl}$

The formula of the complex is $[Cr(H_2O)_5Cl]Cl_2.\,H_2O$

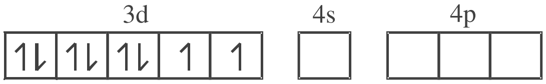
18. **(a)** Conductance depends on number of ions:

Complex	Number of ions
$[Co(NH_3)_6]Cl_3$	4
$[Co(NH_3)_3Cl_3]$	0
$[Co(NH_3)_4Cl_2]Cl$	2
$[Co(NH_3)_5Cl]Cl_2$	3

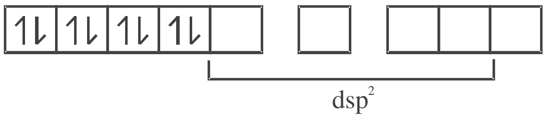
19. **(a)** For octahedral complex of Co^{+3} ion, H_2O and $C_2O_4^{-2}$ act as strong field ligand.

20. **(c)** $[Ni(CN)_4]^{-2}$

$Ni^{+2} = [Ar]\ 4s^{\circ}\ 3d^8$



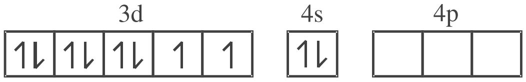
After pairing



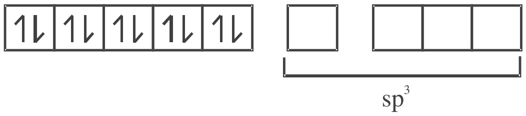
Magnetic behaviour is diamagnetic

$[Ni(CN)_4]^{-4}$

Ni = $[Ar]\ 4s^2 3d^8$



After pairing



21. **(d)** $[Ni(CN)_5]^{-3}$, dsp^3, (Inner orbital), diamagnetic

$[Fe(CN)_6]^{-4}$, d^2sp^3, (Inner orbital), diamagnetic

$[Fe(H_2O)_5, (NO)]\ SO_4$ sp^3d^2, (Outer orbital), paramag netic

$[Fe(CN)_6]^{-3}$, d^2sp^3, (Inner orbital), paramagnetic

22. **(a)** EAN of Fe in $[Fe(CN)_6]^{4-} = 36$

Hybridisation of Fe is d^2sp^3. It has 6 co-ordinate bonds and 12 sigma bonds.

23. **(d)** $[NiCl_4]^{-2}$ Tetrahedral, sp^3, paramagnetic

$[Ni(CN)_4]^{-2}$ Square planar, dsp^2, diamagnetic

24. **(c)** According to VBT, geometry of $[Cu(NH_3)_4]^{+2}$ is tetrahedral but its actual geometry is square planar.

25. **(d)** Splitting energy of square planar complex is higher than octahedral complex.

26. **(c)** In d^8 configuration of square planar all electrons are paired hence, magnetic moment is zero.

27. **(c)** $[Fe(CN)_6]^{4-}$

$Fe^{+2} = [Ar]\ 4s^{\circ}\ 3d^6$

According to CFT, in presence of strong field ligand d^6 configuration is $t_{zg^6eg^{\circ}}$

28. **(c)** $\Delta_t \approx \frac{4}{9}\Delta_0$

$\Delta_t \approx \frac{4}{9} \times 18000 = 8000\ cm^{-1}$

29. **(d)** Order of stability:

3d < 4d < 5d– series central metal

30. **(d)** Cause of colour of a compound:

Polarisation, d-d transition, charge transfer spectra.

31. **(b)** Cause of colour in $KMnO_4$ is ligand to metal charge transfer.

32. **(a)** The colour of an aqueous solution of $CuSO_4$ is blue green. Its complementary colour is orange-red.

33. **(d)** Ma_4b_2 complex does not show optical isomerism.

34. **(d)** $[Co(en)_3]$ $[Cr(CN)_6]$ and $[Co(en)_2\ (CN)_2]$ $[Co(en)\ (CN)_4]$ ⇒ Co-ordination isomers

$[Mn(CO)_5(SCN)]$ and $[Mn(CO)_5(NCS)]$ ⇒ Linkage iosmers

$[Co(NH_3)_5(NO_2)]\ SO_4$ and $[Co(NH_3)_5(SO_4)]$ NO_2 ⇒ Ionization isomers

35. **(b)** $[Co(NH_3)_4Cl_2]^+$ for Ma_4b_2 complex 2 gemetrical isomers

$[Co(en)_2Cl_2]^+$ for $M(AA)_2b_2$ complex 2 geometrical isomers, one geometrical isomer is optically active.

36. **(b)** Pentaamminenitrochromium (III) ion

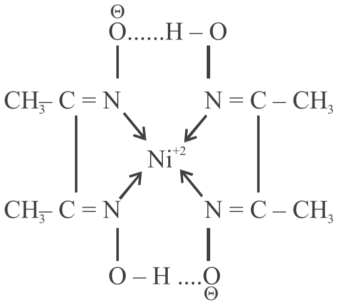
$[Cr(NH_3)_5(NO_2)]^{+2}$

It can display linkage isomerism.

37. **(b)** S^{-2} ion forms violet colour complex, $Na_4[Fe(CN)_5(NOS)]$, with sodium nitroprusside.

38. **(c)** $Cu^{+2} + K_4[Fe(CN)_6] \rightarrow \underset{\text{chocolate ppt.}}{Cu_2[Fe(CN)_6]}$

39. **(b)** This complex is extra stabilized by hydrogen bonding.



40. **(c)** $\underset{\text{(undecomposed)}}{AgBr} + Na_2S_2O_3 \rightarrow \underset{\text{soluble complex}}{Na_3\,[Ag(S_2O_3)_2]}$

LEVEL II

1. **(b)** $\underset{0.1\ mol}{CrCl_3.\ 6H_2O} + \underset{excess}{AgNO_3} \rightarrow \underset{28.7g}{AgCl}$

or

$$\frac{28.7}{143.5} = 0.2\ mol$$

Hence, the formula of the complex would be $[Cr(H_2O)_5Cl]Cl_2.H_2O$

2. **(d)** In metal carbonyls, paired d-orbital of central metal forms π-bond with vacant π^*-orbital of ligand CO.

3. **(d)** EAN of Ni is $[Ni(CO)_4] = 28 - 0 + 8 = 36$

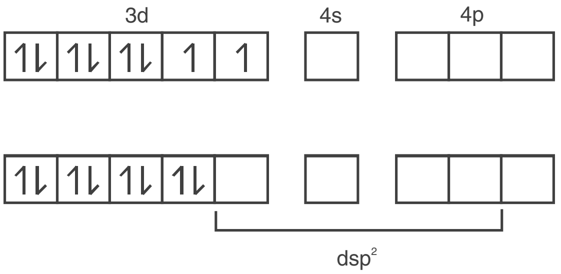
EAN of Ni in $[Ni(CN)_4]^{2-} = 28 - 2 + 8 = 34$

4. **(d)** $K_2\,[Cr(CN)_2\underset{\substack{\uparrow \\ \text{oxo}}}{O_2}\underset{\substack{\uparrow \\ \text{peroxo}}}{(O_2)}NH_3]$

Potassium amminedicyanodioxoperoxochromate (VI)

5. **(c)** $[NiX_4]^{-2}$ has zero unpaired e^- hence, pairing of electrons ocurs. X is a strong field ligand.

$Ni^{+2} = [Ar]\,4s^{\circ}\,3d^{8}$



6. **(a)** Magnetic moment = 2.83 BM

Number of unpaired e^- = 2

Complex	Unpaired e^-
$[V(H_2O)_6]^{+3}$	2
$[Cr(H_2O)_6]^{+3}$	3
$[Cu(CN)_4]^{-2}$	1
$[MnCl_4]^{-2}$	5

7. **(c)** In brown ring complex, $[Fe(H_2O)_5NO]\,SO_4$, Fe has three unpaired e^- hence, magnetic moment = $\sqrt{15}$ BM and, hybridization is sp^3d^2.

8. **(b)** IUPAC name is.

Pentaaminenitrito-N-chromium (III) tetrachlorozincate (II)

This compound shows linkage and co-ordination isomerism but not geometrical isomerism.

9. **(d)** Square planar complex Ma_2b_2 shows geometrical isomerism.

10. **(a)** Cis-platin $[PtCl_2(NH_3)_2]$ is used in cancer chemotherapy.

11. **(a)** $Ag_2S + CN^- + H_2O + O_2 \rightarrow [Ag(CN)_2]^-$

12. **(c)** 1 litre of mixture x + excess $AgNO_3 \rightarrow$ Y

$[Co(NH_3)_5Br]SO_4 + AgNO_3 \rightarrow AgBr$

0.01 mol 0.01 mol

1 litre of mixture x + excess $BaCl_2 \rightarrow$ Z

$[Co(NH_3)_5Br]SO_4 + BaCl_2 \rightarrow BaSO_4$

0.01 mol 0.01 mol

13. **(c)** Sodium nitroprusside, $Na_2[\overset{+2}{Fe}(CN)_5\,\overset{+1}{NO}]$

14. **(b)** Mond's process → $[Ni(CO)_4]$

unreacted AgBr from photographic plate → $[Ag(S_2O_3)_2]^{3-}$

Lead poisoning from the body → $[Pb(EDTA)]^{2-}$

15. **(c)** $NaCl + AgNO_3 \rightarrow \underset{(A)}{AgCl\downarrow} + \underset{(B)}{NaNO_3}$

$AgCl + NH_{3(solution)} \rightarrow \underset{(C)}{[Ag(NH_3)_2]Cl}$

(By adding HNO_3, this reaction shifted in backward direction)

$CuSO_4 + NH_{3(solution)} \rightarrow \underset{(D)}{[\overset{+2}{Cu}(NH_3)_4]SO_4}$

16. **(b)** In MnO_4^-, hybridization of Mn is d^3s

d-orbitals used in this hybridization are d_{xy}, d_{yz}, d_{xz}.

17. **(b)** $\Delta_0 = \frac{hc}{\lambda}$ or $\Delta_0 \propto \frac{1}{\lambda}$

$[M(NH_3)_6]^{2+}$ has greater Δ_0 than $[M(H_2O)_6]^{2+}$

18. **(c)** It is due to charge transfer from 'O' to 'Mn' (L → M).

19. **(d)** In $[Cu(NH_3)_4]^{2+}$, hybridization of Cu^{2+} is dsp^2 and it has square planar geometry.

20. **(d)** IUPAC name is :

(η^6–benzene) tricarbonylchromium (o)

21. **(b)** Ligands with two or more points of attachment to single metal atoms are called as polydentate ligands. They are chelating ligands.

22. **(c)** $[Cu(H_2O)_4]\,SO_4.\,H_2O$; $[Zn(H_2O)_4]\,SO_4.\,H_2O$; $[Fe(H_2O)_6]\,SO_4.\,H_2O$

23. **(b)** If x = 1; y = 1; z = 2. $[Cr(C_2O_4)\,(en)\,(O_2)_2]^-$ then co-ordination number of Cr is 6.

24. **(c)** $\frac{1}{3}$ of total chlorine of $CrCl_3.6H_2O$ is precipitated. It means in ionization sphere one chlorine is present.

25. **(c)** $[Cu(NH_3)_4]\,SO_4$ is a complex salt

$K_2SO_4.Al_2(SO_4)_3.\ 24H_2O$ (potash alum) is a double salt.

26. **(c)** EAN of Mg = 12 – 2 + 12 = 22

27. **(b)** Pentaamminenitrochromium (III) perchlorate

$[Cr(NH_3)_5\,(NO_2)]\,ClO_4$

This compound can show linkage isomerism

28. **(b)** (A) trans-$[Co(NH_3)_4I_2]^+$ optically inactive

(B) cis-$[Co(NH_3)_2(en)_2]^{3+}$ optically active

(C) trans-$[Co(NH_3)_2(en)_2]^{3+}$ optically inactive

(D) $[NiI_4]^{2-}$ coloured

(E) $[TiF_6]^{2-}$ colourless

(F) $[CoF_6]^{3-}$ coloured

29. **(c)** $Cr(NH_3)_5Cl_3 + AgNO_3 \rightarrow AgCl$

1 mol 2 mol 2 mol

Or

$[Cr\,(NH_3)_5Cl]\,Cl_2$

30. **(b)** [Co(en)$_3$]Cl$_3$. M(AA)$_3$
cis-[Co(en)$_2$Cl$_2$] cis-M(AA)$_2$b$_2$; They show optical isomerism

31. **(d)**

Complex	Number of unpaired e$^-$
[MnBr$_4$]$^{2-}$	5
[Fe(CN)$_6$]$^{4-}$	0
[CoBr$_4$]$^{-2}$	3

32. **(b)** Na$_2$[Cd Cl$_4$]
Cd^{+2} = [Kr] 5s° 4d^{10}
Due to fullfilled d-subshell, there is no d-d transition.

33. **(a)** Magnitude of Δ_0 depends on strength of ligand.
order of strength of ligand :
F$^-$ < NH$_3$ < NO$_2^-$ < CN$^-$

34. **(c)** Order of the crystal field splitting power is :
H$_2$O < NH$_3$ < NO$_2^-$ < CN$^-$

35. **(b)** [Fe(CN)$_6$]$^{3-}$
Fe^{+3} = [Ar] 4s°3d^5
Hybridization of Fe^{+3} is d^{2}sp^3 (Inner orbital complex)
Due to presence of strong field ligand pairing occurs (low spin)

36. **(c)** Wilkinson's catalyst is [RhCl (PPh$_3$)$_3$]
Hybridisation of Rh is dsp^2 and geometry is square planar.

37. **(d)** [Cr(H$_2$O)$_6$]Cl$_3$
Cr^{+3} = [Ar] 4s° 3d^3
According to CFT, this configuration is $t_{2g}^3\, e_g^0$
It means, $3d_{xy}^1$, $3d_{yz}^1$, $3d_{xz}^1$

38. **(c)** $\boxed{\Delta_0 \propto \frac{1}{\lambda}}$

Order of Δ_0 is,
[Co(CN)$_6$]$^{3-}$ > [Co(NH$_3$)$_6$]$^{3+}$ > [Co(H$_2$O)$_6$]$^{3+}$
Order of wavelength of absorbed light (λ) is,
[Co(CN)$_6$]$^{3-}$ < [Co(NH$_3$)$_6$]$^{3+}$ < [Co(H$_2$O)$_6$]$^{3+}$

39. **(b)** $\boxed{\Delta_0 \propto \frac{1}{\lambda}}$

Order of Δ_0:
[M(en)$_3$]$^{2+}$ > [M(H$_2$O)$_6$]$^{2+}$ > [MBr$_6$]$^{4-}$
Order of λ (wavelength of abosrbed light):
[M(en)$_3$]$^{2+}$ < [M(H$_2$O)$_6$]$^{2+}$ < [MBr$_6$]$^{4-}$
(green) (orange) (red)

Complex	Colour of absorbed light	Complementary colour (Colour of complex)
[MnBr$_4$]$^{4-}$	Red	Green
[M(H$_2$O)$_6$]$^{2+}$	Orange	Blue
[M(en)$_3$]$^+$	Green	Red

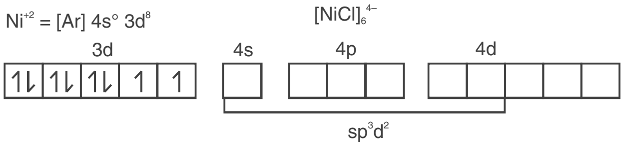
40. **(d)** With CN$^-$, SCN$^-$, I$^-$ etc. the more stable oxidation state for Cu is +1.

LEVEL III

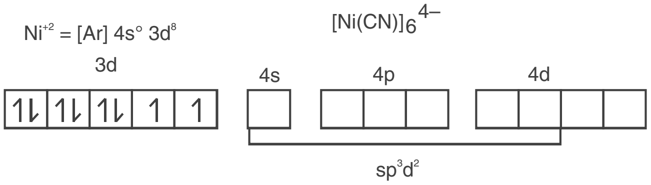
1. (a,b,d) Complex compound [Co(SCN)$_2$ (NH$_3$)$_4$] Cl
Ma$_4$b$_2$ does not show optical isomerism

2. (a, d) Pentaamminecynidochromium (II) hexa nitrito-N-irridate (III)
[Cr(NH$_3$)$_5$(CN)]$_3$ [Ir(NO$_2$)$_6$]
Pentaaminecyanidochromium (III) hexa nitrito-N-irridate (III)
[Cr(NH$_3$)$_5$(CN)]$_3$ [Ir(NO$_2$)$_6$]$_2$

3. (a,b,c)



Number of unpaired e$^-$ = 2
Octahedral geometry



Number of unpaired e$^-$ = 2
Octahedral geometry
Both complex have different ligands hence, they have different colour and stability.

4 (a,b,d)

Complex	EAN
K[Co(CO)$_4$]	27 + 1 + 8 = 36
K$_2$[Fe(CO)$_4$]	26 + 2 + 8 = 36
[Co(NH$_3$)$_6$]Cl$_2$	27 – 2 + 12 = 37
[CoCl$_3$(H$_2$O)$_3$]	27 – 3 + 12 = 36

5. (b,c)

Electronic configuration	**Hybridization of central metal**
$d^0 - d^3$	d^2sp^3
$d^8 - d^{10}$	sp^3d^2

In these cases, magnetic moment remains same either in strong field or in weak field ligand.

6. (a,c,d) In Ma_4b_2 complex both cis and trans-form are optically inactive.

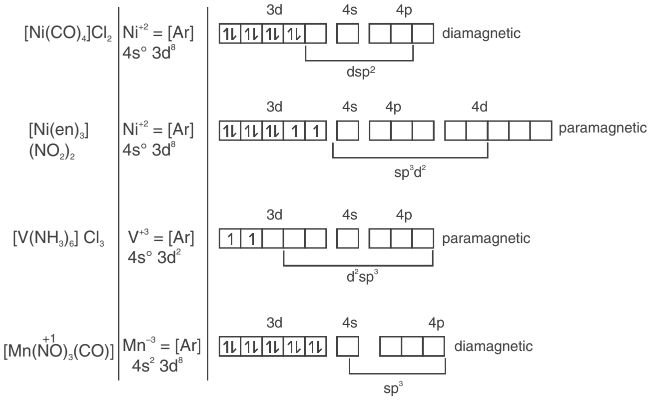
$M(AA)_3$ complex shows optical isomerism but not geometrical isomerism.

Mabcd tetrahedral complex shows optical isomerism but Mabcd square planar complex does not show optical isomerism.

7. (a,d) In sp^3d^2 or d^2sp^3 hybridization, d-orbitals involved are $d_{x^2-y^2}$ and d_{z^2}

8. (a,b,d) Potassium hexacyanidoferrate (III) is $K_3[Fe(CN)_6]$

9. (a,b,d)



10. (b, c)

S_1 is incorrect but S_2 and S_3 are correct.

11. (b, c, d)

I and II are geometrical isomers.

I and III are geometrical isomers.

II and III are identical.

12. (b, c, d)

Order of C – O bond order:

$[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$

Order of M – C bond order:

$[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+$

13. (a)

If, there is no loss in weight with concentrated H_2SO_4 then complex does not have water of crystalisation. complex gives white precipitate of AgCl.

Complex is: $[Co(Br)(H_2O)(en)_2]Cl_2$.

14. (c) Trans form of complex $[Co(Br)(H_2O)(en)_2]Cl_2$ is optically inactive.

15. (b) Ir belongs to 5d-series. In 5d-series central metal, pairing always occurs hence, $\Delta_0 > P$

16. (a) $CH_3COO^- < H_2O < NH_3 < CN^-$

17. (d) Chloridotris-(triphenylphosphine) rhodium (I) $[Rh(PPh_3)_3Cl]$ is used as homogenous catalyst for hydrogenation of alkenes.

18. (d) Complex, $[Co(NH_3)_4Br_2]\ NO_2$ shows ionisation, linkage and geometical isomerism. Its both cis and trans forms have plane of symmetry.

19. $[\overset{+1}{Fe}(H_2O)_5\overset{+1}{NO}]\ SO_4$

20.

Complex	**Denticity**
Glycinate	2
Oxalate	2
O-phenathroline	2
2,2,-bipyridyl	2
diethylenetriamine	3
ethylenediamine	2

21.

Complex	**Number of geometrical isomers**
$[CoCl_2Br_2]^{2-}$	Zero (tetrahedral complex)
$[Rh(en)_3]^{3+}$	Zero
$[Cr(en)_2Br_2]^+$	2
$[Pt(en)Cl_2]$	Zero
$[Co(NH_3)_3(NO_2)_3]$	2

22. Metal carbonyls follow EAN rule and in metal carbonyls oxidation number of central metal is zero.

$[Fe(CO)_x]$

$36 = 26 - 0 + 2x$

$x = 5$

23.

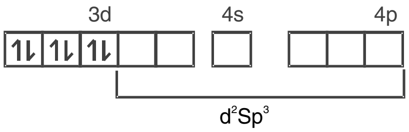
Metal ion	**Electronic configuration**
Co^{+3}	[Ar] 4s° $3d^6$
Ni^{+2}	[Ar] 4s° $3d^8$
Cr^{+3}	[Ar] 4s° $3d^3$
Fe^{+2}	[Ar] 4s° $3d^6$

Fe^{+3}	[Ar] 4s° $3d^5$
Cu^{+2}	[Ar] 4s° $3d^9$
Ti^{+3}	[Ar] 4s° $3d^1$
Co^{+2}	[Ar] 4s° $3d^7$

24. Metal ion having e^- configuraton from d^4 to d^7 can form both low spin and high spin complexes.

$[NiF_6]^{-2}$

Ni^{+4} = [Ar] 4s° $3d^6$



The number of unpaired e^- = 0

In this compound, pairing occurs.

25. A → P, R; B → Q, S; C → P, Q; D → R, S

26. A→Q, R, S; B→P, Q, R, S; C→P, R; D → P, R, S

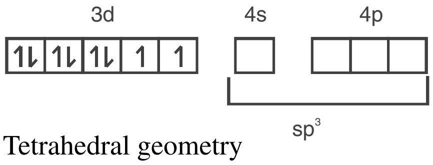
27. A → R; B → Q; C → P ; D → S

28. P → 4; Q → 1; R → 1, 2, 4 ; S → 3

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (d) $[NiCl_4]^{2-}$

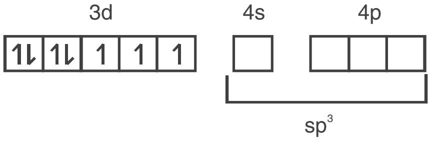
Ni^{+2} = [Ar] 4s° $3d^8$



Tetrahedral geometry

2. (b) $Hg[Co(SCN)_4]$

Co^{+2} = [Ar] 4s° $3d^7$



Number of unpaired e^- = 3

Magnetic moment = $\sqrt{15}$

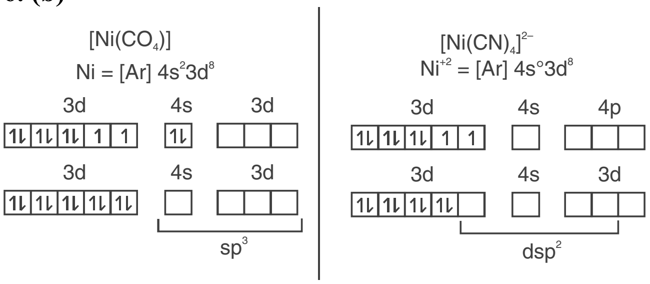
3. (a) $[Co(NH_3)_4Br_2]$ Cl and $[Co(NH_3)_4BrCl]$ Br are isonization isomers. Ma_4b_2 and Ma_4bc complexes show geometrical isomerism but not optical isomerism.

4. (a) In metal carbonyls, bond length of CO increases.

5. (d) In $[V(CO)_6]^-$, chance of back bonding is maximum.

As chance of back bonding increases, bond order of CO decreases.

6. (b)



7. (c) $\overset{+1}{[Cu}(CH_3CN)_4)]BF_4$ Cu^+ = [Ar] 4s° $3d^{10}$

$K_3[\overset{+1}{Cu}(CN)_4]$ Cu^+ = [Ar] 4s° $3d^{10}$

$\overset{+2}{Cu}F_2$ Cu^{+2} = [Ar] 4s° $3d^9$

[It has one unpaird e°]

$[\overset{+1}{Cu}(CH_3CN)_4)]BF_4$ Cu^+ = [Ar] 4s° $3d^{10}$.

8. (c) $[\overset{+2}{Ni}(NH_3)_4][\overset{+2}{Ni}Cl_4]$

Tetraamminenickel (II) tetrachloronickelate (II)

9. (a) $[\overset{+1}{Fe}(H_2O)_5\overset{+1}{NO}]SO_4$

Fe^+ = [Ar] 4s° $3d^7$ (It has three unpaired e^-)

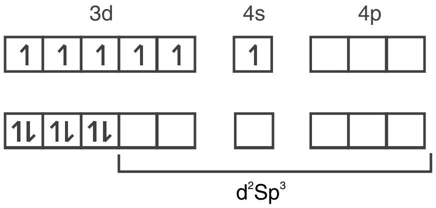
10. (b) u = 2.82 BM

Number of unpaired e^- = 2

In $[NiCl_4]^{-2}$, Ni^{+2} has 2 unpaired e^-.

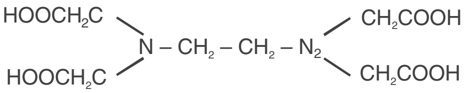
11. (a) $Cr(CO)_6$

Cr° = [Ar] $4s^1$ $3d^5$



Number of unpaired e^- = 0

12. (c) Correct structure of EDTA is



13. (b) The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]$ Cl is $[Cr(H_2O)_4Cl_2](NO_2)$

14. (b) $[NiCl_4]^{2-}$ Tetrahedral

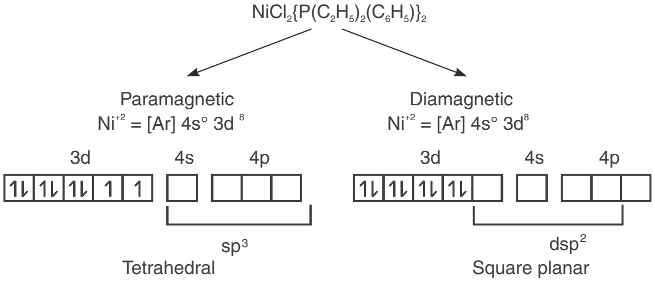
$[Ni(CN)_4]^{2-}$ Square planar

$[Ni(H_2O)_6]^{2+}$ Octahedral

15. (c)

(K)	$K_3[Fe(CN)_6]$	Paramagnetic
(L)	$[Co(NH_3)_6]Cl_3$.	Diamagnetic
(M)	$Na_3[Co(OX)_3]$	Diamagneitc
(N)	$[Ni(H_2O)_6]Cl_2$.	Paramagnetic
(O)	$K_2[Pt(CN)_4]$	Diamagnetic
(P)	$[Zn(H_2O)_6]\ (NO_3)_2$.	Diamagnetic

16. (c)



17. (d) IUPAC name of $[Co(H_2O)_4(NH_3)_2]Cl_3$ is, Diamminetetraaquacoblat (III) chloride

18. (b)

	Number of unpaired e^-
(P) $[FeF_6]^{3-}$	5
(Q) $[V(H_2O)_6]^{2+}$	3
(R) $[Fe(H_2O)_6]^{2+}$	4

19. (b)

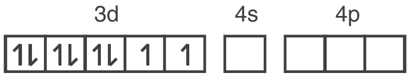
(A) $[Cr(NH_3)_4Cl_2]Cl$	Paramagnetic and cis-trans isomerism
(B) $[Ti(H_2O)_5Cl](NO_3)_2$.	Paramagnetic and exhibits ionisation isomerism
(C) $[Pt(en)(NH_3)Cl]NO_3$.	Diamagnetic and exhibits ionisation isomerism
(D) $[Co(NH_3)_4(NO_3)_2]$ NO_3.	Diamagnetic and exhibits cis-trans isomerism

20. (b) IUPAC name of $[Co(NO_2)(NH_3)_5]Cl_2$ is:
Pentaammine nitro-N-cobalt (III) chloride

21. (d) In metal carbonyls, between metal and CO both σ and π-character are present.

22. (a) EDTA is a hexadentate ligand. To make an octahedral complex one EDTA is required.

23. (c) Ni^{+2} = [Ar] $4s^o$ $3d^8$



Number of unpaired e^- = 2

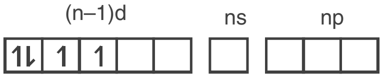
Spin only magnetic moment

$= \sqrt{2(2+2)} \approx 2.84$ BM

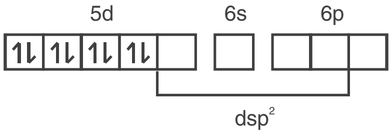
24. (a) 'spin only' magnetic moment = 2.84 BM

Number of unpaired e^- = 2

d^4 (in strong field ligand)



25. (d) In complex $[PtCl_4]^{2-}$
Pt^{+2} = [Xe] 65° $4f^{14}$ $5d^8$



Square planar geometry

26. (d) $[E(en)_2(C_2O_4)]$ NO_2
Co-ordination number of E = 6
$x + 0 - 2 - 1 = 0$
$x = +3$ (oxidation state)

27. (a) Stronger is the ligand, greater will be value of Δ_0

28. (c) cis-form of $[Co(en)_2(NH_3)_2]^{3+}$ is optically active.

29. (a) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers.

30. (a) Correct order of their increasing field strength is :

$NH_3 < en < CN^- < CO$

31. (b) $M(AA)_2b_2$ complex exhibits geometrical isomerism.

32. (a) Formula of dibromido bis-(ethylenediamine) chromium (III) bromide is $[Cr(en)_2Br_2]$ Br

33. (b)

	Number of unpaired e^-
$[Cr(H_2O)_6]^{2+}$	4
$[Co(H_2O)_6]^{2+}$	3
$[Mn(H_2O)_6]^{2+}$	5
$[Fe(H_2O)_6]^{2+}$	4

34. (b) Order of ligands in the spectrochemical series is:

$CN^- > en > NCS^- > Cl^-$

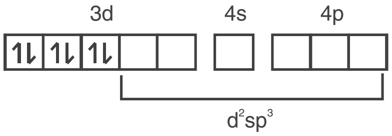
35. (d) All complexes of Pt^{+2} of co-ordination number 4 have square planar geometry.

36. (a) cis-form of $[Co(en)_2Cl_2]$+ is optically active.

37. (a) $[Pd(C_6H5)_2$ $(SCN)_2]$ and $[Pd(C_6H5)_2$ $(NCS)_2]$ are linkage isomers.

38. (b) In presence of Ox ligand, pairing in Co^{+3} take place.

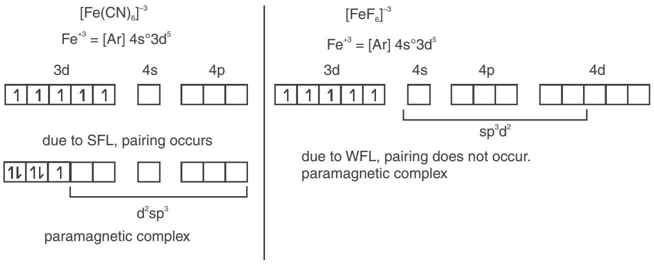
Co^{+3} = [Ar] 4s° $3d^6$



Complex is diamagnetic.

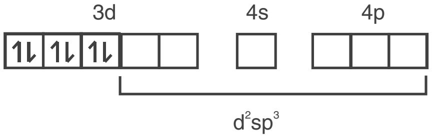
39. (b) Stronger is the ligand, greater will be value of Δ_0

40. (a)



41. (c) Complex of Co^{+3} is diamagnetic, it means pairing occurs.

$Co^{+3} = [Ar]\ 4s^{\circ}\ 3d^{6}$



42. (b) The correct name of complex $[Mn(CN)_5]^{2-}$ is : Pentacyanomanganate (III) ion

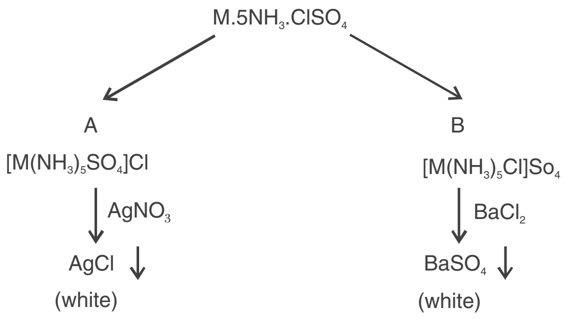
43. (c) Central metal of co-ordination compound acts as the lewis acid.

44. (c)

	Number of unpaired e⁻
$[Sc(H_2O)_6]^{3+}$	0
$[Ti(NH_3)_6]^{4+}$	0
$[V(NH_3)_6]^{3+}$	2
$[Zn(NH_3)_6]^{2+}$	0

To absorb visible light, complex should have unpaired d-electron.

45. (b)

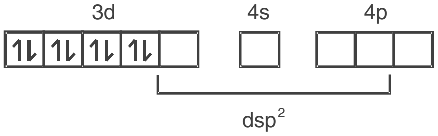


Complex A and B are ionisation isomers.

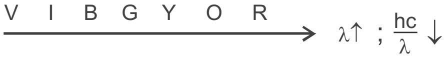
46. (b) $[NiL_4]^{-2}$

$Ni^{+2} = [Ar]\ 4s^{\circ}\ 3d^{8}$

For diamagnetic complex, pairing occurs.



47. (b) Number of unpaired e⁻ = 0



	absorb wavelength (λ)
L_1	Red
L_2	Green
L_3	Yellow
L_4	Blue

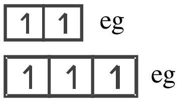
$$\boxed{\Delta \propto \frac{1}{\lambda}}$$

Stronger is the ligand, greater will be the value of Δ.

48. (a) CH_4 can not act as a ligand because it does not have lone pair.

49. (a) In $[FeF_6]^{3-}$ complex, due to presence of WFL t_{2g} and e_g are filled symmetrically.

$Fe^{+3} = [Ar]\ 4s^{\circ}\ 3d^{5}$



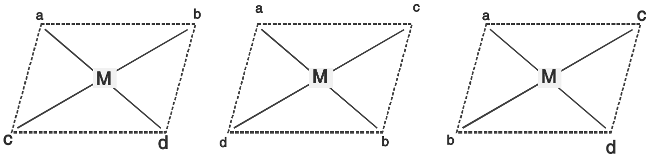
50. (d) $\overset{+2}{Co}Cl_2 + HCl \rightarrow [CoCl_4]^{-2}$

51. (c) Cause of colour in $KMnO_4$ is charge transfer from 'O' to 'Mn' (L → M)

52. (b) $[CoCl(NH_3)_5]^{+} + 5H^{+} \rightarrow Co^{+2} + 5NH_4^{+} + Cl^{-}$

In acidic medium, this complex decomposes.

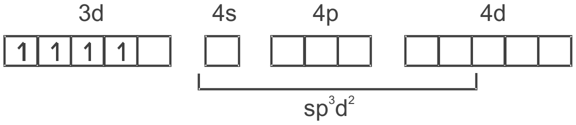
53. (b) For M_{abcd} complex, 3 geometrical isomers are possible.



54. (a)

$[Cr(H_2O)_6]^{2+}$

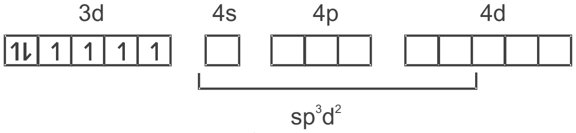
$\overset{+2}{Cr} = [Ar]\ 4s^{\circ}3d^{4}$



Number of unpaired e⁻ = 4

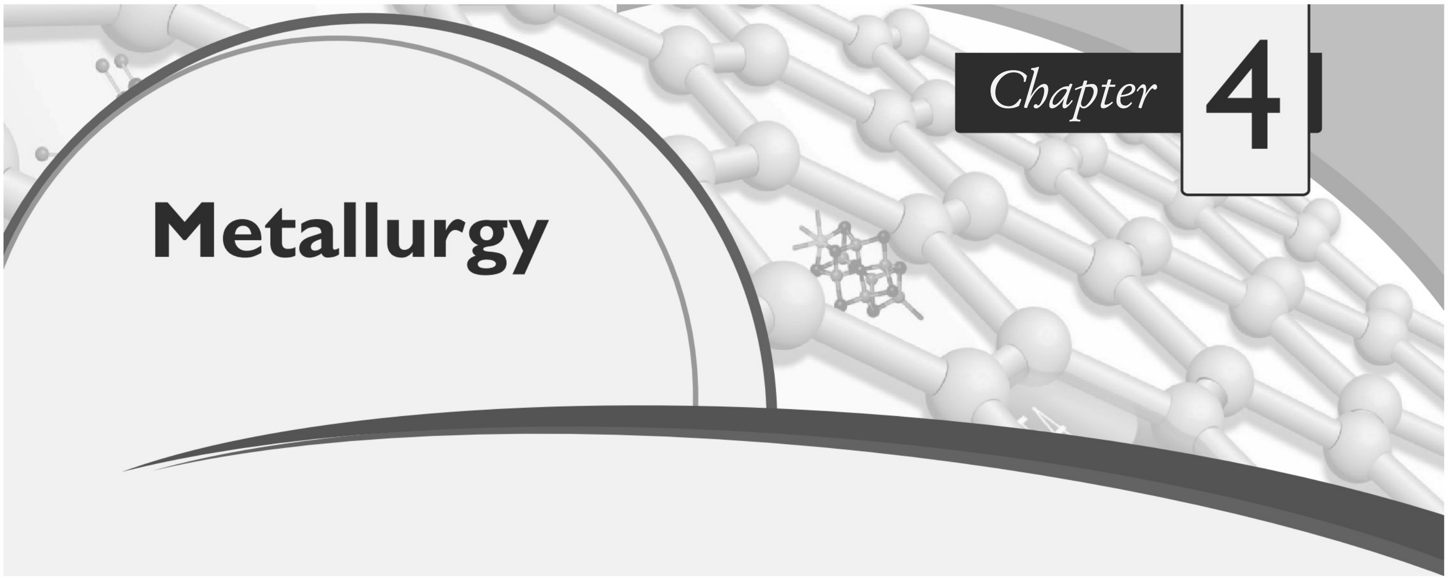
$[Fe(H_2O)_6]^{2+}$

$Fe^{+2} = [Ar]\ 4s^{\circ}3d^{6}$



Number of unpaired e⁻ = 4

55. (a) cis-$[M(AA)_2b_2]$ complex is optically active.



Chapter 4

Metallurgy

Key Concepts

Introduction: The process of extraction of metal from its ore in profitable manner is called metallurgy.

(i) Mineral is a substance in which metal is present in either native state or combined state.

(ii) 'Ore' is the mineral from which the metal can be economically and conveniently extracted.

(iii) 'Gangue or matrix' is the non metallic impurities present in the ore.

COMMON STEPS INVOLVED IN METALLURGY

Crushing and grinding

Operation in which size reduction of large lumps to small pieces followed by finely ground material by the use of crushers and grinders.

Concentration (Dressing) of the ore

Operation in which the removal of impurities (gangue) from ore by the following methods:

(a) Levigation or gravity separation:

(i) This method is based on the difference in densities of the ore particles and gangue particles.

(ii) The powdered ore with gangue particles introduced in the running steam of water.

(iii) Lighter impurity particles washed off with water and heavier ore particles settle down at the bottom

(iv) Usually employed for oxide and carbonate ores.

(b) Magnetic separation:

(i) Ore and gangue are separated, if only one of them having magnetic property

(ii) Mixture of two minerals can also be separated if one of them is non magnetic and the other is magnetic.

(c) Froth floatation process:

(i) Employed for sulphide ores

(ii) It is based on the different wetting characteristics of the ore and gangue particles with water and oil.

(iii) Usually ore particles are making as aerofillic and gangue particles as aerophobic by using different reagents.

(iv) Ore particles raised to the surface along with air bubbles and collected at the surface where as gangue particles are wetted and settled down at the bottom of the tank.

(v) Reagents acts as frothing agents (pine oil), collectors (ethyl xanthate and potassium ethyl xanthate), activators (copper sulphate) and depressors (sodium cyanide, alkali).

(d) Leaching:

- (i) Chemical method of concentration
- (ii) Selective dissolution of ore in strong reagents where as gangue particles are undissolved and gets separated.
- (iii) Employed for concentrating ores of aluminium, silver gold etc.

Working of the concentrated ore:

- (i) It depends upon the nature of the ore as well as the nature of impurities.
- (ii) Processes involved:
  - (a) Conversion of the concentrated ore to its oxide form.
  - (b) Conversion of the oxide to the metallic form
  - (c) Hydrometallurgy

Conversion of the concentrated ore into its oxide form:

(i) Calcination:

- (a) Ore is heated in absence of air to remove water or CO_2 from hydrated oxides or carbonates respectively.
- (b) Process temperature is below the melting points of treated ores.
- (c) During calcination moisture, volatile impurities are removed there by one becomes porous.

Example:

$Al_2O_3.\ 2H_2O \rightarrow Al_2O_3 + 2H_2O$

$2Fe_2O_3.\ 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$

$CaCO_3 \rightarrow CaO + CO_2$

$MgCO_3 \rightarrow MgO + CO_2$

(ii) Roasting:

- (a) Ore is heated strongly with other substances, usually with oxygen
- (b) Employed for sulphide ores
- (c) Process temperature is below the melting points of treated ore
- (d) Chemical conversion of ore is taking place.
- (e) Some of the impurities removed as volatile substances.

$S + O_2 \rightarrow SO_2\uparrow$

$4As + 3O_2 \rightarrow 2As_2O_3\uparrow$

$P_4 + SO_2 \rightarrow 2P_2O_5\uparrow$

Examples:

(a) Conversion of metal sulphides into oxides

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

(b) Metal sulphides converted into sulphates

$PbS + 2O_2 \rightarrow PbSO_4$

$ZnS + 2O_2 \rightarrow ZnSO_4$

(c) Metal sulphides converted into chlorides

$Ag_2S + 2\ NaCl \rightarrow 2AgCl + Na_2S$

(d) Conversion of amalgams

$AgCl + 2Hg \rightarrow Ag - Hg + HgCl$

Conversion of the oxide to metallic form:

The roasted or calcined ore is converted into metallic form through reduction by using different reducing techniques which will depends upon the nature of the ore, some of the methods are mentioned below.

(i) Reduction by carbon (smelting):

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc, are reduced by strongly heating with coal or coke.

- (a) Reduction of the oxide with carbon at high temperature is known are as smelting
- (b) Flux is added smelting, which reduces the melting point of impurities to form as easily fusible substance called as 'slag' and can be separated easily because of its lower density.
- (c) Selection of flux depends upon nature of impurity present. Its impurity is acidic, basic flux is employed and vice versa.
- (d) Smelting is usually carried out in blast furnaces or reverberatory furnace.

(ii) Reduction by aluminium (Alumino-thermite reduction):

- (a) Aluminium acts as reducing agent due to its high electropositive nature.
- (b) Oxides such as Cr_2O_3, Mn_3O_4 are reduced by this method because carbon or CO are not efficiently reduced.
- (c) The process is also known as "**Gold Schmidt thermite process**".

(iii) Reduction by heating in air (Auto-reduction):

- (a) Employed for metals of less active such as Hg, Cu and Pb
- (b) Due to unstable nature in the oxide form at high temperature, no reducing agent is required for their reduction .

Example :

$$HgS + O_2 \xrightarrow{\Delta} Hg + SO_2 \uparrow$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2S + 2O_2 \text{ (Roasting)}$$

$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6C + SO_2 \text{ (Auto-reduction)}$$

(iv) Electrolytic reduction (Electro-metallurgy):

(a) Employed for highly electropositive metals such as Na, K, Ca, Mg, Al, etc.

(b) These metals are extracted by the electrolysis of their oxides hydroxides or chlorides in fused state.

Example:

On fusion:

$NaCl \rightleftharpoons Na^+ + Cl^-$ (ions become mobile)

On electrolysis:

At cathode:

$Na^+ + e^- \rightarrow Na$

At anode:

$Cl^- \rightarrow Cl + e^-$

$Cl + Cl \rightarrow Cl_2$

(c) Aluminium is obtained by the electrolysis of electrolyte which consists of mixture of alumina, cryolite and calcium fluoride. (cryolite and fluorospar are added to reduce melting point of electrolyte and to increase conductivity).

(v) Other methods are:

(a) Reduction by carbon monoxide (employed for iron (III) oxide)

(b) Reduction by water gas (employed for nickel oxide)

(c) Amalgamation method (employed for noble metals)

Hydrometallurgy (Reduction by precipitation):

(i) Process in which more electropositive metals displace less electropositive metals from salt solution.

(ii) First the concentrated ore is dissolved in strong reagent and removed insoluble precipitates.

(iii) Now the metal is precipitated by addition of more electropositive metal.

Example:

Silver sulphide dissolved in sodium cyanide which forms a soluble complex, then silver is precipitated by the addition of zinc powder.

$$Ag_2S + 4\,NaCN \rightarrow \underset{\text{Sodium dicyanoargentate (I)}}{2Na\,[Zn(CN)_2]} + Na_2S$$

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2\,[Zn(CN)_4] + 2Ag \downarrow$$

Note: This type of precipitation process is called **cementation**.

Refining or purification:

(i) The metals after reduction process consists of number of impurities like Si, P, Slag, oxides, other metals etc.

(ii) Removal of all these impurities to get pure metal is called as refining

(iii) Methods as refining are:

(a) Liquation:

(i) This is based on the principle of difference in melting points of metal and impurity.

(ii) Employed for purification of low melting point metals like Pb, Sn, etc.

(b) Distillation process:

(i) This is based on difference in boiling points of metals and impurities.

(ii) Employed for low boiling point metals like Zn, Hg etc.

(c) Oxidation process:

(i) This is a selective oxidation method

(ii) Used for refining those metals in which the impurities have greater tendency to get oxidized than the metals it self

(iii) The impurities converted into oxide and skimmed off from the metal

(iv) Various oxidation processes used for different metals bear different names, eg, poling, pudding, bessemerisation and cupellation (for Ag)

(d) Electrorefining:

(i) Employed for refining of highly electro positive metals like Al, Cu, Ag, Zn, Sn, Cr and Ni

(ii) Impure metal is made as anode, thin pure metal sheet is kept as cathode and the electrolyte is comprising with soluble salt solution of the metal.

(iii) On passing the electric current, pure metal from the anode dissolved and is deposited on the cathode.

(iv) The soluble impurities go into the solution (remains in the solution after the completion of refining) while the insoluble impurities settle down below the anode as 'anode mud'.

(e) Van-Arkel process:

(i) Employed to get metal in very pure form of small quantities.

(ii) In this method, the metal is converted into volatile unstable compound (eg iodide), and impurities are not affected during compound formation.

(iii) The compound thus obtained is decomposed to get the metal.

(iv) Employed for purification of metals like titanium and zirconium

$$\mathrm{Ti\ (s) + 2I_2\ (g) \xrightarrow{523K} TiI_4\ (g)}$$

$$\mathrm{Til_4\ (g) \xrightarrow{1700K} Ti\ (s) + 2I_2\ (g)}$$

(f) Zone refining:

(i) Employed for metals which require very high purity like semi conductors.

(ii) The method is based on the principle that an impure metal on solidification will deposit crystals of pure metal and the impurities will remain behind in the molten part of the metal.

(iii) Used to purify the elements such as silicon, germanium, etc.

Solved Examples

1. Which of the following is not a concentration technique?

(a) Levigation

(b) Froth floatation

(c) Leaching

(d) Calcination

Sol.(d) Concentration is the method employed to remove gangue materials by mechanical separation. In calcination, volatile impurities are removed by heating ore below its melting point in absence or limited supply of air.

2. The ores that are concentrated by froth floatation method are:-

(a) Carbonates

(b) Sulphides

(c) Oxides

(d) Phosphates

Sol.(b) In floatation process, the ore particles should have aerofillic in preference to gangue particles. Sulphide ores having this character.

3. Calcination is the process in which:

(a) Heating the ore in presence of air

(b) Heating the ore in presence of sulphur

(c) Heating the ore in absence of air

(d) Heating the ore in presence of chlorine

Sol.(c) Calcination is the process in which moisture and volatile impurities are removed and process is carried in absence of air or in limited supply of air.

4. The purpose of adding Na_3AlF_6 to Al_2O_3 during electrolysis is:-

(a) To decrease melting point of Al_2O_3

(b) To increase conductivity of electrolyte

(c) To provide reducing conditions in the bath

(d) Both (a) and (b)

Sol.(d) Al_2O_3 is a poor conductor of electricity and having very high melting point. So, to increase the conductivity Na_3AlF_6 is added and to decrease the melting point Na_3AlF_6 and CaF_2, AlF_3 are added so that melting point of electrolyte comes to around 930°C.

5. During the process of electro refining of copper, some metals present as impurity settle down as anode mud. These are:

(a) Sn and Ag

(b) Pb and Zn

(c) Ag and Au

(d) Fe and Ni

Sol.(c) In anode mud, less electropositive elements are present. Ag and Au are less electropositive than Cu.

6. The method of Zone refining of metals is based on the principle of:

(a) Greater solubility of the impurities in the molten state than in the solid.

(b) Greater solubility of pure metal than that of impurity.

(c) Higher melting point of the impurity than that of pure metal.

(d) Greater noble character of the solid metal than that of the impurity.

Sol.(a) Zone refining is used when pure metal has greater melting point than impurities and impurities have greater solubility in molten state than in the solid.

7. Which of the following is not correctly matched?

(a) $ZnCO_3 \rightarrow Zn$ (Calcination followed by smelting)

(b) $Al(OH)_3 \rightarrow$ Al (Calcination followed by smelting)

(c) $PbS \rightarrow Pb$ (Partial roasting followed by self reduction)

(d) $Cu_2S \rightarrow Cu$ (Complete roasting following by carbon reduction)

Sol.(b) $ZnCO_3 \rightarrow Zn$

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$ (Calcination)

$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow$ (Smelting)

$Al(OH)_3 \rightarrow Al$

$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + H_2O\uparrow$ (Calcination)

$Al_2O_3 \xrightarrow{\Delta}$ Al (electrolytic reduction)

$PbS \rightarrow Pb$

$PbS + O_2 \xrightarrow{\Delta} PbO + PbSO_4 + SO_2\uparrow$ (Partial roasting)

$$\left.\begin{array}{l} PbO + PbS \xrightarrow{\Delta} Pb + SO_2\uparrow \\ \text{Or } PbS + PbSO_4 \xrightarrow{\Delta} Pb + SO_2\uparrow \end{array}\right\} \text{(Self reduction)}$$

$Cu_2S \rightarrow Cu$

$Cu_2S + O_2 \xrightarrow{\Delta} Cu_2O + SO_2\uparrow$ (Complete roasting)

$Cu_2O + C \xrightarrow{\Delta} Cu + CO\uparrow$ (Carbon reduction)

8. When an impurity in metal has greater affinity for oxygen and is more easily oxidized than metal itself then the metal is refined by:

(a) Cupellation

(b) Zone refining

(c) Poling

(d) Electrolytic process

Sol.(a) In cupellation process, impure metal is heated with borax and silica. Impurities are removed as their oxide.

9. What is the appropriate process for the extraction of lead from galena?

(A) Froth floatation (B) Calcination (C) Roasting (D) Self reduction (E) Electrolytic reduction (F) smelting (G) Leaching

(a) G → B → D → E

(b) A → C → D

(c) A → C → E

(d) A → C → F

Sol.(b) Galena is a sulphide ore (PbS). It is concentrated by froth floatation. After partial roasting, self reduction process is used.

10. In purification of bauxite ore, it is mixed with coke and heated at 1800°C in presence of nitrogen. This is:

(a) Hall's process

(b) Serpeck's process

(c) Baeyer's process

(d) Electrolytic reduction

Sol.(b) Serpeck's process:-

$Al_2O_3.2H_2O + 3C + N_2 \xrightarrow{\Delta} 2AlN + 3CO + 2H_2O$

$AlN + 3H_2O \rightarrow Al(OH)_3\downarrow + NH_3\uparrow$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$

11. Select the reaction which does not occur in Bessemer's convertor:

(a) $FeS + O_2 \rightarrow FeO + SO_2$

(b) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(c) $FeO + SiO_2 \rightarrow FeSiO_3$

(d) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

Sol.(d) The reaction,

$2CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$

represents partial roasting of ore. It is carried out in reverberatory furnace.

12. Which of the following process is not involved in the extraction of Ag from argentite?

(a) Hydrometallurgy

(b) Formation of cyanide

(c) Levigation

(d) Reduction by Zn metal

Sol.(c) Levigation is a concentration process, used for oxide ores. Concentration process used for argentite ore is cyanide leaching.

$Ag_2S + CN^- + H_2O + O_2 \rightarrow [Ag(CN)_2]^-$

Reduction process used is Hydrometallurgy (reduction by Zn).

$[Ag(CN)_2]^- + Zn \rightarrow Ag + [Zn(CN)_4]^{-2}$

13. Select the incorrect statement:

(a) Based on reactivity series, occurrence of certain elements takes place in native state.

(b) Due to the basic nature of oxides of alkaline earth metals, they combine with atmospheric acidic oxides giving salts.

(c) Chalcopyrite ore contains both Cu and Fe.

(d) Both anglesite and cassiterite contain Pb.

Sol.(d) Due to less reactivity, Au occurs in native state. Due to basic nature of alkaline earth metals oxides, they occur in the form of their salts. Anglesite is $PbSO_4$ and cassiterite is SnO_2.

14. Which of the following is not correctly matched?

(a) Removal of oxide impurity from impure Cu → Poling process

(b) Removal of Pb impurity from impure Ag → Cupellation

(c) Obtaining wrought iron from cast iron → Bessemerisation

(d) Refining of Nickel → Mond's process

Sol.(c) Wrought iron is obtained from cast iron in reverberatory furnace.

15. Which of the following statement is not correct?

(a) Tin stone is separated from non-magnetic impurity of wolframite by electrolytic separation.

(b) CO acts as reducing agent is most parts of blast furnace during extraction of iron.

(c) A silicate slag is obtained during the extraction of Cu from $CuFeS_2$ and iron from haematite.

(d) In Puddling process, impurities present in cast iron are oxidized by haematite.

Sol.(a) Tin stone (SnO_2) is non-magnetic while wolframite ($FeWO_4$) is magnetic Tin stone is separated from wolframite by electromagnetic separation.

Exercise

LEVEL I

1. Three most occurring elements into the earth crust are:

(a) O, Si, Al (b) Si, O, Fe

(c) Fe, Ca, Al (d) Si, O, N

2. An example of an oxide ore is

(a) Bauxite (b) Malachite

(c) Zinc blende (d) Feldspar

3. Which of the following set of elements mostly occur as sulphide ores?

(a) Zn, Cu, Na (b) Zn, Cu, Pb

(c) Fe, Al, Ti (d) Cu, Ag, Au

4. Which of the following is not an ore of Magnesium?

(a) Carnallite (b) Magnesite

(c) Dolomite (d) Gypsum

5. Which one of the following is not an ore of aluminum?

(a) Bauxite (b) Corundum

(c) Epsomite (d) Cryolite

6. Which one contains both Ca and Mg?

(a) Limestone (b) Dolomite

(c) Chalk (d) Feldspar

7. Which of the following minerals does not contain iron?

(a) Magnetite (b) Magnesite

(c) Haematite (d) Limonite

8. Metals which exist as native ore?

(a) Ni, Pt (b) Zn, Cd

(c) Pt, Au (d) Sn, Pb

9. Which of the following contain Fe as well as Cr?

(a) Wolframite (b) Chromite

(c) Pyrolusite (d) Chalcopyrite

10. Which ore is concentrated by 'wetting by oil'?

(a) Oxide ore (b) Sulphate ore

(c) Carbonate ore (d) Sulphide ore

11. Haematite ore is concentrated by:

(a) Gravity separation method

(b) Froth floatation process

(c) Amalgamation

(d) Hand picking

12. In the extraction of copper from its sulphide ore, the metal is formed by reduction of Cu_2O with:

(a) FeS (b) CO

(c) Cu_2S (d) SO_2

13. The element which is recovered from electrolytic process is:

(a) Iron (b) Lead

(c) Aluminium (d) Zinc

14. Refining of silver can be done by:

(a) Cupellation

(b) Electrorefining

(c) Both (a) and (b)

(d) None of these

15. Impure aluminium is purified by:

(a) Baeyer's process

(b) Hall's process

(c) Hoop's Process

(d) Serpeck's process

16. In the alumino-thermite process, Al metal acts as:

(a) Oxidizing agent

(b) Reducing agent

(c) Catalyst

(d) Flux

17. Slag is formed by reaction between:

(a) Impurities and coke

(b) Impurities and ore

(c) Impurities and flux

(d) Flux and coke

m**18.** Which of the following statement is correct?

(a) All ores are minerals

(b) All minerals are ores

(c) Calcination is generally carried out in blast furnace

(d) Oxide ores are concentrated by froth floatation process.

19. Purification of silicon element used in semiconductors is done by:

(a) Zone refining

(b) Heating

(c) Froth floatation

(d) Heating in vacuum

20. Which one of following beneficiation processes is used for the mineral $Al_2O_3.2H_2O$?

(a) Froth floatation (b) Leaching

(c) Liquation (d) Magnetic separation

21. In blast furnace, maximum temperature is in:

(a) Zone of fusion

(b) Zone of combustion

(c) Zone of slag formation

(d) Zone of reduction

22. When a metal is to be extracted from its ore and if the gangue associated with the ore is silica, then:

(a) An acidic flux is needed

(b) A basic flux is needed

(c) Both acidic and basic fluxes are needed

(d) Neither of them is needed

23 Silver containing lead as an impurity is removed by:

(a) Poling (b) Cupellation

(c) Lavigation (d) Distillation

24. Cassiterite is concentrated by:

(a) Levigation

(b) Electromagnetic separation

(c) Froth-floatation

(d) Liquification

25. For which ore of the metal, froth floatation method is used for concentration?

(a) Horn silver (b) Bauxite

(c) Cinnabar (d) Haematite

26. In which of the following minerals, aluminium is not present?

(a) Cryolite (b) Mica

(c) Feldspar (d) Fluorspar

27. Gravity separation process may be used for the concentration of:

(a) Chalcopyrite (b) Bauxite

(c) Haematite (d) Calamine

28. Electrolytic reduction method is used in the extraction of:

(a) Highly electropositive elements

(b) Highly electronegative elements

(c) Transition metals

(d) Noble metals

29. Bauxite is leached with:

(a) KCN (b) NaCN

(c) NaOH (d) Na_2CO_3

30. In the equation:

$4M + 8CN^- + 2H_2O + O_2 \rightarrow 4[M(CN)_2]^- + 4OH^-$

Identify the metal M:

(a) Cu (b) Fe

(c) Au (d) Zn

LEVEL II

1. Which of the following process is not a physical process of separation?

(a) Levigation

(b) Magnetic separation

(c) Leaching

(d) Froth floatation

2. In the extraction of copper from copper pyrites, iron is removed as:

(a) $FeSO_4$ (b) $FeSiO_3$

(c) Fe_3O_4 (d) Fe_2O_3

3. In zone refining method, the molten zone:

(a) Consists of impurities only

(b) Consists more impurity than the original metal

(c) Contains the purified metal only

(d) Moves to either side

4. Bauxite, Siderite and argentite are respectively:

(a) Sulphide, oxide and carbonate ore

(b) Oxide, carbonate and sulphide ore

(c) Oxide, oxide and sulphide ore

(d) Oxide, sulphide and oxide ore

5. Which one of the following reactions is an example for calcination process?

(a) $2Ag + 2HCl + (O) \rightarrow 2AgCl + H_2O$

(b) $2Zn + O_2 \rightarrow 2ZnO$

(c) $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

(d) $MgCO_3 \rightarrow MgO + CO_2$

6. Cupellation process is used in the metallurgy of:

(a) Cu (b)Ag

(c) Zn (d)Al

7. In electrorefining of metal the impure metal is made the anode and a strip of pure metal the cathode during the electrolysis of an aqueous solution of a complex metal salt. This method cannot be used for refining of:

(a) Silver (b) Copper

(c) Aluminium (d) Gold

8. Among the following groups of oxides, the group that cannot be reduced by carbon to give the respective metals is:

(a) Cu_2O, SnO_2 (b) Fe_2O_3, ZnO

(c) CaO, K_2O (d) PbO, Fe_3O_4

9. The reason for floating of ore particles in concentration by froth floatation process is that:

(a) They are light

(b) They are insoluble

(c) They are charged

(d) They are hydrophobic

10. Which of the following statements is correct regarding the slag obtained during the extraction of a metal like copper or iron?

(a) The slag is lighter and has lower melting point than the metal

(b) The slag is heavier and has lower melting point than the metal

(c) The slag is lighter and has higher melting point than the metal

(d) The slag is heavier and has higher melting point than the metal

11. Consider the following reactions at 1000°C.

(i) $Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(g)$; $\Delta G° = -360\ kJ\ mol^{-1}$

(ii) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta G° = -460\ kJ\ mol^{-1}$

(a) ZnO is more stable than CO
(b) ZnO can be reduced to Zn by C
(c) ZnO and CO are formed at equal rate
(d) ZnO can not be reduced to Zn by C

12. ΔG° vs T plot in the Ellingham's diagram slopes downward for the reaction:

(a) $Mg + \frac{1}{2}O_2 \rightarrow MgO$

(b) $2Ag + \frac{1}{2}O_2 \rightarrow Ag_2O$

(c) $C + \frac{1}{2}O_2 \rightarrow CO$

(d) $CO + \frac{1}{2}O_2 \rightarrow CO_2$

13. The incorrect match in the following is:

(a) Purification of Al metal : Baeyer's method
(b) Polling : Reduction of Cu_2O
(c) $FeCr_2O_4$ (Chromite ore) : NaOH/ Na_2CO_3
(d) Ag : Mac Arthur cyanide process

14. An ore after levigation is found to have acidic impurities. Which of the following can be used as flux during smelting operation?

(a) H_2SO_4 (b) $CaCO_3$
(a) SiO_2 (d) Both $CaCO_3$ and SiO_2

15. Which of the following metals never occurs in free sate in nature?

(a) Gold (b) Copper
(c) Silver (d) Sodium

16. Select the incorrect statement in the following:

(a) Silica present in bauxite is removed by addition of NaOH(aq.)
(b) Silica present in haemetite is removed by the addition of $CaCO_3$ during smelting
(c) Fe_2O_3 present in bauxite is removed by Bayer's process
(d) Magnetic separation is used for cassitarite

17. In which of the following process, roasting and self reduction is required?

(a) $Cu_2S \rightarrow Cu_2O$
(b) $CaCO_3 \rightarrow CaO$
(c) $ZnS \rightarrow Zn$
(d) $PbS \rightarrow Pb$

18. Which of the following statement is not correct?

(a) In froth floatation process, pine oil decreases the surface tension of the solution.
(b) In Poling refining, non volatile oxides are removed as sucm.
(c) Dolomite ore can be considered as ore of both Ca and Mg.
(d) Aqueous $Al_2(SO_4)_3$ is used for electrorefining of Al.

19. Which is incorrectly matched for refining of elements?

(a) Si, Ge from impurities ⇒ zone refining method
(b) Sn refined from impurities with high boiling point ⇒ poling method
(c) Zn, Cd from impurities with high boiling point ⇒ distillation
(d) Al from impurities Cu, Fe ⇒ hoop method

20. A mixture of alumina and coke is heated in a current of nitrogen to about 1800°C. And the product obtained is treated with water. A gas is evolved. The gas is:

(a) N_2 (b) N_2O
(c) NH_3 (d) NO

21. The slag obtained during the extraction of copper pyrites is composed mainly of:

(a) $MgSiO_3$ (b) $CuSiO_3$
(c) $FeSiO_3$ (d) $CuFeS_2$

22. Consider the following at 1000°C

(A) $2Zn\ (s) + O_2\ (g) \rightarrow 2ZnO(g);\ \Delta G° = -360 kJ\ mol^{-1}$

(B) $2C\ (gr) + O_2\ (g) \rightarrow 2CO(g);\ \Delta G° = -500 kJ\ mol^{-1}$

Choose the correct statement at 1000°C:

(a) Zinc can be oxidized by carbon monoxide
(b) Zinc oxide can be reduced by graphite
(c) Both statements (a) and (b) are true
(d) Both statements (a) and (b) are False

23. When ZnS and PbS minerals are present together, them NaCN is added to separate them in the froth floatation process as a depressant because:

(a) $Pb(CN)_2$ is precipitated while no effect on ZnS.
(b) ZnS forms soluble complex $Na_2[Zn(CN)_4]$.
(c) PbS forms soluble complex $Na_2[Pb(CN)_4]$.
(d) It decreases the floatation property of PbS by making it hydrophilic

24 The materials mixed, before haemetite ore is subjected to smelting in the extraction of iron, are:

(a) Coke and silica
(b) Coke and limestone
(c) Limestone and silica
(d) Cock, silica and limestone

25. Which of the following reaction forms the basis of Goldschmidt alumino-thermite process?

(a) $2Al + N_2 \rightarrow 2AlN$
(b) $2Al + 3Cl_2 \rightarrow 2AlCl_3$
(c) $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$
(d) $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

26. In the extraction of copper, metal is formed in the Bassemer converter due to reaction:

(a) $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$
(b) $Cu_2S \rightarrow 2Cu + S$
(c) $Fe + Cu_2O \rightarrow 2Cu + FeO$
(d) $2Cu_2O \rightarrow 4Cu + O_2$

27. The extraction of zinc from zinc blende is achieved by:

(a) Electrolytic reduction
(b) Roasting followed by reduction with carbon
(c) Roasting followed by reduction with another metal
(d) Roasting followed by self-reduction

28. Which method is not correct given for refining of crude metals?

(a) Distillation : Zinc and mercury
(b) Liquation : Tin
(c) Van Arkel : Zirconium
(d) Mond process : Lead

29. Poling process is used for:

(a) The removal of Cu_2O from Cu
(b) The removal of Al_2O_3 from Al
(c) The removal of Fe_2O_3 from Fe
(d) All of these

30. Among the following statements, the incorrect one is

(a) Calamine and siderite are carbonates.
(b) Argentite and cuprite are oxides.
(c) Zinc blende and iron pyrites are sulphides.
(d) Malachite and azurite are ores of copper.

LEVEL III

ONE OR MORE THAN ONE CORRECT TYPE

1. Which of the following is (are) manufactured by the electrolysis of their fused salts?

(a) Copper
(b) Sodium
(c) Aluminium
(d) Platinum

2. Complexes formed in the cynide process are:

(a) $[Au(CN)_2]^-$
(b) $[Ag(CN)_2]^-$
(c) $[Cu(CN)_4]^{2-}$
(d) $[Zn(CN)_4]^{2-}$

3. Which of the following process (es) occur(s) during the extraction of copper from chalcopyrites?

(a) Froth floatation
(b) Roasting
(c) Bessemerisation
(d) Calcination

4. Calcium silicate (slag) formed in the slag formation zone in extraction of iron from Haematite ore:

(a) Does not dissolve in molten iron.
(b) Being lighter floats on the molten iron.
(c) Is used in cement industry and as building material.
(d) Prevents the re-oxidation of molten iron.

5. Liquation process may be applied for the purification of:

(a) Copper
(b) Tin
(c) Iron
(d) Zinc

6. Roasting of copper pyrites is done:

(a) To remove moisture.
(b) To oxidize free sulphur and antimony.
(c) To convert pyrites completely into Cu_2O and FeO.
(d) To remove volatile organic impurities.

7. Select the correct statement:

(a) Dolomite contains both magnesium and calcium.
(b) Extraction of lead from galena involves roasting in limited supply of air at moderate temperature followed by self reduction at higher temperature (to melt the charge).

(c) Extraction of zinc from Zinc blende involves roasting followed by reduction with carbon.

(d) The chemical composition of 'slag' formed during the extraction of iron and copper is $FeSiO_3$.

8. Which of the following is a correct statement?

(a) Calamine is the ore of zinc.

(b) Proustite is the ore of silver.

(c) Cassiterite is the ore of tin.

(d) Diaspore is the ore of aluminium.

9. Froth floatation:

(a) Is a physical method of separating mineral from the gangue

(b) Is a method of concentration of ore depending on the difference in wetability of gangue and the ore particles.

(c) Is used for the concentration of sulphide ores

(d) Is a method in which impurities sink to the bottom and ore particles pass on to the surface with froth.

10. Which of the following are correct processes?

(a) $Fe + Al_2O_3 \rightarrow 2Al + Fe_2O_3$

(b) $ZnO + C \rightarrow Zn + CO$

(c) $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$

(d) $2[Ag(CN)_2]^- + Zn \rightarrow 2Ag + [Zn(CN)_4]^{2-}$

11. Which of the following reactions occur during calcination?

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

(c) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

(d) $Cu_2S + 2CuO \rightarrow 4Cu + SO_2$

12. Silver containing lead as an impurity is not purified by:

(a) Poling (b) Cupellation

(c) Levigation (d) Distillation

13. Select the correct statements for Ellingham diagram:

(a) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram.

(b) According to Ellingham diagram, Al will not reduce MgO at temperature below 1350°C

(c) According to Ellingham diagram, Al will reduce MgO at temperature below 1350°C

(d) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram.

PARAGRAPH BASED QUESTIONS

Paragraph # 1 (Q. 14 to 15)

Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated Sodium cyanide solution. During this process metallic gold is slowly converted to $[Au(CN)_2]^-$, which is soluble in water. After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc which is converted to $[Zn(CN)_4]^{2-}$gold in nature is frequently alloyed with silver which is also oxidized by aerated sodium cyanide solution.

14. The correct ionic reaction for the process is:

(a) $4Au + 8CN^- + 2H_2O + O_2(air) \rightarrow 4[Au(CN)_2]^-$ (soluble) + $4OH^-$

(b) $Au + 2CN^- \rightarrow [Au(CN)_2]^-$

(c) $Zn + 2CN^- \rightarrow [Zn(CN)_2]^-$

(d) $Zn + 4CN^- \rightarrow [Zn(CN)_4]^{2-}$

15. The process described above in the paragraph represents:

(a) Ore concentration

(b) Pyrometallurgical extraction

(c) Hydrometallurgical extraction

(d) Purification of metal

Paragraph # 2 (Q. 16 to 17)

Extraction of copper is done using copper pyrites. After roasting, the ore is mixed with silica and coke and then smelted in a blast furnace. The matte obtained from the blast furnace is charged into a silica-lined converter. Some silica is also assed, and a hot air blast is blown into the mixture to obtain blister copper, which is purified by electrorefining.

16. The chemical formula of copper pyrites is:

(a) $CuFeS_2$ (b) Cu_2O

(c) Cu_2S (d) $CuCO_3 . Cu(OH)_2$

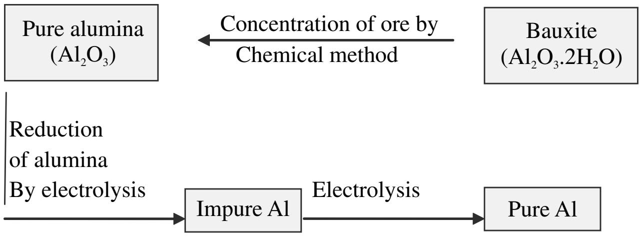
17. The chemical composition of the slag formed during smelting is:

(a) $CuSiO_3$ (b) $FeSiO_3$

(c) $CaSiO_3$ (d) $Cu_2O. SiO_2$

Paragraph # 3 (Q. 18 to 19)

Extraction of aluminium can be understood by:



Using suspended graphite rods an anode and C-lining inside the Fe container.

18. The purpose of adding cryolite is:

(a) To remove the impurities as slag
(b) To lower the melting point of Al_2O_3
(c) To decrease the electrical conductivity of pure aluminium
(d) To increase the Al percentage in the yield

19. The molten electrolytes contain Na^+, Al^{3+} and Ca^{2+} but only Al gets deposited at Cathode because,

(a) Standard reduction potential of Al is more than that of Na and Ca
(b) Standard oxidation potential of Al is more than that Na and Ca
(c) Graphite reacts only with Al^{3+} and not with Na^+ and Ca^{2+}
(d) Discharge potential of Al^{3+} is higher than Na^+ and Ca^{2+}

INTERGER TYPE QUESTIONS

20. Number of metals among following which are obtained by electrometallurgy in molten state are:

Li, Ba, Na, Al, Fe, Cu, Pb, Sn, Ag, Au, Zn, Ca, Mg

21. How many of the following process of refining is/are chemical methods:

(a) Liquation process
(b) Fractional distillation process
(c) Zone refining method
(d) Chromatographic method
(e) Cupellation
(f) Poling process
(g) Hoop's process
(h) Kroll's process

22. How many of the following minerals are oxides of metals/ metalloids.

(a) Bauxite
(b) Corundum
(c) Dolomite
(d) Malachite
(e) Magnetite
(f) Pyrolusite
(g) Argentite
(h) Horn silver
(i) Quartz
(j) Cryolite
(k) Siderite
(l) Zincite
(m) Calamine
(n) Sylvine
(o) Carnellite

23. Poling process is applied when impurity is a compound of a metal and a non-metal. Atomic number of non-metal is…………………

MATCH THE COLUMN TYPE QUESTIONS

24.

	Column I		**Column II**
A	Mond's process	(a)	Refining of Ag
B	Thermite process	(b)	Extraction of Cr
C	Poling	(c)	Refining of Cu
D	Cupellation	(d)	Refining of Zr
E	Van Arkel method	(e)	Extraction and purification of Ni
F	Carbon reduction method	(f)	Iron

25.

	Column I		**Column II**
A	Copper pyrites	(a)	Fluoride ore
B	Cryolite	(b)	Sulphate ore
C	Rock salt	(c)	Oxide ore
D	Alumina	(d)	Sulphide ore
E	Dolomite	(e)	Chloride ore
F	Gypsum	(f)	Carbonate ore

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. Electrolytic reduction of alumina to aluminium by Hall – Heroult process is carried out:

(a) In the presence of NaCl
(b) In the presence of fluorite
(c) In the presence of cryolite which forms a melt with lower melting temperature
(d) In the presence of cryolite which forms a melt with higher melting temperature

[IIT-2000]

2. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is

(a) $Cu_2O + FeS$ (b) $FeSiO_3$

(c) $CuFeS_2$ (d) $Cu_2S + FeO$

[IIT-2001]

3. Which of the following process is used in extractive metallurgy of magnesium?

(a) Fused salt electrolysis

(b) Self - reduction

(c) Aqueous solution electrolysis

(d) Thermite reduction

[IIT-2002]

4. In the process of extraction of gold,

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + HO^-$$

$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y]

(a) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$

(b) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$

(c) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$

(d) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

[IIT-2003]

5. The methods chiefly used for the extraction of lead and tin from their ores are respectively:

(a) Self-reduction and carbon reduction

(b) Self-reduction and electrolytic reduction

(c) Carbon reduction and self-reduction

(d) Cyanide process and carbon reduction

[IIT-2004]

6. Which ore contains both iron and copper:

(a) Cuprite (b) Chalcocite

(c) Chalcopyrite (d) Malachite

[IIT-2005]

7. Match entry in Column (I) is in some way related to the entries in columns (II)

Column I		**Column II**	
A	Self - reduction	(a)	Lead
B	Carbon reduction	(b)	Silver
C	Complex formation and displacement by metal	(c)	Copper
D	Decomposition of iodide	(d)	Boron

[IIT-2006]

8. Extraction of zinc from Zinc blende is achieved by:

(a) Electrolytic reduction

(b) Roasting followed by reduction with carbon

(c) Roasting followed by reduction with another metal

(d) Roasting followed by self-reduction

[IIT-2007]

9. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of

(a) Nitrogen (b) Oxygen

(c) Carbon dioxide (d) Argon

[IIT-2008]

10. Match the conversions in Column I with the type(s) of reaction(s) given in Column II.

Column I		**Column II**	
A	$PbS \rightarrow PbO$	(a)	Roasting
B	$CaCO_3 \rightarrow CaO$	(b)	Calcination
C	$ZnS \rightarrow Zn$	(c)	Carbon reduction
D	$Cu_2S \rightarrow Cu$	(d)	Self-reduction

Passage (Q. 11 to 13)

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4.5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self–reduction. **[IIT-2010]**

11. Partial roasting of chalcopyrite produces:

(a) Cu_2S and FeO

(b) Cu_2O and FeO

(c) CuS and Fe_2O_3

(d) Cu_2O and Fe_2O_3

12. Iron is removed from chalcopyrite as:

(a) FeO (b) FeS

(c) Fe_2O_3 (d) $FeSiO_3$

13. In self-reduction, the reducing species is:

(a) S (b) O^{2-}

(c) S^{2-} (d) SO_2

14. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are:

(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III magnetite
(d) III in haematite and II, III in magnetite

[IIT-2011]

15. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively

[IIT-2012]

16. Sulphide ores are common for the metals

(a) Ag, Cu and Pb
(b) Ag, Cu and Sn
(c) Ag, Mg and Pb
(d) Al, Cu and Pb

[JEE Advanced 2016]

17. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud' these are –

(a) Pb and Zn (b) Sn and Ag
(c) Fe and Ni (d) Ag and Au

[AIEEE- 2005]

18. Heating mixture of Cu_2O and Cu_2S will give

[AIEEE- 2005]

(a) Cu + SO_3 (b) Cu + SO_2
(c) Cu_2SO_3 (d) CuO + CuS

19. Which method of purification is represented by the following equation:

$$Ti\,(s) + 2I_2\,(g) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti\,(s) + 2I_2\,(g)$$

(a) Cupellation (b) Poling
(c) Van Arkel (d) Zone refining

[AIEEE- 2012]

20 Calcination is the process in which –

(a) Ore is heated in absence of air
(b) Used for sulphides ores
(c) Ore is heated in presence of air
(d) None of these

[JEE Main Online – 2013]

21. In Goldschmidt alumino thermite process which of the following reducing agents is used –

(a) Calcium (b) Coke
(c) Al - powder (d) Sodium

[JEE Main Online – 2013]

22. The metal that cannot be obtained by electrolysis of an aqueous solution of its salt is:

(a) Ag (b) Ca
(c) Cu (d) Cr

[JEE Main 2014]

23. The form of iron obtained from blast furnace is:

(a) Steel (b) Cast Iron
(c) Pig iron (d) Wrought Iron

[JEE Main Online – 2014]

24. Calamine is an ore of:

(a) Copper (b) Aluminium
(c) Iron (d) Zinc

[JEE Main Online – 2015]

25. In the context of the Hall – Heroult process for the extraction of Al, which of the following statements is false?

(a) CO and CO_2 are produced in this process
(b) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
(c) Al^{3+} is reduced at the cathode to form Al
(d) Na_3AlF_6 serves as the electrolyte

[JEE Main-2015]

26. Which one of the following ores is best concentrated by froth floatation method?

(a) Siderite (b) Galena
(c) Malachite (d) Magnetite

[JEE Main-2016]

Answer Key

LEVEL I

1. (a) 2. (a) 3. (b) 4. (d) 5. (c) 6. (b) 7. (b) 8. (c) 9. (b) 10. (d)
11. (a) 12. (c) 13. (c) 14. (c) 15. (c) 16. (b) 17. (c) 18. (a) 19. (a) 20. (b)
21. (b) 22. (b) 23. (b) 24. (a) 25. (c) 26. (d) 27. (a) 28. (a) 29. (c) 30. (c)

LEVEL II

1. (c) 2. (b) 3. (b) 4. (b) 5. (d) 6. (b) 7. (c) 8. (c) 9. (d) 10. (a)
11. (b) 12. (c) 13. (a) 14. (b) 15. (d) 16. (a) 17. (d) 18. (d) 19. (b) 20. (c)
21. (c) 22. (b) 23. (b) 24. (b) 25. (d) 26. (a) 27. (b) 28. (d) 29. (a) 30. (b)

LEVEL III

1. (b,c) 2. (a,b,d) 3. (a,b,c) 4. (a,b, c,d) 5. (b,d) 6. (a,b,c,d) 7. (a,b,c) 8. (a,b,c,d)
9. (a,b,c,d) 10. (b,c,d) 11. (a,b) 12. (a,c,d) 13. (a,b) 14. (a) 15. (c) 16. (a)
17. (b) 18. (b) 19. (a) 20. (6)21. (4) 22. (6) 23. (8)
24. A → (e) ; B → (b) ; C → (c) ; D → (a) ; E → (d) ; F → (f)
25. A → (d) ; B → (a) ; C → (e) ; D → (c) ; E → (f) ; F → (b)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (c) 2. (b) 3. (a) 4. (a) 5. (a) 6. (c) 7. A → (a,c) ; B → (a,c) ; C → (b) ; D → (d)
8. (b) 9.(b) 10. A → (a) ; B → (b) ; C → (a,c) ; D → (a,c,d) 11. (a) 12. (d) 13. (c)
14. (d) 15. (b) 16. (a) 17. (d) 18. (b) 19. (c) 20. (a) 21. (c) 22. (b) 23. (c)
24. (d) 25. (d) 26. (b)

Hints and Solutions

LEVEL I

1. **(a)** Three most occurring elements into the earth crust are O, Si, Al

2. **(a)** Bauxite ($Al_2O_3.2H_2O$) is an oxide ore.

3. **(b)** Zinc blende, ZnS
chalcopyrites, $CuFeS_2$
Galena, PbS

4. **(d)** Gypsum is $CaSO_4.2H_2O$

5. **(c)** Epsomite is $MgSO_4.7H_2O$

6. **(b)** Dolomite is $CaCO_3.MgCO_3$

7. **(b)** Magnesite is $MgCO_3$

8. **(c)** Less reactive metals like Au, Pt exist as native ore.

9. **(b)** Chromite ore is $FeCr_2O_4$

10. **(d)** Sulphide ore is concentrated wetting by oil.

11. **(a)** Oxide ore (Haematite, Fe_2O_3) is concentrated by gravity separation method.

12. **(c)** $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$

13. **(c)** Highly electropositive elements are recovered from electrolytic process.

14. **(c)** Refining of silver can be done by cupellation and electrorefining.

15. **(c)** Impure aluminium is purified by Hoop's process.

16. **(b)** In the alumino-thermite process, Al acts as reducing agent.

17. **(c)** Slag is formed by reaction between impurities and flux.

18. **(a)** All ores are minerals but all minerals are not ores.

19. **(a)** Purification of Si is done by zone refining.

20. **(b)** Concetration method used for bauxite ore is leaching (chemical method).

21. **(b)** In blast furnane, maximum temperature is in combustion zone where combustion of coke (C) takes place.

22. **(b)** Silica (SiO_2) is an acidic impurity hence, a basic flux is needed.

23. **(b)** In cupellation method, Pb and Zn impurity present in silver are removed as their oxides.

24. **(a)** Cassiterite (SnO_2) is an oxide ore. It is concentrated by gravity sepatation (Levigation).

25. **(c)** Froth floatation method is used for sulphide ore (cinnabar, HgS).

26. **(d)** Fluorspar is CaF_2.

27. **(a)** Gravity separation is used for oxide ore (Haematite, Fe_2O_3).

28. **(a)** Electrolytic reduction method is used in the extraction of high electropositive elements like Na, Ca, Mg, K, Al etc.

29. **(c)** Bauxite is leached with NaOH

$$Al_2O_3.2H_2O + NaOH \longrightarrow NaAlO_2 + H_2O$$

30. **(c)** Cyanide process is used for Ag and Au.

LEVEL II

1. **(c)** Leaching is a chemical process in which a suitable reagent is used which forms a soluble complex only with desired metal leaving behind impurities.

2. **(b)** $FeO + SiO_2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$

3. **(b)** In zone refining method, the molten zone consists more impurity than the original metal becuase impurities are moving in the direction of movement of furnace.

4. **(b)** Bauxite ($Al_2O_3 . 2H_2O$)
Siderite ($FeCO_3$)
Argentite (Ag_2S)

5. **(d)** $MgCO_3 \longrightarrow MgO + CO_2$

Calcination is heating of ore in absence or limited supply of air.

6. **(b)** Cupellation is refining process for Ag.

7. **(c)** This method can not be used for highly electropositive matals.

8. **(c)** Highly electropositive metals are extrached by electrolysis of their fused salt.

9. **(d)** Ore particles are hydrophobic and they are wetted by oil.

10. **(a)** The slag is lighter and has lower melting point than the metal hence it floats over the molten metal.

11. **(b)** **(i)** $Zn_{(s)} + \frac{1}{2} O_2(g) \longrightarrow ZnO_{(g)}$;

$\Delta G° = -360$ kJ/mol.

(ii) $C_{(s)} + \frac{1}{2} O_2(g) \longrightarrow CO_{(g)}$;

$\Delta G° = -460$ kJ/mol.

(ii–i) $ZnO_{(g)} + C_{(s)} \longrightarrow CO_{(g)} + Zn_{(s)}$;

$\Delta G° = -460 + 360 = -100$ kJ/mol.

For a feasible reaction, $\Delta G°$ must be negative. It means, ZnO can be reduced by C into Zn.

12. **(c)** $\Delta G°$ Vs T plot in the Ellingham's diagram slopes downward for the reaction,

$$C + \frac{1}{2} O_2 \longrightarrow CO$$

13. **(a)** Purification of Al metal is done by Hoop's process. (Baeyer's process is used for purification of bauxite ore).

14. **(b)** To remove acidic impurities, basic flux is used.

15. **(d)** Because Na is highly reactive.

16. **(a)** Silica impurity present in bauxite is removed by sepeck's process (by addition of coke and N_2)

17. **(d)** $PbS \longrightarrow PbO + PbSO_4$ (Roasting)

$$\left.\begin{array}{l} PbS + PbO \rightarrow Pb + SO_2 \\ PbS + PbSO_4 \rightarrow Pb + SO_2 \end{array}\right\} \text{Self Reduction}$$

18. **(d)** Electrorefining process is not used for Al.

19. **(b)** Poling process is used if oxide of metal is present as impurity in metal.

20. **(c)** $Al_2O_3.2H_2O + 3C + N_2 \xrightarrow{\Delta} 2AlN + 3CO + 2H_2O$

$AlN + 3H_2O \longrightarrow Al(OH)_3\downarrow + NH_3\uparrow$

21. **(c)** $FeO + SiO_2 \longrightarrow \underset{\text{(slag)}}{FeSiO_3}$

22. **(b)** A reaction is feasible only when its $\Delta G°$ is negative.

(i): $2Zn_{(s)} + O_2(g) \longrightarrow 2ZnO_{(g)}$; $\Delta G° = -360$ kJ/mol

(ii): $2C_{(gr)} + O_2(g) \longrightarrow 2CO_{(g)}$; $\Delta G° = -500$ kJ/mol

(ii–i): $2ZnO_{(s)} + 2C(gr.) \longrightarrow 2CO_{(g)} + 2Zn_{(s)}$; $\Delta G° = -140$ kJ/mol

Hence, ZnO can be reduced by graphite.

23. **(b)** Impurity ZnS forms a soluble complex $Na_2[Zn(CN)_4]$ with depressant NaCN.

24. **(b)** In extraction of iron, coke (C) and limestone ($CaCO_3$) are added with haematite ore (Fe_2O_3).

25. **(d)** $Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$

It is an example of goldschmidt alumino-thermite process.

26. **(a)** In Bassemer converter copper is extracted by,

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

27. **(b)** ZnS (Zinc blende) $\longrightarrow$ Zn

ZnS $\longrightarrow$ ZnO (Roasting)

ZnO $\longrightarrow$ Zn (C-Reduction process)

28. **(d)** Mond's process is used for nickel (Ni)

29. **(a)** Poling process is used for the removal of Cu_2O from Cu.

30. **(b)** Argentite (Ag_2S)

Cuprite (Cu_2O)

LEVEL III

1. (b,c) Highly electropositive metals like Na, Al etc are extracted by electrolysis of their fused salt.

2. (a,b,d) Cynide process is used for metallurgy of Ag and Au.

3. (a,b,c) Concentration by froth floatation followed by Roasting. Reduction by Bessemerisation

4. (a,b,c,d) Slag ($CaSiO_3$) is lighter than molten Fe

5. (b,d) Liquation is the process used for metal having impurities greater melting point than metal.

6. (a,b,c,d) Aim of roasting :

(a) to convert ore into oxide of metal.

(b) to remove moisture.

(c) to remove volatile organic impurities.

(d) to oxidize free sulphur and antimony.

7. (a,b,c) Slag in the extraction of Fe is $CaSiO_3$ while slag in the extraction of Cu is $FeSiO_3$.

8. (a,b,c,d)

Calamine ($ZnCO_3$)

Proustite (Ag_3AsS_3)

Cassiterite (SnO_2)

Diaspore ($Al_2O_3.H_2O$)

9. (a,b,c,d) Froth floatation, is a physical method, mainly used for sulphide ores, depends on the difference in wetability of gangue and the ore particles.

10. (b,c,d) Al is more electropositive than Fe hence, Fe can not be used as reducing agent for Al_2O_3.

11. (a, b) Calcination is the heating of ore in absence or limited supply of air.

12. (a,c,d) Lead impurity from silver can be removed by cupellation.

13. (a, b) Metal present lower in the Ellingham diagram can reduce metal oxide present higher in this diagram.

14. (a) In cyanide process, Au forms soluble complex with CN^- in the presence of O_2.

15. (c) This process represents hydrometallurgical extraction.

16. (a) Copper pyrites is $CuFeS_2$

17. (b) $\underset{\text{(impurity)}}{FeO} + \underset{\text{(flux)}}{SiO_2} \rightarrow \underset{\text{(slag)}}{FeSiO_3}$

18. (b) Cryolite (Na_3AlF_6) is added to lower the melting point of Al_2O_3.

19. (a) Al has higher SRP (standard reduction potential) than Na and Ca.

20. Li, Ba, Na, Al, Ca, Mg

21. Cupellation, Poling process, Hoop's process, Kroll's process.

22.

Bauxite	(Al_2O_3. $2H_2O$)
Magnetite	(Fe_3O_4)
Quartz	(SiO_2)
Corundum	(Al_2O_3)
Pyrolusite	(SnO_2)
Zincite	(ZnO)

23. Poling is applied when metallic oxide is present as impurity.

The atomic number of 'O' is 8.

24. (A → e ; B → b ; C → c ; D → a ; E → d ; F → f)

25. (A → d ; B → a ; C → e ; D → c ; E → f ; F → b)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **(c)** Cryolite is added into alumina to lower down melting point.

2. **(b)** $\underset{\text{(impurity)}}{\text{FeO}} + \underset{\text{(flux)}}{\text{SiO}_2} \rightarrow \underset{\text{(slag)}}{\text{FeSiO}_3}$

3. **(a)** Highly electropositive metals, like Mg, are extracted by electrolysis of their fused salt.

4. **(a)** [X] is $[\text{Au(CN)}_2]^-$

[Y] is $[\text{Zn(CN)}_4]^{2-}$

5. **(a)** Pb → self reduction process

Sn → carbon reduction process

6. **(c)** Chalcopyrite is CuFeS_2

7. (A → a, c ; B → a, c ; C → b ; D → d)

8. **(b)** $\text{ZnS} \longrightarrow \text{ZnO}$ (Roasting)

$\text{ZnO+C} \longrightarrow \text{Zn+CO}$ (Carbon reduction process)

9. **(b)** $\text{Ag}_2\text{S} + \text{NaCN} + \text{H}_2\text{O} + \text{O}_2 \longrightarrow \text{Na}[\text{Ag(CN)}_2] + \text{S} + \text{NaOH}$

10. (A → a ; B → b ; C → a, c ; D → a, c, d)

11. **(a)** $\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + \text{FeO} + \text{SO}_2$

12. **(d)** $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$

13. **(c)** $\text{Cu}_2\overset{-2}{\text{S}} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \overset{+4}{\text{SO}_2}$

(S^{-2} ion acts as a reducing agent)

14. **(d)** Haematite $(\overset{+3}{\text{Fe}_2}\text{O}_3)$

Magnetite $(\text{Fe}_3\text{O}_4 \text{ or } \overset{+2}{\text{Fe}}\text{O}.\overset{+3}{\text{Fe}_2}\text{O}_3)$

15. **(b)**

$$\text{Ag}_2\text{S+CN}^-\text{+H}_2\text{O+}\underset{\text{oxidizing agent}}{\text{O}_2} \longrightarrow [\text{Ag(CN)}_2]^- + \text{S+OH}^-$$

$$[\text{Ag(CN)}_2]^- + \underset{\text{Reducing agent}}{\text{Zn}} \longrightarrow \text{Ag} + [\text{Zn(CN)}_4]^{2-}$$

16. **(a)** Argentite (Ag_2S)

Chalcopyrite (CuFeS_2)

Galena (PbS)

17. **(d)** Composition of anode mud in electrolytic refining of copper is Ag, Au etc.

18. **(b)** $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$

19. **(c)** Van-Arkel process is used for Zr and Ti.

20. **(a)** Calcination is the process in which ore is heated in absence or limited supply of air.

21. **(c)** In Goldschmidt alumino thermite process, Al is used as reducing agent.

22. **(b)** Higher electropositive metals, like Ca, are extracted by electrolysis of their fused salt.

23. **(c)** The iron abtained from blasat furance is pig iron.

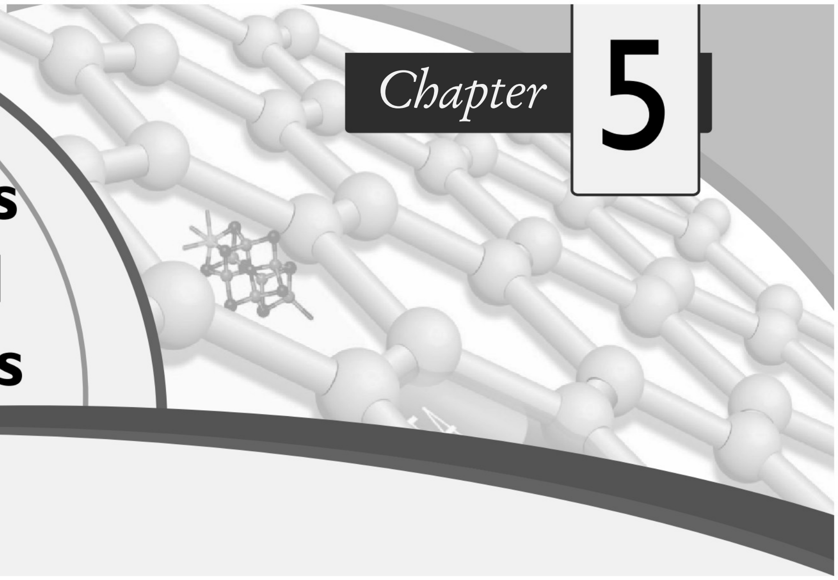
24. **(d)** Calamine is ZnCO_3

25. **(d)** Cryolite $(\text{Na}_3\text{AlF}_6)$ and Fluorospar (CaF_2) are added to lower down melting point and to increase conductivity of electrolyte (Al_2O_3).

26. **(b)** Galena (PbS) is concentrated by froth floatation process.

Chapter 5

Hydrogen and Its Compounds and S-Block Elements



Key Concepts

HYDROGEN

Hydrogen is the first element of the periodic table. Its electronic configuration is $1s^1$ and it behaves like an alkali metal as well as a halogen. There are three isotopes of hydrogen namely, hydrogen (${}_1H^1$), deuterium (${}_1H^2$ or D) and tritium (${}_1H^3$ or T).

Based on the spinning of two nuclei in dihydrogen, two types of dihydrogen may be distinguished. Ortho-dihydrogen involves parallel spinning while para-dihydrogen involves antiparallel spinning of the two nuclei.

Dihydrogen is relatively inactive (because of high enthalpy 435.kJ Mol^{-1}) at ordinary temperature but quite reactive at high temperature or in the presence of catalysts.

HYDRIDES

These are classified as follows:

- *Ionic Hydrides:* When elements of Groups 1 and 2 (except Be and Mg) and lanthanides, (electronegativity in the range 0.9 to 1.2) from compounds with hydrogen, they are called ionic hydrides. These hydrides are crystalline solids with higher melting points. The stability of hydrides decreases with increase in atomic number of the element in a group. Examples are NaH, CaH_2 etc.
- *Covalent Hydrides:* When element of p-block from compound with hydrogen, they are called covalent hydrides. Examples are NH_3, H_2O etc. These are generally gaseous compound. Their stability with increase in atomic number of elements within group decreases.
- *Interstitial Hydrides:* These are formed by some of the transition metals with electronegativity ranging from 1.2 to 1.4. Mostly these are non-stoichiometric solids and may be considered as interstitial compounds. Varying temperature and pressure may vary the proportion of hydrogen in the compound. Examples are $TiH_{1.73}$, $ZrH_{1.92}$, $VH_{0.6}$ etc.
- *Polymeric Hydrides:* Some elements with electronegativity in the range 1.4 to 2.0 form polymeric hydrides. These are solids containing molecules linked by hydrogen-bridged bonds. Examples include $(BeH_2)_n$, $(MgH_2)_n$ and $(AlH_3)_n$

  Hydrogen finds many uses. For example, for the preparation of NH_3, CH_3OH, synthetic petrol, acetylene, vegetable ghee, $H_2 - F_2$ flame, an oxy-hydrogen flame etc.

WATER

Water (H_2O) is the most abundant liquid i.e., 75% of the earth's surface is full oceans, lakes and rivers. It has bent angular structure with H-O-H bond angle of 104.5°. Because of hydrogen bondings, water unusually has high melting and boiling points. Because of these bonds, ice is less dense than liquid water. When ice (density = 0.917 g cm^{-3}) is heated, its density increases to 1 g cm^{-3} at 4°C followed by decrease in density as the temperature is further increased.

Water is termed as soft water if it is free from calcium or magnesium salts. If these salts are present, it is termed as hard water. The latter is not useful for washing purposes as soap forms insoluble scum of calcium or magnesium state in hard water.

Temporary hardness in water is due to dissolved bicarbonates of calcium or magnesium. It can removed by boiling water when carbonates are precipitated out. Permanent hardness is due to soluble chloride or sulphate of calcium or magnesium. This hardness can be removed by adding sodium hydroxide, carbonate or sodium phosphate. Ion exchange resins are also used to soften the water.

HYDROGEN PEROXIDE

The two O-H groups in hydrogen peroxide (H_2O_2) do not lie in the same plane. The angle between two planes is 111.5° and it reduces to 90.2° in the crystalline phase. The O-O-H bond on the other hand changes from 94.8° to 101.9°.

Hydrogen peroxide is a strong oxidizing agent. It oxidizes ferrous to ferric, iodide to iodine, lead sulphide to lead sulphate, potassium ferrocyanide to potassium ferricyanide (in acidic medium) and manganese (II) to manganese (IV).

Hydrogen peroxide also acts as a reducing agent. It reduces permanganate to manganese (II), iron (III) to iron (II), ferricyanide to ferrocyanide (in alkaline medium), periodate to iodate, ozone to oxygen and silver to metallic.

SUMMARY OF PREPARATION AND PROPERTIES OF DIHYDROGEN

H_2
DIHYDROGEN

PREPARATION

From water (H_2O)

(a) By reaction with metals

- Active metals (Na, K, Ca) react at room temperature
- Metals like Mg, Zn, Al react on heating
- Metals like Fe, Ni, Sn react with steam

$H_2O + Na \xrightarrow{} NaOH + H_2$

$H_2O + 2Mg \xrightarrow{} 2MgO + H_2$

$4H_2O + 3Fe \xrightleftharpoons{1000k} Fe_3O_4 + 4H_2$

(b) Electrolysis of acidic or alkaline water

$2H_2O \xrightarrow{\text{Electricity}} O_2 + 2H_2$

From Acids by reaction with active metals

$2HCl + Mg \xrightarrow{} MgCl_2 + 2H_2$

$H_2SO_4 + Zn \xrightarrow{} ZnSO_4 + H_2$

From Conc. Alkalies by reaction with elements like

Zn, Sn, Al, Be, B, Si etc.

$2Al + 2NaOH + 2H_2O \xrightarrow{} NaAlO_2 + 3H_2$

$Sn + 2NaOH + H_2O \xrightarrow{} Na_2SnO_3 + 2H_2$

Laboratory Preparation

$\underset{\text{dil.}}{H_2SO_4} + Zn \xrightarrow{} ZnSO_4 + H_2$

Uses

- In Preparation of ammonia
- Hydrogenation of oils
- In oxy-hydrogen and atomic hydrogen torch
- Liquid H_2 is used as prospective fuel.

PROPERTIES

Physical Properties

- Colourless
- Tasteless
- Odourless
- Highly combustible
- High value of $\Delta H_{H\text{-}H}$ (436 KJ mol^{-1})

Chemical Properties

Metals react to form respective hydrides

$H_2 + 2Na \xrightarrow{525K} 2NaH$

$H_2 + Ca \xrightarrow{525K} CaH_2$

Non-Metals form respective hydrides

$2H_2(g) + O_2(g) \xrightarrow[\text{or sunlight}]{970K} 2H_2O$

$3H_2(g) + N_2(g) \xrightarrow{Fe/Mo,\ 770K} 2NH_3$

$H_2(g) + S(I) \xrightarrow{} H_2S$

$2H_2(g) + 2C(s) \xrightarrow{1275K} C_2H_2$

$H_2(g) + X_2(g) \xrightarrow[3000K]{\text{Electric arc}} 2HX(X = F,Cl,Br\ I)$

Metals Oxides are reduced to metals

$H_2 + PbO \xrightarrow{} Pb + H_2O$

$2H_2 + CO \xrightarrow[ZnO/Cr_2O_3]{700K,\ 200atm.} CH_3OH$

Unsaturated hydrocarbons get hydrogenated

$H_2 + CH_2 = CH_2 \xrightarrow{Pt} CH_3\text{-}CH_3$

$2H_2 + CH \equiv CH \xrightarrow{Pt} CH_3\text{-}CH_3$

$H_2 + \text{Vegetable oils} \xrightarrow{Ni} \text{Fats}$

H_2O
WATER

Physical Properties

- The composition of hydrogen and oxygen elements by mass is 1:8 and by volume it is 2:1.
- It is a covalent compound with bent structure. The O-H bonds are sp^3-$s\sigma$ - bonds and angle around O is 104.5°.
- Its dipole moment is 1.83D and dielectric constant is 82.5.
- Excellent solvents for large number of ionic as well as covalent substances.
- Interpartical forces in **water** and **ice** are **H-bonds.**
- Density of ice is less than water because of open cage like structure of ice.
- Density of water is maximum (1.0 g cm^{-3}) at 277 K.
- Dissociation constant (K_w) of water at 25° C is 1×10^{-14} and $pK_w = 14$.

Chemical Properties

Dissociation of water

$$H_2O \xrightarrow{\text{High temp.}} H_2 + \frac{1}{2}O_2$$

Dissociation is 0.2% even at 1500 K

Amphoteric nature of water

$$\underset{\text{Acid}}{H_2O} + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

$$\underset{\text{Base}}{H_2O} + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Self ionization of water

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

Active metals decompose water to liberate H_2

$$H_2O + 2Na \longrightarrow 2NaOH + H_2$$

$$H_2O + Zn \xrightarrow{\text{Heat}} ZnO + H_2$$

In these reactions H_2O acts as a weak oxidant.
It can reduce highly electronegative elements such as halogens, carbon, etc.

$$2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$$

$$\underset{\substack{\text{Red Hot}\\\text{Coke}}}{C} + H_2O(g) \longrightarrow CO + H_2$$

Hydrolytic Reactions

$$3H_2O + PBr_3 \longrightarrow H_3PO_3 + 3HBr$$

$$2H_2O + SiCl_4 \longrightarrow SiO_2 + 4HCl$$

$$6H_2O + Ca_3P_3 \longrightarrow Ca(OH)_2 + 2PH_3$$

$$2H_2O + CaH_2 \longrightarrow Ca(OH)_2 + H_2$$

$$2H_2O + CaC_2 \longrightarrow Ca(OH)_2 + C_2H_2$$

$$12H_2O + Al_4C_3 \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$H_2O + CaNCN \longrightarrow CaCO_3 + 2NH_3$$

$$6H_2O + Mg_3N_2 \longrightarrow 3Mg(HO)_2 + 2NH_3$$

Hydrate Reactions

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$$

$$AlCl_3 + 6H_2O \longrightarrow AlCl_3.6H_2O$$

$$BeCl_2 + 2H_2O \longrightarrow BeCl_2.2H_2O$$

H_2O_2
HYDROGEN PEROXIDE

PREPARATION

- **Merck's method**

$Na_2O_2 + H_2SO_4 \xrightarrow{\quad} Na_2SO_4 + H_2O_2$

- **From Barium peroxide**

$BaO_2.8H_2O + H_2SO_4 \xrightarrow{\quad} BaSO_4\downarrow + 8H_2O + H_2O_2$

$BaO_2.8H_2O + H_3PO_4 \xrightarrow{\quad} Ba_3(PO_4)_2\downarrow + 8H_2O + 3H_2O_2$

- **Electrolysis 50% H_2SO_4**

$H_2SO_4 \xrightarrow{\quad} H^+ + HSO_4$

Cathode:- Anode:-

$2H^+ + 2e^- \xrightarrow{\quad} H_2$ $2HSO_4^- \xrightarrow{\quad} H_2S_2O_8 + 2e$

$H_2S_2O_8 + H_2O \xrightarrow{\quad} 2H_2O_2 + H_2SO_4$

- **Electrolysis of $(NH_4)_2SO_4$ (H_2SO_4 mixture)**

$(NH_4)_2SO_4 + H_4SO_4 \xrightarrow{\quad} 2NH_4HSO_4$

$NH_4SO_4^- + H^+$

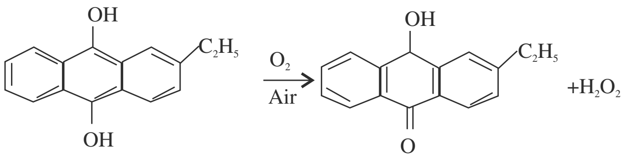
Cathode:- Anode:-

$2H^+ + 2e^- \longrightarrow H_2$ $2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$

$(NH_4)_2S_2O_8 + H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$

Amm. Persulphate

- **Air oxidation of 2-enthraquinol**



Concentration

Dilute solution of H_2O_2 is concentrated by various steps like slow evaporation on water bath, evaporation in vacuum decicator, distillation under reduced pressure and finally freezing.

Storage: It is stored in a dark bottle and its decomposition is retarded by stabilizers like glycerol, acetanilide, uric acid, barbituric acid, etc.

PROPERTIES

Physical Properties

- Colourless, syrupy liquid with odour like nitric acid
- Soluble in alcohol, ether
- Density 1.44 g/cm^3
- BP = 423K at 670 mm; 358K at 68 mm

Chemical Properties

- **Decomposition**

$2H_2O_2 \xrightarrow{\quad} 2H_2O + O_2; \Delta H = - 196 \text{ kJ}$

Decomposition is felicitated by Pt carbon

- **Acidic Nature** ($K_a = 1.5 \times 10^{-12}$)

$H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + 2H_2O$

$H_2O_2 + NaCO_3 \longrightarrow Na_2O_2 + H_2O + CO_2$

- Oxidising behaviour

$4H_2O_2 + PbS \xrightarrow{\quad} PbSO_4 + 4H_2O$

$H_2O_2 + NO_2^- \xrightarrow{\quad} NO_3^- + H_2O$

$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\quad} I_2 + H_2O$

$H_2O_2 + 2Fe^{2+} + 2H^+ \xrightarrow{\quad} 2Fe^{3+} + 2H_2O$

$H_2O_2 + AsO_3^{3-} \xrightarrow{\quad} AsO_4^{3-} + H_2O$

$H_2O_2 + 2[Fe(CN)_6]^{4-} \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$

$4H_2O_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow CrO_5 + H_2O$

- Reducing Nature

$H_2O_2 + Ag_2O \xrightarrow{\quad} 2Ag + H_2O + O_2$

$H_2O_2 + PbO_2 \xrightarrow{\quad} PbO + H_2O + O_2$

$H_2O_2 + O_3 \xrightarrow{\quad} H_2O + 2O_2$

$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

$H_2O_2 + Cl_2 \xrightarrow{\quad} 2HCl + O_2$

$H_2O_2 + 2[Fe(CN)_6]^{3-} \xrightarrow{2OH^-} 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

$H_2O_2 + NaOBr \xrightarrow{\quad} NaBr + H_2O + O_2$

$H_2O_2 + CaOCl_2 \xrightarrow{\quad} CaCl_2 + H_2O + O_2$

Bleaching action H_2O_2: H_2O_2 is used to bleach delicate articles like ivory silk, feather, wool, etc. The bleaching action is due to its ability to oxidise the colouring matter.

$H_2O_2 \xrightarrow{\quad} H_2O + O$

Coloring matter + (O) $\xrightarrow{\quad}$ Oxidised matter (Colourless)

S-Block Elements

(a) Element of group 1 (or I A) and 2(or II A) are known as s-block elements.

(b) General electronic configuration are

Group 1 [Inert gas]ns^1 Alkali metals
Group 2 [Inert gas]ns^2 Alkaline Earth metals

Property	Alkali metal	Alkaline earth metal
Physical state	(a) All are silvery white.	(a) All are grayish white.
	(b) Light soft, malleable and ductile metals with metallic luster.	(b) Relatively harder.
	(c) Both are diamagnetic and colourless.	
Flame colour	(a) Both produce characteristic colours in Bunsen flame due to easy excitation of electron to higher energy levels.	(a) Be and Mg do not show any colour as their electrons are more strongly bound.
	(b) Characteristic flame colours are Li – Crimson, Na – Golden Yellow, K – Pale violet, Rb and Cs – Violet	(b) Ca – Brick red, Sr - Crimson Ba – apple green, Ra - Crimson
	(c) Energy released $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$	(c) Be and Mg atoms due to their small size, bind their electrons more strongly because of higher effective nuclear charge. Hence these posses high excitation energy and are not excited by the flame energy and do not show any colour.
	(d) The flame energy cause an excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light.	
Ionisation energy	(a) Due to unpaired lone electrons in ns sub shell as well as due to their larger size, the outermost electron is far from the nucleus, the removal of electron is easier and these have low values of ionization potential.	(a) Due to smaller size, electrons are tightly held as compared to alkali metal.
	(b) IP of these metals decreases from Li to Cs	(b) The IP value decreases with increase of atomic radii from Be to Ba.
Hydration of ions	(a) Hydration represents for the dissolution of a substance in water to absorb water molecule by weak valency forces. Hydration of ions in the process when ions on dissolution in water get hydrated.	
	(b) Smaller the cation greater is the degree of hydration. Hydration energy- $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	(b) Hydration energy- $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$
	(c) Li^+ being smallest in size has maximum Degree of hydration and that is why lithium Salts are mostly hydrated and moves very slowly under the influence of electric field.	

Property	Alkali metal	Alkaline earth metal
Oxidation numbers and valency	These metals easily form univalent +ve ion by losing solitary ns^1 electron due to low IP value.	The IP_1 of these metals are much lower than IP_2 and thus it appears that these metals should form univalent ion rather than bivalent ions but in actual practice, all these give bivalent ions.
Electro negativity	(a) These metals are highly electropositive thereby posses low values of electro-negativities	(a) Their electro negativities are also small but are higher than of alkali metals.
	(b) Electro-negativity of alkali metals decreases down the group Li > Na > K > Rb > Cs	(b) Electro-negativity decrease form Be to Ba.
Standard oxidation potentials are reducing properties	(a) Since alkali metals easily loose ns^1 electron they have high value of oxidation potential i.e., $M \longrightarrow M^+_{(aq)} + e^-$	(a) They lose two electrons to give M^{+2} ion.
	(b) Standard oxidation potential are listed below Li Na K Rb Cs 3.05 2.71 2.93 2.99 2.99	(b) Standard oxidation potential are Be Mg Ca Sr 1.69 2.35 2.87 2.90
	(c) Li have greatest reducing nature due to maximum hydration energy of Li^+ ion.	
Action with air	(a) On exposure to moist air, all alkali metals except lithium tarnish quickly.	(a) Except beryllium these metals are easily tarnish in air as a layer of oxide is formed on their surface.
	(b) They generally form oxides and peroxides. $M+O_2 \longrightarrow M_2O \xrightarrow{O_2} M_2O_2 \xrightarrow{O_2} MO_2$	(b) They give oxides of ionic nature $M^{+2}O^{-2}$ which are crystalline in nature.
Action with water	(a) Alkali metals decompose water with the evolution of hydrogen $2M + 2H_2O \rightarrow 2MOH + H_2$	(a) Ca, Sr, Ba and Ra decompose cold water readily with evolution of hydrogen. $2M + 2H_2O \rightarrow 2M(OH)_2 + H_2$
	(b) Li decompose water slowly, sodium reacts water quickly. K, Rb and Cs react with water vigorously.	(b) Magnesium decomposes boiling water beryllium is not attacked even at high temperatures.
	(c) Alkali metals react with alcohols forming alkoxides with the evolution of hydrogen: $2Li + 2C_2H_5OH \longrightarrow 2C_2H_5OLi + H_2$ Ethy alcohol Lithium ethoxide	
Hydride	(a) These metals combine with H_2 to give white crystalline ionic hydrides of the general formula MH.	(a) Except Be, all alkaline earth on heating directly with H_2.
	(b) The metal hydrides react with water to give MOH and H_2: $MH + H_2O \longrightarrow MOH + H_2$	(b) BeH_2 is prepared by the action of $LiAlH_4$ on $BeCl_2$: $BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$
		(c) The ionic hydrides of Ca, Sr, Ba liberate H_2 at anode and metal at cathode.

Property	Alkali metal	Alkaline earth metal
Carbonates And bicarbonates	(a) The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) are highly stable to heat, where M stands for alkali metals	(a) All these metal carbonates MCO_3 are insoluble in neutral medium but soluble in acids and decompose on heating.
	(b) The stability of these salts increases with the increasing electropositive character from Li To Cs. Therefore Li_2CO_3 decompose on heating.	(b) The stability of carbonates increase in electropositive character metal.
	(c) Bicarbonates are decomposed at relatively high temperature. $2MHCO_3 \xrightarrow{300°C} M_2CO_3 + H_2O + CO_2$	(c) Bicarbonates of alkaline earth metals do not exit in solid state but are known in solution only on heating their solution bicarbonate decomposed to liberate: $M(HCO_3)_2 \longrightarrow MCO_3 + CO_2 + H_2O$
Halides	(a) Alkali metals combine directly with halogens to from ionic halide MX.	(a) The alkaline earth metals directly combine with halogens on heating to give metal halides MX_2.
	(b) The ease with which the alkali metals form halides increases form Li to Cs due to increase in electropositive character.	(b) The ionic character of halides increases from Be to Ra.
	(c) LiX has more covalent character.	(c) Beryllium halides have covalent Character due to size and high effective nuclear charge and thus do not conduct electricity in molten state.
	(d) Halides having ionic nature high melting point and are good conductor of current in fused state. These are readily soluble in water.	(d) The solubility of halides in water decreases down the group. Except fluorides, all are fairly soluble in water.
	(e) Halides of potassium, rubidium and ceasium have property of combining with extra halogen atoms forming polyhalides: $KI + I_2 - KI_3$	(e) The decrease is solubility of halide down the group is due to decreas in hydration energy because of increasing size of metal cation. Solubility OH increase down the group
		(f) The halides are hygroscopic and readily form hydrates $CaCl_2.6H_2O$, $BaCl_2.\ 2H_2O$ Otherwise down the group lattice and hydration energy incomplete
Sulphates	(a) All these form sulphates of type M_2SO_4.	(a) MSO_4
	(b) Except Li_2SO_4 rest are soluble in water. Down the group stability and solubility increases.	(b) The solubility of sulphates decreases on moving down the group. $BeSO_4$ is soluble in water while $BaSO_4$ is completely insoluble
Nitrates	(a) Nitrates of both are soluble in water and decompose on heating.	
	(b) $LiNO_3$ decompose to give NO_2 and O_2 rest all give nitrites and oxygen. $2MNO_3 \rightarrow 2MNO_2 + O_2$ (except Li) $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$	(b) On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen $M(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$
Solution of Liquid NH_3	Forms deep blue solution with liquid Ammonia which is conducting and paramagnetic in nature.	Except Be and Mg, all others form a deep blue-black solution with liquid ammonia.

Solved Examples

1. Incorrect statement for H_2O_2 is:
- (a) Decomposition of H_2O_2 is a disproportionation reaction.
- (b) Aqueous solution of H_2O_2 is weakly acidic.
- (c) Bleaching action of H_2O_2 is due to its reducing nature.
- (d) H_2O_2 is used in refreshing old lead paintings PbS (black) converts into $PbSO_4$ (white) in presence of H_2O_2.

Sol. (c) $2H_2O_2 \rightarrow 2H_2O + O_2$ (disproportionation)

H_2O_2 is very good oxidizing and poor reducing agent. Its bleaching action is due to its oxidising nature.

$$\underset{\text{(black)}}{PbS} + H_2O_2 \rightarrow \underset{\text{(white)}}{PbSO_4} + H_2O$$

2. In which property listed below hydrogen does not resemble alkali metals?
- (a) Tendency to form cation
- (b) Nature of oxide
- (c) Combination with halogens
- (d) Reducing character

Sol. (b) H_2O is neutral while alkali metal oxides are basic in nature.

3. Calgon causes the softening of hard water by:
- (a) Sequestraction of Ca^{2+} and Mg^{2+} ion
- (b) Sequestraction of Cl^- and SO_4^{2-} ion
- (c) Precipitation the Ca^{2+} and Mg^{2+} ions as phosphates
- (d) Precipitation the Ca^{2+} and Mg^{2+} ions as sulphates

Sol. (a) Calgon is sodium hexametaphosphate $Na_6(PO_3)_6$ or $Na_2[Na_4(PO_3)_6]$

$$2Ca^{+2} + Na_2[Na_4(PO_3)_6] \rightarrow \underset{\text{Soluble complex}}{Na_2[Ca_2(PO_3)_6]} + 4Na^+$$

It is sequestraction of Ca^{+2} and Mg^{+2}

4. Which elements out of the following do not produce hydrogen on treatment with caustic soda?

A (Zn); B (Sn); C (Mg); D (Cu); E (Al)

(a) A, E (b) C, D (c) D, E (d) B, D

Sol. (b) Mg and Cu do not produce hydrogen on treatment with caustic soda (NaOH)

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$$

$$Sn + 2NaOH + H_2O \rightarrow Na_2SnO_3 + 2H_2\uparrow$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow$$

5. In which reaction, hydrogen peroxide neither acts as oxidizing agent nor reducing agent?
- (a) $Na_2CO_3 + H_2O_2 \rightarrow$
- (b) $PbS + H_2O_2 \rightarrow$
- (c) $Cr_2O_7^{2-} + H^+ + H_2O_2 \rightarrow$
- (d) $SO_3^{2-} + H_2O_2 \rightarrow$

Sol. (a) $Na_2CO_3 + H_2O_2 \rightarrow Na_2O_2 + CO_2 + H_2O$
Here, H_2O_2 acts as acid.

6. Alkali metals dissolve in liquid ammonia to give a blue colored solution which is due to the presence of –

(a) M – atoms (b) M^+ ions

(c) Solvated anions (d) Solvated electrons

Sol. (d) The blue colored solutions of an alkali metal in ammonia is explained on the basis of formation of ammoniated (solvated) metal cations and ammoniated (solvated) electrons in the metal ammonia solution in the following way:

$$M \longrightarrow M^+ + e^-$$

$$M^+ + xNH_3 \longrightarrow [M(NH_3)_x]^+$$

$$e^- + yNH_3 \longrightarrow [e(NH_3)_y]^-$$

$$M + (x+y)NH_3 \longrightarrow \underset{\text{(Solvated metal cation)}}{[M(NH_3)_x]^+} + \underset{\text{(solvated electron)}}{[e(NH_3)_y]^-}$$

The blue colour of the solution is due to excitation of free electrons to higher energy levels. The absorption of photons takes place in the red region of the spectrum and hence, the solution appears blue in the transmitted light. As the concentration of the alkali metal increases, the metal ion cluster formation takes place and at very high concentration the solution becomes colored like that of metallic copper.

7. Which of the following is an incorrect statement?
- (a) Sodium oxide is more basic then magnesium oxide.
- (b) Beryllium oxide is amphoteric.
- (c) The thermal stability of beryllium carbonate is more than of calcium carbonate.
- (d) Beryllium is amphoteric.

Sol. (c) The thermal stability of calcium carbonate is more as compared to that of beryllium carbonate. The ionic potential (Φ) value of Be^{2+} is more than that Ca^{2+}. So Be^{2+} attracts the oxygen of CO_3^{2-} more and on heating beryllium carbonate looses CO_2 more easily.

8. In the Solvay process of manufacture of sodium carbonate, the raw materials used are:
- (a) aqueous NaOH, NH_3 and CO_2
- (b) molten NaOH, NH_3 and CO
- (c) brine NaCl, NH_3 and CO
- (d) brine NaCl, NH_3 and CO_2

Sol. (d) The chemical reactions involved in Solvay process are as below:

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4\,HCO_3$$

$$NH_4HCO_3 + NaCl \xrightarrow{30°C} NaHCO_3\downarrow + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{250°C} Na_2CO_3 + H_2O + \underset{\text{(used again)}}{CO_2}$$

$$2NH_4Cl + \underset{\text{Slaked lime}}{Ca(OH)_2} \longrightarrow CaCl_2 + 2H_2O + \underset{\text{(used again)}}{2NH_3}$$

9. The ion of which of the following metals has least ionic conductivity in the aqueous solution?

(a) Lithium (b) Sodium

(c) Potassium (d) Rubidium

Sol. (a) Li^+ forms $[Li(H_2O)_4]^+$ in water because of its smallest size and highest charge to size ratio. The size of this hydrated ion is biggest and thus ionic conductivity is least.

10. The compound X on heating gives a colorless gas. The residue is dissolved in water to obtain Y. Excess of CO_2 is bubbled through aqueous solutions of Y and Z is formed. Z on gentle heating gives back X. The compound X is:

(a) $CaCO_3$ (b) Na_2CO_3

(c) $CaSO_4.\ 2H_2O$ (d) K_2CO_3

Sol. (a) $\underset{[X]}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2$

$$CaO + H_2O \longrightarrow \underset{[Y]}{Ca(OH)_2}$$

$$\underset{[Y]}{Ca(OH)_2} + \underset{\text{(excess)}}{CO_2} \longrightarrow \underset{[Z]}{Ca(HCO_3)_2}$$

$$\underset{[Y]}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{[X]}{CaCO_3} + H_2O + CO_2$$

11. Number of crystal water in Gypsum, Plaster of Paris and Epsom salt respectively are:

(a) 2, 0.5, 7 (b) 7, 2,1

(c) 7, 0.5, 2 (d) 3, 4, 2

Sol. (a) The formulae of Gypsum, Plaster of Paris and Epsom salt are-

$CaSO_4.2H_2O$, $CaSO_4.0.5H_2O$ and $MgSO_4.\ 7H_2O$

12. Nitrolim (a nitrogenous fertilizer) is a mixture of:
- (a) Calcium carbide and calcium cyanamide
- (b) Calcium oxide and calcium carbide
- (c) Calcium cyanamide and carbon
- (d) Calcium oxide and carbon

Sol. (c) $CaC_2 + N_2 \xrightarrow{1000°c} \underbrace{\underset{\text{Cal. Cynamide}}{CaCN_2 + C}}_{\text{Nitrolim}}$

13. On exposure to air, sodium hydroxide becomes liquid and after sometimes it changes to whites powder. Why?

Sol. Sodium hydroxide continuously absorbs carbon dioxide of atmosphere and is converted into sodium carbonate. A stage reaches when the solution becomes saturated and the crystals are formed. These crystals, with the crystallization (efflorescence) and crumble to white powder.

14. An aqueous solution of iodine becomes colourless on adding excess of sodium hydroxide solution. Why?

Sol. Iodine reacts with NaOH forming colourless compounds. Thus, the color of iodine disappears on addition of NaOH.

$$2NaOH + I_2 \longrightarrow \underbrace{NaI + NaIO}_{\text{Colourless products}} + H_2O$$

15. The addition of NaOH solution to a solution of $ZnCl_2$ produces a white precipitate which dissolves on further addition of NaOH. Why?

Sol. $ZnCl_2$ reacts with NaOH to gives white precipitate of $Zn(OH)_2$ which later on gets dissolved in excess of NaOH because of formation of soluble sodium zincate.

$$ZnCl_2 + 2NaOH \longrightarrow 2NaCl + \underset{\text{(Insoluble)}}{Zn(OH)_2}$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(Soluble)}}{Na_2ZnO_2} + 2H_2O$$

16. NaCl in earlier days used to manufacture NaOH and Cl_2 involving following steps. Identify (A) to (I) in the following:

$$NaCl + \text{conc. } H_2SO_4 \xrightarrow{\Delta} (A) + (B)\text{ (gas)}$$

$$(B)\text{ gas} \xrightarrow{MnO_2} (C)\text{ gas}$$

$$(A) + NaCl \xrightarrow{\Delta} (D) + (C)\text{ gas}$$

$$(D) + \text{carbon} + CaCO_3 \longrightarrow (E) + (F)$$

$$CaCO_3 \xrightarrow{\Delta} (G) + (H)\text{ gas}$$

$$(G) + H_2O \longrightarrow (I)$$

$$(I) + (E) \longrightarrow NaOH + CaCO_3$$

Sol. $$NaCl + \text{conc.}H_2SO_4 \longrightarrow \underset{(A)}{NaHSO_4} + \underset{(B)}{HCl}$$

$$\underset{(B)}{HCl} \xrightarrow{MnO_2} Cl_2$$

$$\text{Or } MnO_2 + \underset{(B)}{4HCl} \xrightarrow{\Delta} MnCl_2 + \underset{(C)}{Cl_2} + 2H_2O$$

$$\underset{(A)}{NaHSO_4} + NaCl \xrightarrow{\Delta} \underset{(D)}{Na_2SO_4} + HCl$$

$$\underset{(D)}{Na_2SO_4} + \text{carbon} + CaCO_3 \xrightarrow{\Delta} \underset{(E)}{Na_2CO_3} + \underset{(F)}{CaSO_4}$$

$$\underset{(G)}{CaCO_3} \xrightarrow{\Delta} \underset{(H)}{CaO} + CO_2$$

$$\underset{(G)}{CaO} + H_2O \longrightarrow \underset{(I)}{Ca(OH)_2}$$

$$\underset{(I)}{Ca(OH)_2} + \underset{(E)}{Na_2CO_3} \longrightarrow 2NaOH + CaCO_3$$

17. Magnesium metal burns in air to give a white ash. When ash is treated with water, the odour of ammonia can be detected. What is the reason?

Sol. Mg burns in air to form MgO and Mg_3N_2. It is the Mg_3N_2 which on hydrolysis gives NH_3

$$2Mg + O_2 \longrightarrow 2MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

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

18. Element (A) burns in nitrogen to give an ionic compound, (B) reacts with water to give (C) and (D). A solution of (C) becomes milky on bubbling carbon dioxide. Identify (A), (B), (C) and (D).

Sol. (a) Since element (A) burns in nitrogen to give an ionic compound, therefore (B) must be a metal nitride

(b) Since (B), a metal nitride reacts with water, (B) is ionic nitride and the product formed, i.e., (C) and (D) are metal hydroxides and ammonia, (NH_3)

(c) Since (C) become milky on bubbling CO_2, (C) must by calcium hydroxide, $Ca(OH)_2$.

All reactions involved in the question can be explained as follows:

$$\underset{(A)}{3Ca_{(s)}} + N_{2(g)} \xrightarrow{\Delta} \underset{\underset{(B)}{\text{Calcium nitride}}}{Ca_3N_{2(s)}}$$

$$\underset{(B)}{Ca_3N_2} + 6H_2O \longrightarrow \underset{\text{Calcium Hydroxide(C)}}{3Ca(OH)_2} + \underset{\underset{(D)}{\text{Ammonia}}}{2NH_3(g)}$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\substack{\text{Calcium}\\ \text{Carbonate}\\ \text{(milkiness)}\\ \text{(D)}}}{CaCO_3\downarrow} + H_2O$$

Thus, (A) = Ca, (B) = Ca_3N_2, (C) = $Ca(OH)_2$ (D) = NH_3

19. An aqueous compound of an inorganic compound (X) shows the following reactions:

(a) It decolourises an acidified $KMnO_4$ solution accompanied by the evolution of oxygen.

(b) It liberates I_2 from an acidified KI solution.

(c) It gives a brown precipitate with alkaline $KMnO_4$ solution with evolution of oxygen.

(d) It removes black stains from old oil paintings.

Identify X and give chemical equation for the reactions at steps (a) to (d).

Sol. (X) is H_2O_2.

a. $$\underset{\text{Purple Coloured}}{2KMnO_4} + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + \underset{\text{Colourless}}{2MnSO_4} + 8H_2O + 5O_2$$

b. $$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$

c. $$2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + \underset{\text{Brown}}{2MnO_2} + 2H_2O + 3O_2$$

d. $$\underset{\text{Black}}{PbS} + 4H_2O_2 \longrightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$

20. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce gas A and alkaline solution. The solution on exposure to air produces a thin solid layer of on the surface. Identify the compounds A and B.

Sol. $Ca + N_2 \xrightarrow{\Delta}$ white powder

$\downarrow H_2O$

Gas (A) + alkaline solution

$\downarrow$ Air

thin solid layer

(B)

Ca on heating with N_2 produces calcium nitride, Ca_3N_2, a white powder. Ca_3N_2 on reacting with water produces ammonia gas NH_3, i.e. A and alkaline solution, atmospheric CO_2 to give insoluble $CaCO_3$.

$$3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2$$

$$Ca_3N_2 + 6H_2O \longrightarrow \underset{\substack{\text{Calcium}\\ \text{hydroxide}\\ \text{(alkaline solution)}}}{3Ca(OH)_2} + 2NH_3$$

$$Ca(OH)_2 + \underset{\text{(air)}}{CO_2} \longrightarrow \underset{\text{(B)}}{CaCO_3\downarrow} + H_2O$$

Exercise

LEVEL I

1. Which pair of species can undergo chemical reaction with each other?
(a) CO and NO
(b) LiH and H_2O
(c) CO_2 and HCl
(d) CaH_2 and SiH_4

2. Which type of element forms ionic hydrides?
(a) Transition elements
(b) Metalloids
(c) Elements with high electronegativity
(d) Elements with high electropositivity

3. The three isotopes of hydrogen differ from one another in:
(a) Atomic number
(b) Number of protons
(c) Nuclear charge
(d) Nuclear mass

4. Electrolysis of which of the following liberates hydrogen gas at anode?
(a) Aq. H_2SO_4
(b) Aq. $CuSO_4$
(c) Molten calcium hydride
(d) Aq. barium hydroxide

5. Which of the following operation would cause removal of temporary hardness of water?
(a) passing CO_2 gas through it
(b) passing SO_2 gas through it
(c) adding calculated amount of $Ca(OH)_2$
(d) adding calculated amount of sodium hypophosphate.

6. When temporary hard water containing $Mg(HCO_3)_2$ is boiled the percipitate formed is of:
(a) $MgCO_3$
(b) MgO
(c) $Mg(OH)_2$
(d) None of these

7. In which of the following reactions hydrogen act as oxidizing agent?
(a) $Ca + H_2 \rightarrow$
(b) $H_2 + O_2 \rightarrow$
(c) $H_2 + F_2 \rightarrow$
(d) $CuO + H_2 \rightarrow$

8. Which forces of attraction are responsible for liquefication of H_2?
(a) Dispersion forces
(b) Hydrogen bonding
(c) Dipole force
(d) All of these

9. Adsorbed hydrogen by Palladium is known as:
(a) Atomic (b) Nascent
(c) Occuluded (d) Heavy

10. Which of the following is not a peroxide?

(a) Na_2O_2 (b) BaO_2

(c) PbO_2 (d) H_2O_2

11. The ortho and para-hydrogens possess:

(a) Same physical properties but different chemical properties

(b) Different physical properties but same chemical properties

(c) Same chemical and physical properties

(d) Different physical and chemical properties

12. Which is correct about the reaction between H_2O_2 and O_3?

(a) It is a case of mutual reduction

(b) O_3 will oxidise H_2O_2 into O_2

(c) It is not a redox reaction

(d) H_2O_2 being a stronger oxidizing agent will decompose ozone into oxygen

13. Alkali metal superoxides contain the (O_2^-) ion. They are:

(a) Paramagnetic

(b) Coloured compounds

(c) Oxidizing agents

(d) All of these

14. On heating sodium metal in the current of dry ammonia leads to the formation of which gas?

(a) $NaNH_2$ (b) NaN_3

(c) NH_3 (d) H_2

15. Which of the following s-block elements react with NaOH to give water soluble complex?

(a) Al (b) Ca

(c) Be (d) Li

16. Which of the following element is common in microcosmic salt and Glauber's salt?

(a) N (b) Na

(c) K (d) Both (a) and (b)

17. Which of the following elements does not form hydride by direct heating with dihydrogen?

(a) Be (b) Mg

(c) Sr (d) Ba

18. A metal chloride, when placed on a platinum wire in Bunsen flame, does not produce any distinctive colour. The cation of chloride is:

(a) Li^+ (b) Mg^{2+}

(c) Na^+ (d) Ca^{2+}

19. Which of the following properties of IA group metals increases as the atomic number rises?

(I) Metallic character

(II) Ionic radius

(III) Melting point

(IV) Density

(V) Ionization potential

(a) I, II, III (b) I, II

(c) III, IV, V (d) All

20. Which of the following statements is not true about the dilute solutions of alkali metals in liquid ammonia?

(a) They are deep blue coloured solutions

(b) They are highly conducting in nature

(c) They are diamagnetic in nature

(d) Ammoniated cation and ammoniated anion are formed in the solution.

21. Which of the following equations is not involved in the Solvay process?

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) $NaCl + NH_3 + H_2O + CO_2 \rightarrow NH_4Cl + NaHCO_3$

(c) $CaO + 2NH_4Cl \rightarrow 2NH_3 + H_2O + CaCl_2$

(d) $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

22. Which of the following property of alkaline earth metals increases with increasing atomic number?

(a) Ionization potential

(b) Solubility of hydroxides

(c) Solubility of sulphates

(d) Density

23. Among the carbonates of alkali metals which one has highest thermal stability?

(a) Cs_2CO_3 (b) Rb_2CO_3

(c) K_2CO_3 (d) Na_2CO_3

24. A solution of sodium in liquid ammonia is blue in colour due to:

(a) The presence of ions Na^+

(b) The presence of ammoniated electron

(c) The formation of $NaNH_2$

(d) The formation of sodium hydride

25. The order of basic strength of the hydroxides of alkali metals is:

(a) Li > Na > Rb > Cs

(b) Na > Li > Rb > Cs

(c) Cs > Rb > Na > Li
(d) Rb > Cs > Na > Li

26. Which of the following compounds liberate(s) oxygen on heating?

(a) Li_2CO_3 (b) LiOH
(c) $LiNO_3$ (d) NaOH

27. When $MgCl_2.6H_2O$ is strongly heated, then it forms:

(a) MgO (b) $Mg(OH)_2$
(c) Mg(OH)Cl (d) $MgCl_2$

28. Magnesium liberates H_2 on reaction with:

(a) dil. HCl
(b) dil. H_2SO_4
(c) very dil. HNO_3
(d) all of these

29. Calcium hydride on hydrolysis forms:

(a) $CaO + H_2$
(b) $Ca(OH)_2$ only
(c) $Ca(OH)_2 + H_2$
(d) Only CaO

30. Which one on reaction with NaOH solution gives inflammable gas?

(a) S (b) Zn
(c) NH_4Cl (d) I_2

31. Which of the following is the most important factor in making lithium metal, the strongest reducing agent?

(a) Ionization energy
(b) Hydration energy
(c) Heat of sublimation
(d) None of these

32. Compound having highest melting point:

(a) LiCl (b) CsCl
(c) NaCl (d) KCl

33. The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to:

(a) Ionic nature of lithium fluoride
(b) High lattice enthalpy of lithium and fluoride ion
(c) High hydration enthalpy of lithium ion
(d) Low ionisation enthalpy of lithium atom

34. Which of the following compound is consumed during the preparation of Na_2CO_3 by Solvay's Process?

(a) $NH_3 + CaCO_3 + NaCl$
(b) $NH_4Cl + CaO + NaCl$
(c) $CaCO_3 + NaCl$
(d) $NaCl + NH_4HCO_3$

35. Select the correct statement:

(a) Be and Al show diagonal relationship
(b) Be forms tetrahedral complexes $[Be(C_2O_4)_2]^{2-}$
(c) Al forms AlF_6^{-3}, an octahedral complex
(d) All are correct statements

LEVEL II

1. When a mixture of ammonium sulphate and 50% H_2SO_4 is electrolysed the products formed at anode and cathode are:

(a) H_2 and H_2O_2
(b) $(NH_4)_2S_2O_8$ and H_2
(c) H_2 and NH_4HSO_4
(d) H_2O_2 and H_2

2. When H_2O_2 is added to ice cold solution of acidified potassium dichromate containing ether. The contents are shaken and allowed to stand then

(a) a blue colour is obtained in ether due to formation of $Cr_2(SO_4)_3$
(b) a blue colour is obtained in ether due to formation of CrO_5
(c) CrO_3 is formed which dissolves in ether to give blue colour
(d) Chromyl chloride is formed.

3. Which of the following species is reduced by H_2O_2?

(a) $[Fe(CN_6)]^{4-}$
(b) $[Fe(CN_6)]^{3-}$ in alkaline medium
(c) NO_2^-
(d) I^-/HCl

4. Which of the following on oxidation gives H_2O_2?

(a) 2-Ethylanthraquinol
(b) 2-Ethylanthraquinone
(c) Anthracene
(d) 2-Ethylanthracene

5. One of the following is an incorrect statement. Point out the incorrect one:

(a) Hardness of water depends upon its soap consuming power

(b) Temporary hardness is due to bicarbonates of calcium and magnesium

(c) Permanent hardness is due to soluble sulphates and chlorides of Ca and Mg

(d) Permanent hardness can be removed by boiling water.

6. Incorrect statement about ortho and para hydrogen:

(a) Para hydrogen is present in pure state at low temperature (zero kelvin)

(b) The ratio of ortho : para hydrogen at room temperature is 3:1

(c) Entropy of ortho hydrogen is more than para hydrogen at high temperature.

(d) 100% pure ortho hydrogen may be obtained at high temperature

7. Which of the following is an incorrect statement for heavy water?

(a) It is used as moderator in nuclear reactor

(b) It gives deuteromathane when react with Al_4C_3

(c) Ionic compounds are more soluble in D_2O than in H_2O

(d) Bond energy of D_2O is higher than that of H_2O

8. In which of the following reaction hydrogen peroxide is a reducing agent?

(a) $2FeCl_2 + 2HCl + H_2O_2 \rightarrow 2FeCl_3 + 2H_2O$

(b) $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$

(c) $HI + H_2O_2 \rightarrow 2H_2O + I_2$

(d) $H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$

9. Which one of the following removes temporary hardness of water?

(a) Slaked lime

(b) Plaster of Paris

(c) $CaCO_3$

(d) Hydrolith

10. Which physical constant for H_2O has higher magnitude than D_2O?

(a) Boiling point

(b) Temperature of maximum density

(c) Dielectric constant

(d) Bond dissociation energy

11. Identify incorrect statement regarding H_2O_2:

(a) It can be prepared by acidifying BaO_2 and hydrolyzing $H_2S_2O_8$ and H_2SO_5.

(b) It is thermodynamically stable.

(c) It has non planar structure.

(d) It is oxidizing as well as reducing agent.

12. In which of the following method of the removal of hardness, Ca^{+2} and Mg^{2+} are not separated from sample of hard water?

(a) By boiling of temporary hard water

(b) Addition of sodium carbonate

(c) Using sodium hexametaphosphate

(d) Synethetic resins and zeolite method.

13. Which of the following statement is not correct regarding the diagonal relationship between Al and Be?

(a) BeO and Al_2O_3 are amphoteric in nature.

(b) Al_4C_3 and Be_2C give same gas on hydrolysis.

(c) Both can from complexes with same maximum co-ordination.

(d) Both form electron deficient and covalent hydride.

14. $A+H_2O \rightarrow NaOH$

$B+H_2O \rightarrow NaOH+O_2$; A and B are respectively:

(a) Na_2O_2 and Na_2O

(b) Na_2O and Na_2O_2

(c) NaO_2 and Na_2O_2

(d) Na_2O and NaO_2

15. Which of the following pair of metal form nitride on reaction with Nitrogen?

(a) Li, Mg (b) Mg, Na

(c) Al, K (d) Al, Na

16. Which gas responsible for leaving holes in cakes or pastries and making them light and fluffy?

(a) O_2 (b) CO_2

(c) H_2 (d) CH_4

17. When sodium is placed in moist air, finally change into:

(a) NaOH (b) Na_2O_2

(c) Na_2O (d) Na_2CO_3

18. Which of the following statement is not correct?

(a) $AlCl_3$ is soluble in excess NaOH and form soluble complex.

(b) $LiHCO_3$ is not found in solid state.
(c) K_2O_2 is diamagnetic but KO_2 is paramagnetic.
(d) Hydrated $MgCl_2$ gives anhydrous $MgCl_2$ on heating in dry air.

19. Which of the following statement is not correct?
(a) BeF_2 forms complex ion with NaF in which Be goes with cation.
(b) $BeCO_3$ is kept in the atmosphere of CO_2 since it is least thermally stable.
(c) Be dissolves in alkali forming $[Be(OH)_4]^{-2}$.
(d) BeH_2 can exist as planar dimer in vapour state.

20. CO_2 gas along with solid Y is obtained when sodium salt X is heated, X is again obtained when CO_2 gas is passed into aqueous solution of Y. X and Y are:
(a) Na_2CO_3, Na_2O
(b) Na_2CO_3, NaOH
(c) $NaHCO_3$, Na_2CO_3
(d) Na_2CO_3, $NaHCO_3$

21. Which of the following statement is not correct?
(a) Lithium halide are most covalent among alkali metal halides.
(b) Li_2O is more thermal stable than Li_2CO_3.
(c) Except Be halides, all other halides of II A metals are ionic in nature.
(d) Charge and size ratio for Be^{+2} and Al^{+3} is nearly same.

22. $NH_3 + H_2O + CO_2 \rightarrow A$;
$A + H_2O + CO_2 \rightarrow B$
$B + NaCl \rightarrow C + NH_4Cl$;
$C \rightarrow D + H_2O + CO_2$.
Which of the following is incorrect statement?
(a) A is $(NH_4)_2CO_3$
(b) D is Na_2CO_3
(c) C is $NaHCO_3$
(d) B is $(NH_4)_2C_2O_4$

23. When powered Be is heated with air, it form A and B. Compound A gives C after reductive chlorination. C produces white fumes in presence of moisture and forms D. Then A, B, C and D, respectively, are:
(a) BeO, Be_3N_2, $BeCl_2$, $Be(OH)_2$
(b) Be_3N_2, BeO, $BeCl_4^{-2}$, $Be(OH)_2$
(c) BeO, $Be(OH)_2$, Be_3N_2, $BeCl_2$
(d) BeO, Be_3N_2, Be, $Be(OH)_2$

24. A solid compound X on heating gives CO_2 gas and a residue. The residue mixed with water forms Y on passing an excess of CO_2 through Y in water, a clear solution, Z is obtained. On boiling Z compound X is reformed. The compound X is:
(a) $CaCO_3$ (b) Na_2CO_3
(c) K_2CO_3 (d) $Ca(HCO_3)_2$

25. Select the incorrect choice:
(a) Solubility of alkaline earth metal's carbonates, sulphates and chromates decreases from Be to Ba.
(b) Solubility of alkaline earth metal's hydroxides is less than alkali metal hydroxides.
(c) Solubility of alkaline earth Metal's oxides decreases from Be to Ba.
(d) SO_2 on passing in lime water turns lime water milky.

26. Which of the following statement is not correct?
(a) All alkali-metal salts impart a characteristic colour to the Bunsen flame.
(b) The correct order of increasing thermal stability of the carbonates of alkali metals is $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$.
(c) Among the alkali metal's cesium is the most reactive
(d) The reducing character of the alkali metal hydrides follow the order:
LiH > NaH > KH > RbH > CsH.

27. Identify the product A,B,C,D of reaction sequence respectively:

$$\text{X}\quad NaCl \rightarrow A + B + Cl_2$$
$$\downarrow Al$$
$$NaAlO_2 + B_{(g)}$$
$$\text{Y}\quad A + Cl_2 \rightarrow C + D + H_2O$$

(a) NaOH, NaCl, NaClO, H_2O
(b) Na_2CO_3, H_2, NaCl, $NaClO_3$
(c) NaOH, H_2, NaCl, $NaClO_3$
(d) Na, H_2, $NaClO_3$, NaCl

28. Which of the following metal, on burning in moist air, does not give smell of ammonia?
(a) Mg (b) Ca
(c) K (d) Li

29. Mg_2C_3 reacts with water forming propyne gas. C_3^{4-} ions has:
(a) Two sigma and two pi bonds
(b) Three sigma and one pi bond
(c) Two sigma and one pi bond
(d) Two sigma and three pi bonds

30. The fluoride which is most soluble in water is:
(a) CaF_2 (b) BaF_2
(c) SrF_2 (d) BeF_2

31. Amongst the following hydroxides, the one which has the highest value of Ksp at ordinary temperature?
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Ba(OH)_2$

32. At high temperature, nitrogen combines with CaC_2 to give:
(a) Calcium cyanide
(b) Calcium cyanamide
(c) Calcium carbonate
(d) Calcium nitride

33. Which metal bicarbonates does not exist in solid state?
(i) $LiHCO_3$ (ii) $Ca(HCO_3)_2$
(iii) $Zn(HCO_3)_2$ (iv) $AgHCO_3$
(a) i, ii, iii, iv (b) i, ii, iii
(c) i, ii, iv (d) ii, iii, iv

34. The reaction of sodium highly exothermic with water. The rate of reaction is lowered by:
(a) Lowering the temperature
(b) Mixing with alcohol
(c) Mixing with acetic acid
(d) Making an amalgam

35. The alkali metals dissolve in liquid NH_3, it is found that:
(a) The dilute solution are blue but the colour changes to bronze with increasing concentration.
(b) The blue solutions is due to the presence of solvated electrons.
(c) The blue solutions are paramagnetic but the bronze coloured solutions are diamagnetic.
(d) All the facts given above are found.

LEVEL III

ONE OR MORE THAN ONE CORRECT TYPE

1. The reagent(s) used for softening the temporary hardness of water is (are):
(a) $Ca_3(PO_4)_2$ (b) $Ca(OH)_2$
(c) Na_2CO_3 (d) NaOCl

2. The oxidation states of the most electronegative element in the products of the reaction between BaO_2 with dilute H_2SO_4 are:
(a) -1 (b) +1
(c) -2 (d) 0

3. Which of the following reaction(s) is/are correct?
(a) $Cl_2 + NaOH \rightarrow NaCl + NaClO_3 + H_2O$
(b) $P_4 + NaOH + H_2O \rightarrow NaH_2PO_2 + PH_3$
(c) $S + NaOH \xrightarrow{\Delta} Na_2S_2O_3 + Na_2S + H_2O$
(d) $Si + NaOH \xrightarrow{\Delta} Na_2SiO_3 + H_2$

4. Which of the following is/are correct?
(a) Sodium thiosulphate is called hypo.
(b) Sodium peroxide is called oxone.
(c) Potassium carbonate is called pearl ash.
(d) Sodium nitrate is called Indian nitre.

5. Which of the following is/are found in the solid state?
(a) $LiHCO_3$ (b) $KHCO_3$
(c) $NaHCO_3$ (d) NH_4HCO_3

6. Which of the following compound(s) will impart a golden yellow colour to the Bunsen flame?
(a) KCl (b) K_2CO_3
(c) NaCl (d) Na_2CO_3

7. Nitrogen dioxide cannot be obtained by heating:
(a) KNO_3 (b) $NaNO_3$
(c) $AgNO_3$ (d) $Cu(NO_3)_2$

8. Which of the following metals dissolve in liquid ammonia?
(a) Sr (b) Ca
(c) Ba (d) Be

9. In which of the following, hydration enthalpy is greater than the lattice enthalpy?
(a) $BaSO_4$ (b) $BaCO_3$
(c) Na_2SO_4 (d) Na_2CO_3

PASSAGE BASED QUESTIONS

Passage # 1 (Q. 10 and 11)

Hydrogen peroxide is a powerful oxidizing agent, both in the acidic and alkaline medium.

In acidic medium: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

In alkaline medium: $H_2O_2 + 2e^- \rightarrow 2^-OH$

Hydrogen peroxide acts as a reducing agent towards powerful oxidizing agents.

In acidic medium: $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$

In alkaline medium, however, its reducing nature is more effective.

$H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^-$

10. On addition of H_2O_2 to acidified $KMnO_4$, $KMnO_4$ gets decolourised due to:
(a) Oxidation of $KMnO_4$
(b) Reduction of $KMnO_4$
(c) Both oxidation and reduction
(d) None of the above of $KMnO_4$

11. H_2O_2 behaves as a bleaching agent due to:
(a) Oxidizing nature
(b) Reducing nature
(c) Acidic nature
(d) Unstable nature

Passage # 2 (Q. 12 to 14)

Red hot coke + Steam $\xrightarrow{1000^{\circ}c}$ (X) $\xrightarrow[500^{\circ}c \text{ catalyst (y)}]{\text{Steam}}$ (Z) + H_2.

12. 'X' is:
(a) Water gas (b) Producer gas
(c) Coal gas (d) Oil gas

13. Catalyst 'Y' is:
(a) V_2O_5 (b) Cr_2O_3
(c) Fe_2O_3 (d) $Fe_2O_3 + Cr_2O_3$

14. 'Z' is removed by passing the gaseous mixture through
(a) acidic solution
(b) alkaline solution
(c) water under high pressure of 25 atm
(d) an organic solvent

Passage # 3 (Q. 15 and 16)

On exposure to air, alkali metals get tarnished due to formation of oxides, hydroxides and carbonates on their surface. When heated in air or oxygen they burn vigorously forming different types of oxides depending upon the nature of the metal.

The formation and stability of these metals can be explained on the basis of size of alkali metal ion and the anion. Peroxides are colourless, while superoxides are coloured. The normal oxides are basic while peroxides and superoxides. Act as oxidizing agents.

15. On heating in excess of oxygen, lithium gives:
(a) Li_2O (b) LiO
(c) Li_2O_2 (d) LiO_2

16. On heating excess of oxygen, potassium gives:
(a) K_2O (b) KO
(c) K_2O_2 (d) KO_2

Passage # 4 (Q. 17 and 18)

According to Fajan's rules, the percentage of covalent character in an ionic compound increases if the cation is highly charged or small in size and the anion is large or cation has pseudo inert gas configuration. As a result of the increased covalent character, solubility in less polar solvent increases and the melting point decreases.

17. Which of the following has the lowest melting point?
(a) KCl (b) LiCl
(c) CsCl (d) RbCl

18. The correct order of increasing ionic character is:
(a) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
(b) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
(c) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
(d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

INTEGER VALUE TYPE QUESTIONS

19. What is the sum of protons, electrons and neutrons in the lightest isotope of hydrogen?

20. How many moles of phosphine are produced when one mole of the calcium phosphide reacts with water?

21. Potassium iodide reacts with acidified $K_2Cr_2O_7$. How many moles of KI are required for one mole of $K_2Cr_2O_7$?

22. How many water molecules are associated with washing soda?

MATCH THE COLUMN TYPE QUESTIONS

23.

Column I		Column II	
A	Calgon	1.	More reactive form of hydrogen as compared to H_2
B	D_2O	2.	Open book-type structure
C	Nascent hydrogen	3.	Sodium polymetaphosphate
D	H_2O_2	4.	Heavy water

24.

Column I		Column II	
A	Sodium ion in zeolite gets exchanged with	1.	Ca^{2+}
B	Hardness	2.	Mg^{2+}
C	Temporary hardness	3.	$Ca(HCO_3)_2$
D	Permanent hardness	4.	$MgSO_4$

25.

Column I		Column II	
A	Gives CO_2 on heating	1.	Na
B	Pink-violet flame colouration	2.	Cs
C	Forms superoxide on heating With O_2	3.	K_2CO_3
D	Used in photoelectric cells	4.	$NaHCO_3$
E	Form monoxide on heating with oxygen	5.	K
F	Forms peroxide on heating with oxygen	6.	Li

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **Statement-1:** Alkali metals dissolve in liquid ammonia to give blue solutions.

   Statement-2: Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals).

   (a) Statement-1: is True, statement-2 is True; Statement-2 is a correct explanation for statement-1.

   (b) Statement-1: is True, statement-2 is True; Statement-2 is not a correct explanation for statement-1.

   (c) Statement-1 is True, statement-2 is False

   (d) Statement-1 is False, statement-2 is True

[IIT-2007]

2. The reagent(s) used for softening the temporary hardness of water is (are):

(a) $Ca_3(PO_4)_2$ (b) $Ca(OH)_2$

(c) Na_2CO_3 (d) NaOCl **[IIT-2010]**

3. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a:

(a) Reducing agent, oxidizing agent

(b) Reducing agent, reducing agent

(c) Oxidizing agent, oxidizing agent

(d) Oxidizing agent, reducing agent

[JEE Advanced - 2014]

4. A piece of magnesium ribbon was heated to redness in an atmosphere of nitrogen and on cooling water was added, the gas evolved was-

(a) Ammonia (b) Hydrogen

(c) Nitrogen (d) Oxygen

[AIEEE - 2005]

5. The ionic mobility of alkali metal ions in aqueous solution is maximum for-

(a) Rb^+ (b) Li^+

(c) Na^+ (d) K^+

[AIEEE - 2006]

6. In context with the industrial preparation of hydrogen from water gas ($CO+H_2$), which of the following is the correct statement?

(a) CO is removed by absorption in aqueous Cu_2Cl_2 solution

(b) H_2 is removed through occlusion with Pd

(c) CO is oxidized to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali

(d) CO and H_2 are fractionally separated using difference in their densities

[AIEEE - 2008]

7. The products obtained on the heating $LiNO_3$ will be-

(a) $Li_2O + NO_2 + O_2$

(b) $Li_3N + O_2$

(c) $Li_2O + NO + O_2$

(d) $LiNO_2 + O_2$

[AIEEE - 2011]

8. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water?

(a) Oxide ion accepts a pair of electrons

(b) Oxide ion donates a pair of electrons

(c) Oxidation number of oxygen increases

(d) Oxidation number of sodium decreases

[AIEEE - 2011]

9. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?

(a) $KClO_3$ (b) $CaCO_3$

(c) NH_4NO_3 (d) $NaNO_3$

[AIEEE - 2012]

10. Pure hydrogen (99.9%) can be made by which of the following processes?

(a) Mixing natural hydrocarbons of high molecular weight

(b) Electrolysis of water

(c) Reaction of slat like hydrides with water

(d) Reaction of methane with steam

[AIEEE - 2012]

11. The solubility order for alkali metal fluoride in water is-

(a) $LiF < RbF < KF < NaF$

(b) $RbF < KF < NaF < LiF$

(c) $LiF > NaF > KF > RbF$

(d) $LiF < NaF < KF < RbF$

[JEE Main Online - 2013]

12. In which of the following reactions H_2O_2 acts as a reducing agent?

(i) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

(ii) $H_2O_2 - 2e^- \rightarrow O_2 + 2H^+$

(iii) $H_2O_2 + 2e^- \rightarrow 2OH^-$

(iv) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

(a) (iii), (iv) (b) (i), (iii)

(c) (ii), (iv) (d) (i), (ii)

[JEE Main - 2014]

Answer Key

LEVEL I

1. (b) 2. (d) 3. (d) 4. (c) 5. (c) 6. (a) 7. (a) 8. (a) 9. (c) 10. (c)
11. (b) 12. (b) 13. (d) 14. (d) 15. (c) 16. (b) 17. (a) 18. (b) 19. (b) 20. (c)
21. (d) 22. (b) 23. (a) 24. (b) 25. (c) 26. (c) 27. (a) 28. (d) 29. (c) 30. (b)
31. (b) 32. (c) 33. (b) 34. (c) 35. (d)

LEVEL II

1. (b) 2. (b) 3. (b) 4. (b) 5. (d) 6. (d) 7. (c) 8. (b) 9. (a) 10. (c)
11. (b) 12. (c) 13. (c) 14. (b) 15. (a) 16. (b) 17. (d) 18. (d) 19. (a) 20. (c)
21. (c) 22. (d) 23. (a) 24. (a) 25. (c) 26. (d) 27. (c) 28. (c) 29. (a) 30. (d)
31. (d) 32. (b) 33. (a) 34. (d) 35. (d)

LEVEL III

1. (b, c, d) 2. (a, c) 3. (a, b, c, d) 4. (a, b, c) 5. (b, c, d) 6. (c, d) 7. (a, b) 8. (a, b, c)
9. (c, d) 10. (b) 11. (a) 12. (a) 13. (d) 14. (c) 15. (a) 16. (d)
17. (b) 18. (a) 19. (2) 20. (2) 21. (6) 22. (10)
23. (A → 3; B → 4; C → 1; D → 2)
24. (A → 1, 2; B → 1, 2; C → 3; D → 4)
25. (A → 4; B → 3; C → 2, 5; D → 2; E → 1,2,5, 6; F → 1)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (a) 2. (b, c, d) 3. (a) 4. (a) 5. (a) 6. (c) 7. (a) 8. (b) 9. (b) 10. (c)
11. (d) 12. (c)

Hints and Solutions

LEVEL I

1. (b) $LiH + H_2O \rightarrow LiOH + H_2$

2. (d) Highly electropositive elements (s-block metals) can form ionic hydrides.

3. (d) Isotopes have different nuclear mass.

4. (c) CaH_2 (Molten) $\rightarrow Ca^{+2} + 2H^-$

at anode:- $2H^- \rightarrow H_2\uparrow + 2e^-$

5. (c) Temporary hardness of water can be removed by adding calculated amount of $Ca(OH)_2$.

6. (a) $Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\downarrow + CO_2\uparrow + H_2O$

7. (a) $Ca + H_2 \rightarrow CaH_2$

R.A O.A

8. (a) Intermolecular interaction present in H_2 is dispersion forces.

9. (c) Adsorption of H_2 by various metals is also known as occulusion.

10. (c) In PbO_2, oxidation state of 'O' is '-2'.

11. (b) Ortho and para – hydrogen possess different physical properties but same chemical properties.

12. (b) O_3 is a stronger oxidizing agent than H_2O_2. O_3 will oxidize H_2O_2 into O_2

13. (d) Due to presence of unpaired e- in superoxide ion, they are paramagnetic, coloured and oxidizing agents.

14. (d) $Na + NH_3 \xrightarrow{\Delta} NaNH_2 + \frac{1}{2} H_2\uparrow$

15. (c) $Be + 2NaOH \rightarrow \underset{\text{water soluble}}{Na_2BeO_2} + H_2$

16. (b) Microcosmic salt is $Na(NH_4)HPO_4 . 4H_2O$

Glauber's salt is $Na_2SO_4 . 10H_2O$

17. (a) Be is less reactive s-block metal. It does not form hydride by direct heating with H_2.

18. (b) Due to high ionisation energy, salts of Be^{+2} and Mg^{+2} do not give flame test.

19. (b) In alkali metals (IA), metallic character and ionic radius increases as the atomic number rises.

20. (c) Solutions of alkali metals in liquid ammonia are paramagnetic in nature.

21. (d) $Na_2CO_3 + CO_2 + H_2O \rightarrow NaHCO_3$

(this reaction is not possible)

The actual reaction is,

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

22. (b) Order of solubility of hydroxides:-

$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

23. (a) Order of thermal stability:-

$Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

24. (b) Cause of blue colour is presence of ammoniated electron.

25. (c) Down the group, basic strength of hydroxides increases.

26. (c) $2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2\uparrow + \frac{1}{2} O_2\uparrow$

27. (a) $MgCl_2 . 6H_2O \xrightarrow{\Delta} MgO + HCl\uparrow$

28. (d) Mg displaces H_2 from acids

29. (c) $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

30. (b) $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$ (Inflammable gas)

31. (b) Li is the strongest reducing agent because Li^+ has exceptionally high hydration energy.

32. (c) Order of melting point is,

$NaCl > KCl > CsCl > LiCl$

33. (b) Both Li^+ and F^- ions are very small in size. Hence, lattice energy of LiF is very high and it has lowest solubility in water amongst alkali metal fluorides.

34. (c) Raw materials used in Solvay process are $CaCO_3$, NH_3 and NaCl but only $CaCO_3$ and NaCl are consumed during the preparation of Na_2CO_3.

35. (d) Be and Al show diagonal relationship. Maximum co-ordination number of Be is 4 while that of Al is 6.

LEVEL II

1. (b) at anode, $(NH_4)_2S_2O_8$ is formed.
at cathode, H_2 is formed.

2. (b) a blue colour is obtained due to formation of chromic peroxide, CrO_5 or $CrO(O_2)_2$.

3. (b) $[Fe(CN)_6]^{3-}$ is reduced into $[Fe(CN)_6]^{4-}$

4. (b) 2-Ethylanthraquinol on oxidation give H_2O_2

5. (d) Permanent hardness can not be removed by boiling water. Only temporary hardness can be removed by boiling water.

6. (d) 100% pure orthohydrogen can not be obtained even at high temperature.

7. (c) Ionic compounds are more soluble in polar solvents having higher value of dielectric constant. H_2O has higher dielectric constant than D_2O.

8. (b) Cl_2 acts as oxidizing agent and H_2O_2 acts as reducing agent.

9. (a)

$$\underset{\text{(Hardness)}}{Ca(HCO_3)_2} + \underset{\text{(Slaked lime)}}{Ca(OH)_2} \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

10. (c) H_2O has higher dielectric constant than D_2O.

11. (b) It is thermodynamically unstable.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

12. (c) Sodium hexametaphosphate (Calgon) forms soluble complex with Ca^{+2} and Mg^{+2}.

$$Na_2[Na_4(PO_3)_6] + 2Ca^{+2} \longrightarrow Na_2[Ca_2(PO_3)_6] + 4Na^{+}$$

13. (c) Be shows maximum co-ordination number 4 while due to pressence of vacant d-orbitals Al shows maximum co-ordination number 6.

14. (b)

$$\underset{\text{(A)}}{Na_2O} + H_2O \longrightarrow NaOH$$

$$\underset{\text{(B)}}{Na_2O_2} + H_2O \longrightarrow NaOH + O_2$$

15. (a) Na, K, Rb and Cs do not form nitride on reaction with nitrogen.

Li and Mg form nitride with nitrogen.

16. (b) In cakes or pastries, $NaHCO_3$ (baking soda) is added. During baking of cake, CO_2 gas is released which makes cake light and fluffy.

17. (d)

$$Na + O_2 \longrightarrow Na_2O$$

$$Na_2O + H_2O \longrightarrow NaOH$$

$$NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

18. (d) Hydrated $MgCl_2$ ($MgCl_2.6H_2O$) gives MgO on heating in dry air.

19. (a) $BeF_2 + 2NaF \longrightarrow Na_2[BeF_4]$
In this complex, Be present in anionic part.

20. (c) Salt (X) is $NaHCO_3$.

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{(Y)}}{Na_2CO_3} + CO_2\uparrow + H_2O$$

21. (c) Halides of Mg are also covalent.

22. (d) B is NH_4HCO_3.

23. (a)

$$Be + \text{air} \xrightarrow{\Delta} \underset{\text{(A)}}{BeO} + \underset{\text{(B)}}{Be_3N_2}$$

$$BeO + \text{chlorination} \longrightarrow \underset{\text{(C)}}{BeCl_2}$$

$$BeCl_2 + \text{moisture} \longrightarrow \underset{\text{(D)}}{Be(OH)_2}$$

24. (a)

$$\underset{\text{(X)}}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + H_2O \longrightarrow \underset{\text{(Y)}}{Ca(OH)_2}$$

$$Ca(OH)_2 + \text{excess } CO_2 \longrightarrow \underset{\text{(Z)}}{Ca(HCO_3)_2}$$

25. (c) Order of solubility :

$BeO < MgO < CaO < SrO < BaO$

26. (d) Correct order of reducing character :

$LiH < NaH < KH < RbH < CsH$

27. (c)

$$\begin{tikzcd} NaCl_{(aq)} \arrow[r, "\text{Electrolysis}"] & \underset{\text{(A)}}{NaOH} + \underset{\text{(B)}}{H_2} + Cl_2 \arrow[d, "Al"] \\ & NaAlO_2 + \underset{\text{(B)}}{H_2} \end{tikzcd}$$

$$NaOH + Cl_2 \longrightarrow NaCl + NaClO_3 + H_2O$$

28. (c) Potassium (K) does not form nitride on burrning in air.

29. (a) Structure of C_3^{4-} is,
$^{-}C \equiv C - C^{-3}$
It has 2 sigma and 2 pi bonds.

30. (d) Order of solubility in water :

$BeF_2 > BaF_2 > SrF_2 > CaF_2$

31. (d) $K_{sp} \propto$ solubility

Order of solubility :

$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

32. (b) $CaC_2 + N_2 \xrightarrow{\Delta} \underset{\text{(Calcium cyanamide)}}{CaCN_2}$

33 (a) Only bicarbonates of Na^+, K^+, Rb^+ and Cs^+ exist is solid state.

34 (d) Hg is less reactive metal. Hence, by making an amalgam the rate of reaction of Na with water is lowered.

35 (d) The alkali metals dissolve in liquid NH_3. This solution is blue coloured due to solvated electrons. As concentration of metal increases, colour changes to bronze.

LEVEL III

1.(b, c, d)

$Ca(OH)_2$ (slaked lime), Na_2CO_3 (washing soda) and NaOCl are used for softening the temporary hardness.

$NaOCl + H_2O \rightarrow NaOH + HOCl$

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$

2.(a, c) $BaO_2 + H_2SO_{4\,(dilute)} \rightarrow BaSO_4 + H_2O_2$

The most electronegative element in products is oxygen. In H_2O_2, oxidation state of 'O' is –1 and in $BaSO_4$, oxidation state of 'O' is –2.

3. (a, b, c, d)

All reactions are correct.

4. (a, b, c)

Indian nitre is potassium nitrate (KNO_3)

5. (b, c, d)

$LiHCO_3$ exists only in solution.

6. (c, d) Na^+ will impart a golden yellow colour to the Bunsen flame.

7. (a, b) Nitrates of Na^+, K^+, Rb^+ Cs^+ do not release NO_2 gas by heating.

8. (a, b, c)

In s-block, Be and Mg do not dissolve in liquid ammonia.

9.(c, d) For salts, which are soluble in water, hydration enthalpy is greater than the lattie enthalpy.

Na_2SO_4 and Na_2CO_3 are soluble in water.

10. (b) With H_2O_2, $KMnO_4$ behaves as oxidising agent.

11. (a) H_2O_2 behaves as a bleaching agent due to its oxidizing nature.

12. (a) Red hot coke + steam $\xrightarrow{\Delta} \underset{\text{(X)}}{\underbrace{CO + H_2}_{\text{Water gas}}}$

$$\xrightarrow[\text{Catalyst}]{\text{Steam}} \underset{\text{(Z)}}{CO_2 + H_2}$$

13. (d) Catalyst 'Y' is $Fe_2O_3 + Cr_2O_3$

14. (c) CO_2 is removed by passing the gaseous mixture through water under high pressure of 25 atm.

$CO_2 + H_2O \longrightarrow H_2CO_3$

15. (a) $Li + O_{2(excess)} \xrightarrow{\Delta} Li_2O$

16. (d) $K + O_{2(excess)} \xrightarrow{\Delta} KO_2$

17. (b) Order of melting point:

$KCl > RbCl > CsCl > LiCl$

18. (a) Covalent character $\propto$ polarising power of cation.

Order of ionic character is reverse of order of covalent character.

19. Lightest isotope of hydrogen is protium. It has 1 proton, 1 electron and zero neutron.

20. $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

1 mole 2 moles

21. $K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow Cr_2(SO_4)_3 + 3I_2 + 7H_2O + 4K_2SO_4$

1 mole 6 moles

22. Washing soda is $Na_2CO_3.10H_2O$

23. (A →3; B →4 ; C →1; D → 2)

24. (A →1, 2; B →1, 2 ; C →3; D →4)

25. (A →4; B →3 ; C →2, 5 ; D →2 ; E →1, 2, 5, 6; F →1]

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (b) Both statements are correct but blue colour is due to presence of solvated e^-.

2. (b, c, d)

$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$

$Na_2CO_3 + Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + 2NaHCO_3$

$NaOCl + H_2O \longrightarrow NaOH + HOCl$

$OH^- + HCO_3^- \longrightarrow CO_3^{-2} + H_2O$

3. (a) $\overset{+7}{KIO_4} + \underset{\text{Reducing agent}}{H_2O_2} \rightarrow \overset{+5}{KIO_3} + H_2O + O_2$

$\overset{-1}{NH_2}OH + \underset{\text{Oxidizing agent}}{H_2O_2} \rightarrow \overset{+3}{N_2}O_3 + H_2O$

4. (a) $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$

$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$

5. (a) Hydrated ion of Rb^+ is smallest among these four.

6. (c) $CO + H_2 \xrightarrow{\text{Steam, Catalyst}} \underset{\substack{\downarrow \\ \text{absorption in alkali}}}{CO_2} + H_2$

7. (a) $2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2\uparrow + \frac{1}{2}O_2\uparrow$

8. (b) $Na_2O + H_2O \longrightarrow 2NaOH$

$O^{-2} + H^+ \longrightarrow OH^-$

Oxide ion (O^{-2}) donates a pair of electrons

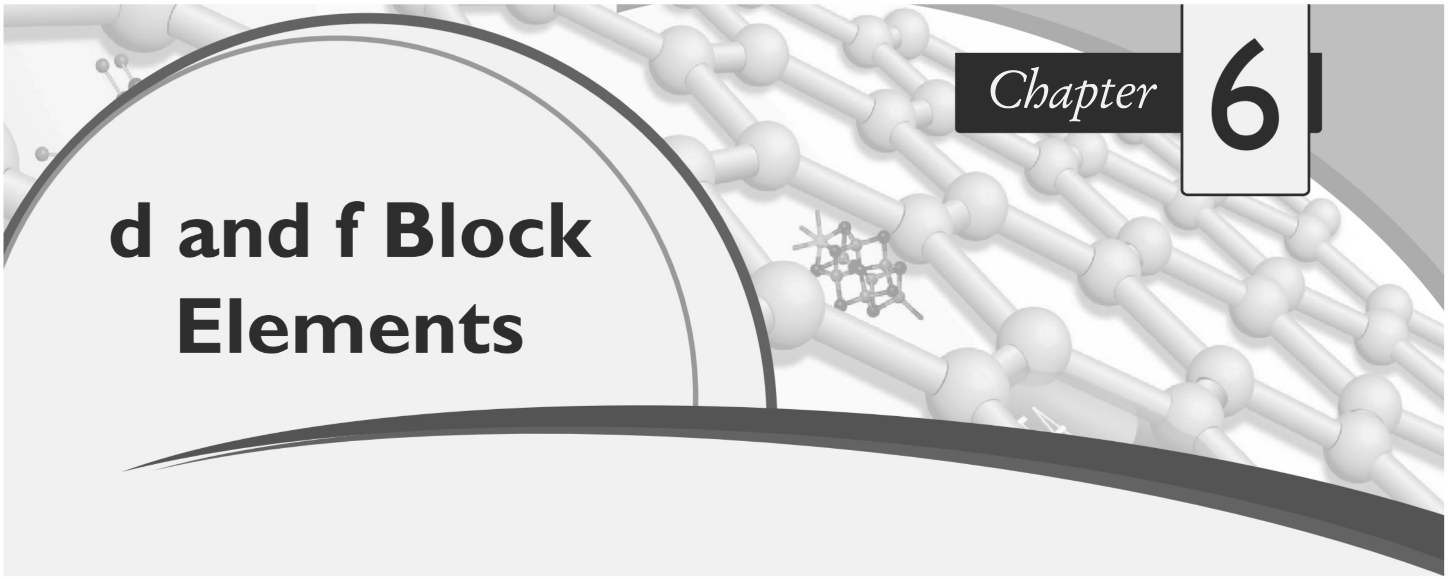
9. (b) $CaCO_3 \xrightarrow{\Delta} \underset{\text{(Basic)}}{CaO} + \underset{\text{(acidic)}}{CO_2}$

10. (c) $NaH + H_2O \longrightarrow NaOH + H_2\uparrow$

11. (d) Order of solubility in water:

LiF < NaF < KF < RbF

12. (c) Removal of e^- is known as oxidation.



Chapter 6

d and f Block Elements

Key Concepts

TRANSITION ELEMENTS

- The elements lying in the middle of the periodic table between group 2 and group 13 are known as d-block elements.
- These d-block elements are called transition elements because they exhibit transitional behaviour between s-block and p-block elements.
- Depending upon the subshell (3d, 4d, 5d) involved, transition elements are mainly classified into three series.
  1. First transition series or 3d series.
  2. Second transition series or 4d series.
  3. Third transition series or 5d series.

Outer electronic configuration of the transition elements

3d-series or I transition series:-

Atomic number	21	22	23	24	25	26	27	28	29	30
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

4d-series or II transition series:-

Atomic number	39	40	41	42	43	44	45	46	47	48
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

5d-series or III transition series:-

Atomic number	57	72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Properties of transition elements

1. **Metallic character:-** All the transition elements are metallic in nature and nearly all of them have simple hcp, ccp or bcc lattices. Due to their greater effective nuclear charge and the large number of valence electrons, the metallic bond is quite strong and hence they are hard, posses high densities and high enthalpies of atomization.
2. **Oxidation states:-** Transition elements exhibit variable oxidation state due to the participation of ns as well as (n –1) d electrons.

   Except scadium, the most common oxidation state of the first row (3d series) elements is +2 which arises from the loss of two 4s electrons, which means that after scandium, d-orbital become stable than s-orbital.

   In the +2 and +3 oxidation states, bond formed are generally ionic while in higher oxidation states the bond formed are essentially convalent. For example in MnO_4^-, CrO_4^{2-}, etc. the bond formed between metal and oxygen are covalent.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					(+1)	
	+2	+2	+2	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)
(+3)	(+3)	(+3)	(+3)	+3	(+3)	(+3)	(+3)		
	(+4)	+4	+4	+4	+4	+4	+4		
		(+5)	+5	+5					
			(+6)	+6	+6				
				(+7)					

Oxidation states of the first row of transition metals (the most common ones are in circles)

3. **Complex formation (complexation):-** Transition metal ions form variety of complex due to the following reasons:
   (i) Small size and high nuclear charge
   (ii) Availability of vacant d-orbital of suitable energy, which can accept lone pair of electrons donated by the molecule or ion (ligand).
4. **Magnetic Properties:-** Two types of magnetic behaviour are found in substances diamagnetism and paramagnetism. Paramagnetic substances are attracted by the magnetic field and weigh more while the diamagnetic substances are slightly repelled by the magnetic field and weight less.

   As the transition metal ions generally contain one or more unpaired electrons in them and hence their complexes are generally paramagnetic. Paramagnetic character increases with increase in number of unpaired electrons. Paramagnetism is expressed in terms of magnetic moment.

   $\mu = \sqrt{n(n+2)}$ BM (Bohr magneton)

   n – number of unpaired electrons

   More the magnetic moment, more will be the paramagnetic character.
5. **Formation of Alloys:-** As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.
6. **Interstitial compound:-** Transition metal form number of interstitial compounds, in which they take up atoms of small size, e.g., H, C and N in the vacant spaces in the their lattices. The presence of these atoms results in decrease in ductility and malleability of the metals but increases their tensile strength.
7. **Catalytic properties:-** Transition metals and their compounds are known to act as a good catalyst due to the following reasons:
   (i) Due to their variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (intermediate compound formation theory).
   (ii) In some cases the finely divided metal or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact (Adsorption theory).
8. **Ionization energy:-** The ionization energies of transition elements are higher than those of S-block elements but lower than p-block elements.
   - In a particular transition series, ionization energy increases gradully as we move from left to right, and it is due to the increase in nuclear charge.
   - Further the magnitudes of ionization energies provide an indication of the energy needed to raise the metal to a particular oxidation state in a compound. From the knowledge of values of ionization energies of the metal it is possible to rationalize the relative stabilities of various oxidation state.
   - Ni(II) compounds are thermodynamically more stable than Pt(II) compounds, on the other hand Pt(IV) compounds are more stable than Ni(IV) compounds. It is due to that sum of first four ionization energies is less for platinum whereas sum of the first two ionization energies is less for nickel.
9. **Coloured compounds:-** Compounds of transition elements are usually coloured due to the promotion of an electron from one d-orbital to another by the absorption of visible light. It can be clearly explained as follows:

   In the transition elements which have partly filled d-orbitals, the transition of electron can take from one of the lower d-orbitals to some higher d-orbital within the same subshell. The energy required for this transition falls in the visible region. So when white light falls on these complexes they absorb a particular colour from the radiation for the promotion of electron and the remaining colours are emitted. The colour of the complex is due to this emitted radiation.

   A few of the transition metal ions such as Cu^+, Ag^+, Sc^{3+} are colourlesss. In these ions, the d-orbital are either completely filled or empty.

Oxides, chlorides and sulphates of Iron, copper and Zinc

(A) Ferric Oxide, Fe_2O_3

Preparation:

1. In lab, it can be prepared by heating ferrous sulphate or ferric hydroxide.

$$2\,FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow\ + SO_3\uparrow$$

$$2Fe\,(OH)_3 \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3\uparrow$$

2. $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$

3. Hydrolysis of $FeCl_3$ actually gives a red-brown gelatinous precipitute of the hydrous oxide $Fe_2O_3(H_2O)_n$ which on heating at 200°C gives red-brown Fe_2O_3 (which occurs as the mineral haematite).

Properties:

1. It is reddish brown powder, insoluble in water but soluble in acid. Amphoteric in nature and reacts with acids and alkalies.

$$Fe_2O_3 + 6HCl \longrightarrow 2\,FeCl_3 + 3H_2O$$

$$Fe_2O_3 + Na_2CO_3 \longrightarrow \underset{\text{Sodium ferrite}}{2NaFeO_2} + CO_2$$

$$Fe_2O_3 + 2NaOH \longrightarrow 2NaFeO_2 + H_2O$$

2. It liberates oxygen at 1300° C.

$$6Fe_2\,O_3 \xrightarrow{1300°C} 4Fe_3O_4 + O_2$$

3. It is reduced to Fe as:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

(B) Zinc Oxide (ZnO)

Preparation:

1. It is prepared by burning zinc metal in air or by heating the zinc carbonate, zinc nitrate or zinc hydroxide.

$$2Zn + O_2 \longrightarrow 2ZnO$$
$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$
$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$
$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

2. $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

Properties:

1. It is a white, light powder insoluble in water and known as philospher's wool. On heating it becomes yellow and on cooling it becomes white (this is due to change in the structure of lattice).

2. It is reduced to Zn by the reaction of charcoal or dry H_2.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$
$$ZnO + C \longrightarrow Zn + CO$$

3. It dissolves readily in mineral acids forms the corresponding salts and with alkalies, it forms zincates $[Zn\,(OH)_4]^{2-}$ or $ZnO_2^{\,2-}$.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
$$ZnO + 2NaOH + H_2O \longrightarrow Na_2\,[Zn(OH)_4]$$
$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

(C) Ferric chloride ($FeCl_3$)

Preparation:

1. Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron filling

$$2Fe + 3Cl_2 \xrightarrow{\Delta} Fe_2Cl_6 \text{ or } 2FeCl_3$$

(anhydrous)

2. Hydrated $FeCl_3.6H_2O$ can be prepared by dissolving iron in aqua regia or iron oxide in hydrochloride acid then the crystallization of the solution.

$$2Fe + 4HCl + Cl_2 \longrightarrow 2FeCl_3 + 2H_2$$
$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

Properties:

1. Anhydrous $FeCl_3$ is deep red-black flaky crystals but hydrated $FeCl_3.6H_2O$ is yellowish brown, deliquescent solid, soluble in water, alcohol and ether.

2. It dissociates on heating above 973 K first into $FeCl_3$ and then into $FeCl_2$ and Cl_2

$$Fe_2Cl_6 \xrightarrow{973\,K} FeCl_3 \xrightarrow{\Delta} FeCl_2 + Cl_2\uparrow$$

3. Its aqueous solution is acidic in nature due to hydrolysis.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

4. Fe^{3+} solution gives deep blue ppt. of Prussian blue with $K_4[Fe(CN)_6]$, potassium ferrocyanide:

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + 3KCl$$

5. $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$ (oxidizing)

6. Fe^{3+} solution gives blood red colour with SCN^- ions:

$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$

(D) Zinc Chloride, ($ZnCl_2.2H_2O$)

Preparation:

1. $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

$$ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + CO_2 + H_2O$$

$$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$$

The solution on concentration and cooling give hydrated zinc chloride crystals $ZnCl_2.2H_2O$.

2. Anhydrous $ZnCl_2$ is obtained by heating zinc in the atmosphere of dry Cl_2 or Dry HCl gas.

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

3. Anhydrous $ZnCl_2$ can also be formed by distilling zinc powder with mercuric chloride.

$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$$

Properties:

1. Anhydrous zinc chloride is white solid, deliquescent and soluble in water. It melts at 660° and boils at 730°C.
2. Hydrated $ZnCl_2$ on heating from zinc hydroxychloride or zinc oxychloride.

$$ZnCl_2.2H_2O \longrightarrow Zn(OH)\,Cl + HCl + H_2O$$

$$2ZnCl_2.2H_2O \longrightarrow \underset{\text{Zinc oxychloride}}{Zn_2OCl_2} + 2HCl + 3H_2O$$

3. $4ZnCl_2 + 4Na_2CO_3 + 3H_2O \longrightarrow ZnCO_3.3Zn(OH)_2 + 8NaCl + 3CO_2$

$$ZnCl_2 + 2NaHCO_3 \longrightarrow ZnCO_3 + 2NaCl + H_2O + CO_2$$

4. $ZnCl_2 + 4NH_3 \longrightarrow ZnCl_2.4NH_3$

(E) Ferrous sulphate ($FeSO_4.7H_2O$) or green vitriol

Preparation:

1. It is prepared by the action of dil. H_2SO_4 on iron.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

This should be mode in a reducing atmosphere in order to prevent the oxidation of Fe^{2+} into Fe^{3+}.

2. $FeCO_3 + H_2SO_4 \longrightarrow FeSO_4 + H_2O + CO_2$
3. $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ (kipp's apparatus)

Properties:

1. It is pale green crystalline solid, soluble in water. It turns brown due to oxidation into the ferric compound by atmospheric oxygen.
2. It is an efflorescent substance, and in isomorphous with Epson salt ($MgSO_4.7H_2O$) and white vitriol ($ZnSO_4.7H_2O$).
3. On heating, green $FeSO_4$ $7H_2O$ gives a white anhydrous salt. On strong heating it forms Fe_2O_3, SO_2 and SO_3.

$$FeSO_4.7H_2O \xrightarrow{\Delta} \underset{\text{White}}{FeSO_4} + 7H_2O$$

$$2FeSO_4 \xrightarrow{\Delta} \underset{\text{Brown}}{Fe_2O_3} + SO_2\uparrow + SO_3\uparrow$$

4. $FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr salt)
5. Aqueous solution of $FeSO_4$ is acidic due to hydrolysis of Fe^{2+}:

$$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

6. Acidified MnO_4^- and $Cr_2O_7^{2-}$ oxidize Fe^{2+} to Fe^{3+}.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(F) Copper sulphate($CuSO_4.5H_2O$) or Blue vitriol

Preparation:

1. It is prepared by dissolving copper (II) oxide or copper (II) carbonate in dil Sulphuric acid.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow Cu\ SO_4 + CO_2 + H_2O$$

On evaporation, solution is concentrated, blue crystal of $CuSO_4.5H_2O$ separate out on cooling.

2. On a large scale, copper (II) sulphate is obtained by passing air through a hot mixture of copper and dil H_2SO_4

$$2Cu + 4H^+ + O_2 \longrightarrow 2Cu^{2+} + 2H_2O$$

3. $CuFeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4$

Properties:

1. On heating $CuSO_4$. $5H_2O$ looses water molecules as follows.

$$CuSO_4.5H_2O \xrightarrow{373\,K} CuSO_4.H_2O \xrightarrow{432\,K} CuSO_4 \xrightarrow[\text{heating}]{\text{strong}} CuO + SO_3$$

2. $CuSO_4 + 6NH_4OH \longrightarrow \underset{\text{Schweitzer's reagent}}{[Cu(NH_3)_4](OH)_2} + (NH_4)_2SO_4 + 4H_2O$
3. $2CuSO_4 + 4KI \longrightarrow Cu_2I_2\downarrow + I_2\uparrow + 2K_2SO_4$ (CuI is not formed)
4. A mixture of copper sulphate and lime, under the name of Bordeaux mixture is used as fungicide in agriculture.

5. $2CuSO_4 + 2KSCN + SO_2 + 2H_2O \longrightarrow 2CuSCN\downarrow + K_2SO_4 + 2H_2SO_4$

(G) Zinc sulphate: $ZnSO_4.7H_2O$ (white vitriol)

Prepareation:

1. It is prepared by the action of dil. H_2SO_4 on Zn metal or its oxide or carbonate

$$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$$

$$2ZnS + 3.5O_2 \xrightarrow{\Delta} ZnO + ZnSO_4 + SO_2$$

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

Properties:

1. It is highly soluble in water. The solution is acidic in nature due to hydrolysis.

$$ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4$$

2. $ZnSO_4.7H_2O \xrightarrow[\Delta]{100°C} ZnSO_4.6H_2O \xrightarrow[\Delta]{280°C} ZnSO_4$

3. $ZnSO_4 \xrightarrow{760°C} ZnO + SO_3$

4. It is isomorphous with Epsom salt and green vitriol.

(H) Silver Nitrate, $AgNO_3$ (Lunar Caustic):-

Preparation:

1. It is prepared by dissolving the metal in dilute nitric acid and crystallizing the solution

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO\uparrow$$

Properties:

1. It is a colourless crystalline solid, soluble in water and alcohol; melting point 212°C.
2. On heating, it gives metallic silver and nitrogen dioxide.

$$2AgNO_3 \xrightarrow[450°C]{\Delta} 2Ag + 2NO_2 + O_2$$

3. It reacts with iodine in two ways

$$5AgNO_3 + 3I_2\,(\text{excess}) + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$$

$$6AgNO_3\,(\text{excess}) + 3I_2 + 3H_2O \longrightarrow AgIO_3 + 5AgI + 6HNO_3$$

4. It gives turbidity with tap water (Cl^-) and turbidity is soluble in NH_4OH.

$$\underset{\text{tap water}}{AgNO_3 + Cl^-} \longrightarrow \underset{\text{turbidity}}{AgCl\downarrow} + NO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(soluble)}}{Ag(NH_3)_2Cl} + 2H_2O$$

5. When treated with alkali, it gives precipitate of silver oxide, which dissolves in excess of NH_4OH.

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Brown ppt.}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O\downarrow + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

6. Ammonical $AgNO_3$ is called Tollen's reagent and is used to identify reducing sugars (including aldehydes). It is called silver mirror test of aldehydes and reducing sugar (like glucose, fructose).
7. It dissolves in excess of KCN:

$$AgNO_3 + KCN \longrightarrow \underset{\text{White ppt.}}{AgCN} + KNO_3$$

$$AgCN + KCN \longrightarrow \underset{\text{Soluble potassium argentocyanide}}{K[Ag(CN)_2]}$$

(I) Silver (I) oxide (Ag_2O)

Preparation:

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O$$

Properties:

1. It is brownish powder, insoluble in water, thermally unstable and soluble in aqueous ammonia.
2. It decomposes to silver and oxygen.

$$2Ag_2O \longrightarrow 4Ag + O_2$$

(J) Silver thiosulphate ($Ag_2S_2O_3$)

Preparation:

1. With $Na_2S_2O_3$,

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{white ppt.}}{Ag_2S_2O_3\downarrow} + 2NaNO_3$$

$$2AgBr + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3\downarrow + 2NaBr$$

Properties:

1. $Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow \underset{\text{sodium argentothiosulphate}}{2Na_3[Ag(S_2O_3)_2]}$

(K) Potassium Dichromate ($K_2Cr_2O_7$)

Preparation:

1. It is prepared from chromite ore ($FeCr_2O_4$)

$$4FeCr_2O_4 + 16NaOH + 7O_2(\text{air}) \longrightarrow \underset{\text{Sodium chromate}}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$$

Or, $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$$2Na_2CrO_4 + \text{dil. } H_2SO_4 \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties:

1. It is orange-red crystalline compound having melting point 670 K.
2. It is moderately soluble in cold water but readily soluble in hot water.
3. $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2\uparrow$

   Potassium chromate chromic acid
4. $$\underset{\text{chromate (yellow)}}{2CrO_4^{2-}} + 2H^+ \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\text{Hydrogen chromate}}{2HCrO_4^-} \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\text{dichromate (orange)}}{Cr_2O_7^{2-}} + H_2O$$
5. Action with HCl:

   $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$

   Chlorine
6. Chromyl chloride Test (This is the test of chloride):

   $K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

   chromyl chloride

   $4NaOH + CrO_2Cl_2 \longrightarrow \underset{\text{yellow solution (sod. Chromate)}}{Na_2CrO_4} + 2NaCl + 2H_2O$
7. Oxidising character:
   (a) Both $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are oxidizing agents but $K_2Cr_2O_7$ is preferred since it is not hygroscopic and can be used as primary standard.

   (b) The dichromates act as powerful oxidising agent in acidic medium.

   $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

   nascent oxygen

   (c) Some examples are:

   $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

   $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

   $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$

   $K_2Cr_2O_7 + \underset{\text{(sod. Sulphite)}}{3Na_2SO_3} + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + \underset{\text{(sod. Sulphate)}}{3Na_2SO_4} + 4H_2O$

   $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(L) Potassium Permanganate ($KMnO_4$)

Preparation:

1. Potassium permanganate is prepared from mineral pyrolusite (MnO_2).
2. Steps involved are:
   (a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} \underset{\text{Pot. Manganate (Green mass)}}{2K_2MnO_4} + 2H_2O$

   or, $2MnO_2 + 2K_2CO_3 + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2CO_2$

   (b) $2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$

   or, $2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$

   or, $2K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + 2MnO_2\downarrow + 2KMnO_4$

Properties:

1. It is a dark violet crystalline solid having a metallic luster (meeting point 523 K). It is fairly soluble in water giving a purple solution.
2. $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2\uparrow$
3. Action of alkalies:

   $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2\uparrow$
4. Oxidizing character:

   Potassium permanganate acts as an oxidizing agent in neutral, alkaline and acidic solutions.

   (a) In neutral medium MnO_2 is formed.

   $2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 3S + 2H_2O$

   $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

   $2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3S$

   (b) In alkaline medium, MnO_2 is formed.

   $2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$

   (c) In acidic medium, Mn^{2+} is formed.

   $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

   $2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 2MnSO_4 + 6K_2SO_4 + 8H_2O + 5I_2$

   $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5S$

   $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

$$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$$

$$2KMnO_4 + 10HI + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

LANTHANIDES AND ACTINIDES

The elements from atomic number 58 (cerium) to 71 (lutetium) are known as lanthanides as they follow the element lanthanum (atomic number 57). These elements are placed together at the bottom of the periodic table. These elements are characterized by the filling up of the antipenultimate 4f energy levels. The compound of these elements show +III oxidation state and form ionic compounds. Some of the elements also show +II and +IV oxidation states.

Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. The colour seems to depend on the number of unpaired electrons. Elements with nf electrons offer a similar colour to those with (14-n) f electrons. The atomic and ionic sizes of lanthanides progressively decreases from the first element to the last element. The contraction is about 20 pm and is known as the lanthanide contraction. This is due to the poor shielding effect of 4f electrons causing more and more attraction between the nucleus and the outer electrons.

The properties of an ion depends on its size and its charge. Because of the very small decrease in ionic size, the chemical properties of lanthanides are very similar. The sizes of the last four elements of the lanthanide series become lower than that of the element Y of the preceding trasition series. Also the elements which follows in the third transition series are considerable smaller than the expected value. The pairs Zr-Hf, Nb-Ta and Mo-W have almost identical sizes. The sizes of the third row of transition elements are very similar to those of the second row elements.

The elements from atomic numeber 90 (Thorium) to 103 (Lawrencium) are known as actinides as they follow the element actinium (atomic number 89). The actiinides also have an oxidation state of +III but this state is not always the most stable state. All the actinides are very reactive and show the phenomenon of radioactivity. Their melting points are moderating high but are considerable low as compared to those of transition elements. They also show actinide contraction to the lanthanide contraction.

Outer Electronic configuration of Lanthanum and Lanthanides

Atomic Number	Element Name	Electronic Configuration
57	La	$5d^1\ 6s^2$
58	Ce	$4f^1\ 5d^1\ 6s^2$
59	Pr	$4f^3\ 6s^2$
60	Nd	$4f^4\ 6s^2$
61	Pm	$4f^5\ 6s^2$
62	Sm	$4f^6\ 6s^2$
63	Eu	$4f^7\ 6s^2$
64	Gd	$4f^7\ 5d^1\ 6s^2$
65	Tb	$4f^9\ 6s^2$
66	Dy	$4f^{10}\ 6s^2$
67	Ho	$4f^{11}\ 6s^2$
68	Er	$4f^{12}\ 6s^2$
69	Tm	$4f^{13}\ 6s^2$
70	Yb	$4f^{14}\ 6s^2$
71	Lu	$4f^{14}\ 5d^1\ 6s^2$

Outer Electronic configuration of Actinium and Actinoids

Atomic Number	Element Name	Electronic Configuration
89	Ac	$6d^1\ 7s^2$
90	Th	$6d^2\ 7s^2$
91	Pa	$5f^2\ 6d^1\ 7s^2$
92	U	$5f^3\ 6d^1\ 7s^2$
93	Np	$5f^4\ 6d^1\ 7s^2$
94	Pu	$5f^6\ 7s^2$
95	Am	$5f^7\ 7s^2$
96	Cm	$5f^7\ 6d^1\ 7s^2$
97	Bk	$5f^9\ 7s^2$
98	Cf	$5f^{10}\ 7s^2$
99	Es	$5f^{11}\ 7s^2$
100	Fm	$5f^{12}\ 7s^2$
101	Md	$5f^{13}\ 7s^2$
102	No	$5^{14}\ 7s^2$
103	Lr	$5f^{14}\ 6d^1\ 7s^2$

Solved Examples

1. The oxidation number is changed in which of the following case-

(a) SO_2 gas is passed into $Cr_2O_7^{2-}/H^+$

(b) Aqueous solution of CrO_4^{2-} is acidified

(c) CrO_2Cl_2 is dissolved in NaOH

(d) $Cr_2O_7^{2-}$ solution is made alkaline

Sol.(a)

(a) $\overset{+6}{Cr_2O_7^{2-}} + \overset{+4}{SO_2} + 2H^+ \rightarrow \overset{+3}{2Cr^{3+}} + \overset{+6}{3SO_4^{2-}} + H_2O$

(b) $\overset{+6}{2CrO_4^{2-}} + 2H^+ \rightarrow \overset{+6}{Cr_2O_7^{2-}} + H_2O$

(c) $\overset{+6}{CrO_2Cl_2} + 2NaOH \rightarrow \overset{+6}{Na_2CrO_4}$

(d) $\overset{+6}{CrO_7^{2-}} + 2OH^- \rightarrow \overset{+6}{2CrO_4^{2-}} + H_2O$

2. What happen when $FeSO_4$(X) is subjected to heating, compound R,S,T are obtained. R is red-brown solid, S can be oxidized to (T). Identify R,S,T.

Sol. $\underset{(X)}{2FeSO_4} \xrightarrow{\Delta} \underset{\substack{(R)\\ \text{Red-Brown}}}{Fe_2O_3} + \underset{(S)}{SO_2} + \underset{(T)}{SO_3}$

3. Heating of Ag with dil. HNO_3 give

(a) NO (b) NO_2

(c) N_2O (d) N_2O_3

Sol.(a) $2HNO_3(\text{dil.}) \rightarrow 2NO + H_2O + 3[O]$

$6Ag + 8HNO_3 \longrightarrow 6AgNO_3 + 2NO + 4H_2O$

4. When excess of $SnCl_2$ is added to $HgCl_2$, the substance formed is –

(a) Hg_2Cl_2 (b) Sn

(c) Hg (d) Cl_2

Sol.(c) $SnCl_2$ reduces $HgCl_2$ to Hg_2Cl_2 and finally to Hg-

$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$

5. A mixture of Mn^{2+} & Zn^{2+} can be separated by using an excess of-

(a) NH_4OH (b) NaOH

(c) H_2SO_4 (d) HNO_3

Sol.(b) $Mn^{2+} + 2NaOH \longrightarrow \underset{(\text{ppt.})}{Mn(OH)_2} + 2Na^+$

$Zn^{2+} + 2NaOH \longrightarrow \underset{\substack{(\text{ppt.})\\ (\text{Amphoteric in nature})}}{Zn(OH)_2} + 2Na^+$

$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2[Zn(OH)_4]}$

6. Black coloured solid (A) $\xrightarrow[\Delta]{KNO_3+KOH}$ green coloured solution (B) $\xrightarrow{CO_2}$ $\underset{\text{Pink}}{(C)}$ + (A)

(C) is decolorised by Fe^{2+}. Identify (A), (B) and (C). Explain the reaction.

Sol. **(A)** MnO_2 (B) K_2MnO_4 (C) $KMnO_4$

$MnO_2 + KOH + O_2\ (KNO_3) \xrightarrow{\Delta} \underset{(B)}{K_2MnO_4} \xrightarrow{CO_2} \underset{(C)}{MnO_4^-} + \underset{(A)}{MnO_2}$

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$

7. Explain why mercury (I) ion exists as Hg_2^{2+} ion white copper (I) ion exists as Cu^+ ion.

Sol. $Hg(Z = 80) \Rightarrow 4f^{14}\,5d^{10}\,6s^2$; $Hg^{\oplus} \Rightarrow 4f^{14}\,5d^{10}\,6s^1$

Hg^+ has one electron in its valence 6s-orbital, due to this, Hg^+ compounds should be paramagnetic but actually they are diamgnetic. Hence, the single filled 6s-orbitals of the two $Hg^{\oplus}$ ions overlap from a Hg–Hg covalent bond. Thus, $Hg^{\oplus}$ ions exist as dimeric species, i.e., Hg_2^{2+}.

$Cu(Z = 29) \Rightarrow 3d^{10}\,4s^1$

$Cu^{\oplus} \Rightarrow 3d^{10}$

Therefore, $Cu^{\oplus}$ ion has no unpaired electron to form dimeric species. i.e., Cu_2^{2+} and hence, it always exists as $Cu^{\oplus}$ ion.

8. Why hydrated copper sulphate is blue while unhydrous copper sulphate is white?

Sol. In $CuSO_4 . 5H_2O$, four water molecules are present as ligand. In the presence of these ligands d-orbitals are no longer degenerate in energy. Hence d-d transition takes place absorbing red wavelength. The complementary colour, viz, blue is reflected. In anhydrous $CuSO_4$, d-orbitals remain degenerate. Hence, no d-d transition can occur. The white light is completely reflected back. Hence, it looks white.

9. (a) Of the lanthanides, cerium (Z = 58) forms a tetrapositive ion, Ce^{4+} in aqueous solution. Why?

(b) The +3 oxidation states of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?

(c) Why do Zr and Hf or Nb and Ta exhibit similar properties ?

(d) Which out of the two, $La(OH)_3$ and $Lu(OH)_3$, is more basic and why?

Sol. (a) Ce^{3+} having the configuration $4f^1 5d^0 6s^0$ can easily loose an electron to acquire the configuration $4f^0$ and form Ce^{4+}. In fact, this is the only +4 state lanthanide which exists in solution.

(b) This is because they have empty, half-filled and completely filled 4f subshells respectively.

(c) Due to the consequence of lanthnoid contraction, Hf (Z = 72) has size similar to that of Zr (Z = 40). Hence, their properties are similar. For the same reason. Nb and Ta have similar size and hence similar properties.

(d) $La(OH)_3$ is more basic than $Lu(OH)_3$. As the size of the lanthanid ions decreases from La^{3+} to Lu^{3+}, the covalent chracter of the hydroxides increases (Fajan's rules). Hence, the basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.

10. Identify A to F.

(a) A powdered substance A on fusion with (Na_2CO_3 + KNO_3) mixture gives a green coloured compound B.

(b) The solution of B in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound C.

(c) The aqueous solution of A on treatement with NaOH and Br_2 - water gives a compound D.

(d) A solution of D in conc. HNO_3 on treatment with lead peroxide at boiling temperature produced a compound E which was of the same colour as that of C.

(e) A solution of A in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound F which was insoluble in conc. HNO_3 and conc. HCl.

Sol. A is $MnSO_4$

(a) $\underset{(A)}{MnSO_4} + Na_2CO_3 + 2KNO_3 \rightarrow \underset{(B)\ \text{Green coloured}}{Na_2MnO_4} + 2KNO_2$

(b) $3Na_2MnO_4 + 2H_2SO_4 \rightarrow \underset{(C)\ \text{Pink coloured}}{2NaMnO_4} + MnO_2 + 2Na_2SO_4 + 2H_2O$

(c) $MnSO_4 + 4NaOH + Br_2 \rightarrow \underset{(D)}{MnO_2} + Na_2SO_4 + 2NaBr + 2H_2O$

(d) $2MnO_2 + 10HNO_3 + 5PbO_2 \rightarrow \underset{(E)\ \text{Pink coloured}}{2HMnO_4} + 5Pb(NO_3)_2$

(e) $MnSO_4 + BaCl_2 \rightarrow \underset{(F)\ (\text{Insoluble in conc. } HNO_3 \text{ and conc. HCl})}{BaSO_4} + MnCl_2$

Exercise

LEVEL I

1. Which of the following statements concerning transition elements, is not true?

(a) They are all metals.

(b) They easily form complexes.

(c) Compounds containing their ions are coloured.

(d) They show multiple oxidation states always differing by two units.

2. The stability of particular oxidation state of a metal in aqueous solution is determined by:

(a) Enthalpy of sublimation of the metal

(b) Ionization energy

(c) Enthalpy of hydration of the metal ion

(d) All of these

3. Which of the following is likely to form white salts?

(a) Cu^{2+} (b) Sc^{3+}

(c) Ti^{3+} (d) Fe^{2+}

4. Brass is an alloy of

(a) Silver and copper (b) Copper and zinc

(c) Copper and tin (d) Copper, zinc and tin

5. Zr and Hf have almost equal atomic and ionic radii because:
(a) of diagonal relationship.
(b) both are in the same group.
(c) of lanthanide contraction.
(d) they have same outermost shell.

6. Which of the following compounds is expected to be coloured?
(a) Ag_2SO_4 (b) CuF_2
(c) MgF_2 (d) CuCl

7. Stainless steel contains
(a) Fe + Cr + Cu (b) Fe + C + Ni
(c) Fe + Cr + Ni (d) Fe + Ni + Cu

8. The catalytic activity of the transition metals and their compounds is ascribed to
(a) Their chemical reactivity
(b) Their magnetic behavior
(c) Their unfilled d-orbitals
(d) Their ability to adopt multiple oxidation states and their complexing ability.

9. In the reaction $Zn + NaOH \xrightarrow{\Delta} X$, the product X is:
(a) Na_2ZnO_2 (b) $2NaZnO_2$
(c) $Zn\ (OH)_2$ (d) None of these

10. Which of the following is not correctly matched?
(a) SiC – Covalent carbide
(b) WC – Interstitial carbide
(c) Al_4C_3 – Ionic carbide
(d) B_4C – Molecular carbide

11. Which of the following is not a property of intersitial compounds?
(a) Neither ionic nor covalent
(b) High chemically reactivity
(c) Retain metallic conductivity
(d) Non-stoichiometric compound

12. K_2MnO_4 can be converted into $KMnO_4$ by:
(a) Passing CO_2 gas
(b) By passing Cl_2
(c) Electrolytic oxidation
(d) All of these

13. Which of the following metals of 3d series do not show variable oxidation state?
(a) Sc, Ti (b) Ti, Cu
(c) Sc, Zn (d) Co, Ni

14. The metals which are present in insulin and vitamin B_{12} respectively are:
(a) Zn, Co (b) Fe, Cr
(c) Co, Fe (d) Zn, Fe

15. $CrO_4^{2-} \underset{pH\ =\ Y}{\overset{pH\ =\ X}{\rightleftharpoons}} Cr_2O_7^{2-}$

The pH values of X and Y are respectively:
(a) 4 and 5 (b) 4 and 8
(c) 8 and 4 (d) 8 and 9

16. In which of the following oxoanions, the oxidation state of the central atom is not the same as that of its group number in the periodic table?
(a) MnO_4^- (b) $Cr_2O_7^{2-}$
(c) VO_4^{3-} (d) FeO_4^{2-}

17. Interstitial compounds are not formed by:
(a) Co (b) Ni
(c) Fe (d) Ca

18. Which compound does not exist?
(a) MnF_6 (b) MnF_4
(c) MnO_3F (d) MnO_4^{-2}

19. The incorrect match is:
(a) CrO_5 peroxide
(b) Mn_2O_7 Acidic oxide
(c) CrO_3 Amphoteric
(d) FeO Basic oxide

20. Solder is an alloy of:
(a) Pb + Sn (b) Mg + Al
(c) Cu + Sn (d) Al + Mn + Cu

21. Most common oxidation states are matched below with the elements. Which one is mismatched ?
(a) Iron (+2, +3)
(b) Chromium (+1, +2)
(c) Manganese (+2, +7)
(d) Titanium (+3, +4)

22. Which of the following pair of ions has same value of "spin-only" magnetic moment:
(a) Cu^+, Cu^{2+} (b) Co^{3+}, Fe^{2+}
(c) Ti^{2+}, Cu^{2+} (d) Sc^{2+}, Zn^{+2}

23. CO_2 and SO_2 gas can be distinguish by:
(a) Slaked lime (b) Beryta water
(c) Acidified $KMnO_4$ (d) All of these

24. Acidified $K_2Cr_2O_7$ can not oxidise:

(a) Green vitriol (b) Mohr's salt

(c) Ferric oxalate (d) Ferric sulphate

25. In which of the following oxo-anion, all M–O bond length are not identical?

(a) MnO_4^- (b) MnO_4^{-2}

(c) $Cr_2O_7^{-2}$ (d) CrO_4^{-2}

26. Which of the following is not a similarity between sulphur and chromium?

(a) Both exhibit hexacovalency

(b) Sulphate and chromate of Ba^{2+} are water insoluble

(c) Trioxide (MO_3) both are acidic

(d) Sulphate (SO_4^{2-}) and chromate (CrO_4^{2-}) have same colouration

27. Copper (II) ions gives reddish brown precipitate with potassium ferrcroyanide. The formula of the precipitate is:

(a) $Cu[Fe(CN)_6]$ (b) $Cu_2[Fe(CN)_6]$

(c) $Cu_3[Fe(CN)_6]$ (d) $Cu_3[Fe(CN)_6]_2$

28. CeO_2 is:

(a) A good oxidising agent

(b) Diamagnetic in nature

(c) Colourless compound

(d) All of these

29. Which of the following show highest oxidation state?

(a) Cl (b) Mn

(c) Np (d) All of these

30. Which of the following ion has maximum complex forming tendency?

(a) La^{+3} (b) Ce^{+3}

(c) Eu^{+3} (d) Lu^{+3}

LEVEL II

1. Number of Cr—O bonds in dichromate ion ($Cr_2O_7^{2-}$) is:

(a) 6 (b) 7

(c) 8 (d) 4

2 Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in the three conditions are, respectively

(a) MnO_4^{2-}, Mn^{3+} and Mn^{2+}

(b) MnO_2, MnO_4^{2-} and Mn^{2+}

(c) MnO_2, MnO_2^+ and Mn^{3+}

(d) MnO_2 , MnO_2 and Mn^{3+}

3. Amongst TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (Atomic numbers : Ti = 22, Co = 27, Cu = 29, Ni = 28) the colourless species are

(a) TiF_6^{2-} and Cu_2Cl_2

(b) Cu_2Cl_2 and $NiCl_4^{2-}$

(c) TiF_6^{2-} and CoF_6^{3-}

(d) CoF_6^{3-} and $NiCl_4^{2-}$

4. CrO_3 dissolves in aqueous NaOH to give:

(a) CrO_4^{2-} (b) $Cr(OH)_3$

(c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

5. A compound of a metal ion M^{x+} (Z = 24) has a spin only magnetic moment of $\sqrt{15}$ Bohr Magnetons. The number of unpaired electrons in the compound are:

(a) 2 (b) 4

(c) 5 (d) 3

6. Which one of the following statement is not correct?

(a) $La(OH)_3$ is less basic than $Lu(OH)_3$.

(b) In lanthanide series, ionic radius of Ln^{3+} ions decreases.

(c) La is actually an element of transition series rather than lanthanide series.

(d) Atomic radii of Zr and Hf are same because of lanthanide contraction.

7. Which of the following compounds has colour but no unpaired electrons?

(a) $KMnO_4$ (b) K_2MnO_4

(c) $MnSO_4$ (d) $MnCl_2$

8. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because:

(a) Zn acts as an oxidising agent when react with HNO_3.

(b) HNO_3 is weaker acid than H_2SO_4 and HCl.

(c) In electrochemical series Zn is above hydrogen.

(d) NO_3^- ion is reduced in preference to hydronium ion.

9. Which of the following is incorrectly matched?

	Catalyst	**Process**
(a)	V_2O_5	Contact process
(b)	Cu_2Cl_2	Sandmeyer reaction
(c)	Finely divided Fe	Vegatable oil to ghee
(d)	$TiCl_4 + Al(CH_3)_3$	Zieglar Natta Catalyst

10. An inorganic molecule X on heating gives green colouration and evolve O_2 gas. The X is:

(a) $(NH_4)_2Cr_2O_7$ (b) $K_2Cr_2O_7$

(c) $RbCrO_4$ (d) CrO_2Cl_2

11. Consider the following reaction:

$2Cu^{2+} + X^- \longrightarrow Cu_2X_2(s) + X_2$

Then X^- can be:

(a) F^- (b) Cl^-

(c) Br^- (d) I^-

12. In which reaction no colour change will be observed?

(a) $K_2Cr_2O_7 \xrightarrow{CO_2}$

(b) $K_2Cr_2O_7 \xrightarrow{SO_2}$

(c) $Na_2CrO_4 \xrightarrow{CO_2}$

(d) $Na_2S \xrightarrow{Na_2[Fe(CN)_5NO]}$

13. Which of the following property first increases then decreases on moving from Sc to Zn?

(a) Paramagnetism

(b) Heat of atomisation

(c) Maximum oxidation state

(d) All of these

14. Coloured and paramagnetic oxoanion is:

(a) MnO^-_4 (b) CrO_4^{-2}

(c) MnO_4^{-2} (d) $Cr_2O_7^{-2}$

15. Product formed when Au react with aquaregia is:

(a) AuCl (b) $AuCl_3$

(c) $Au(NO_3)_3$ (d) $HAuCl_4$

16. When $KMnO_4$ react with H_2O_2 in slightly alkaline and acidic medium, the respective products obtained:

(a) K_2MnO_4 and Mn^{2+}(aq)

(b) MnO_2 and MnO_2

(c) MnO_2 and Mn^{2+}(aq)

(d) Mn^{2+} (aq) and MnO_2

17. $K_2Cr_2O_7$ when reacts cold conc. H_2SO_4 gives red crystal of:

(a) CrO_4^{-2} (b) CrO_3

(c) $Cr_2(SO_4)_3$ (d) Cr_2O_3

18. $(X) + K_2CO_3 + \text{Air} \xrightarrow{\text{Heat}} (Y)$.

$(Y) + Cl_2 \longrightarrow (Z)$ Pink.

Which of the following is correct?

(a) X = Black, MnO_2, Y = Blue, K_2CrO_4, Z = $KMnO_4$.

(b) X = Green, Cr_2O_3, Y = Yellow, K_2CrO_4, Z = $K_2Cr_2O_7$.

(c) X = Black, MnO_2, Y = Green, K_2MnO_4, Z = $KMnO_4$.

(d) X = Black, Bi_2O_3, Y = Colourless, $KBiO_2$, Z = $KBiO_3$.

19. When acidified $KMnO_4$ is added to hot oxalic acid solution, the decolourization is slow in the beginning but becomes very rapid after some time. This is because:

(a) Mn^{+2} acts as autocatalyst

(b) CO_2 is formed as the product

(c) Reaction is exothermic

(d) MnO_4^- catalyses the reaction

20. Which of the following statements are 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

(a) A, B, D (b) A, B, C

(c) B, C, D (d) all are correct

21. Mercury (II) chloride solution on reaction with gaseous ammonia forms:

(a) $Hg(NH_2)Cl.HgO$

(b) $Hg(NH_3)Cl_2$

(c) $[Hg(NH_3)_4]Cl_2$

(d) $[Hg(NH_3)_2]Cl$

22. $AgNO_3 \xrightarrow{\Delta} (W) + (X) + O_2$

$(X) + H_2O \longrightarrow HNO_2 + HNO_3$

$(W) + HNO_3 \longrightarrow Y + NO + H_2O$

$(Y) + Na_2S_2O_3 \text{ (excess)} \longrightarrow (Z) + NaNO_3$

Identify (W) to (Z).

(a) W = Ag; X = N_2O; Y = $AgNO_3$; Z = $Na_2[Ag(S_2O_3)_2]$

(b) W = Ag_2O; X = NO; Y = $AgNO_3$; Z = $Na_3[Ag(S_2O_3)_2]$

(c) W = Ag; X = NO_2; Y = $AgNO_3$; Z = $Na_3[Ag(S_2O_3)_2]$

(d) W = AgO ; X = N_2; Y = $AgNO_3$; Z = $Na[Ag(S_2O_3)_2]$

23. Which of the following electronic configuration is associated with the highest stable oxidation state?

(a) [Ar] $3d^1 4s^2$ (b) [Ar] $3d^5 4s^1$

(c) [Ar] $3d^5 4s^2$ (d) [Ar] $3d^6 4s^2$

24. A white precipitate of AgCl dissolves in excess of:

(I) NH_3(aq) (II) $Na_2S_2O_3$

(III) NaCN

(a) III only (b) I, II, III

(c) I, II (d) I only

25. Zinc (II) ion on reaction with NaOH first gives a white precipitate which dissolves in excess of NaOH due to the formation of:

(a) ZnO (b) $Zn(OH)_2$

(c) $[Zn(OH)_4]^{2-}$ (d) $[Zn(H_2O)_4]^{2+}$

26. Dilute nitric acid on reaction with silver liberates:

(a) NO gas (b) NO_2

(c) N_2 gas (d) O_2 gas

27. Acidified permanganate solution does not oxidize:

(a) $C_2O_4^{2-}$ (aq.) (b) NO_2^- (aq.)

(c) S^{2-} (aq.) (d) F^-(aq.)

28. Which of the following characteristic is not the point of resemblance between lanthanoids and actinoids?

(a) Reducing property

(b) Oxidation state of +3

(c) Trends of ionic radii for M^{+3} ions

(d) Radioactivity

29. Which of the following statement is not correct?

(a) Lu^{+3} has the strongest tendency toward complex formation among trivalent lanthanoid ions.

(b) Ce has maximum composition in misch metal.

(c) f-block elements can have electrons from f^0 to f^{14}.

(d) Nd, Np and Nb all are f-block elements.

30. Which of the following lanthanoid has one electron in 6d subshell?

(a) La (b) Ce

(c) Gd (d) None of these

LEVEL III

One or more than one correct type

1. The metal oxide which decomposes on heating is/are:

(a) ZnO (b) Al_2O_3

(c) Ag_2O (d) HgO

2. Which of the following acids attack(s) on copper and silver?

(a) dilute HNO_3 (b) dilute HCl

(c) conc. H_2SO_4 (d) aqua regia

3. Which statements are correct regarding copper sulphate?

(a) It reacts with NaOH and glucose to give Cu_2O.

(b) It reacts with KCl to give Cu_2O.

(c) It gives CuO on strong heating in air.

(d) It reacts with KI to give brown colouration.

4. Pick out the correct statements (s):

(a) MnO_2 dissolves in conc. HCl, but does not form Mn^{4+} ions.

(b) Decomposition of acidic $KMnO_4$ is not catalysed by sunlight.

(c) MnO_4^{2-} is strongly oxidising and stable only in very strong alkali. In dilute alkali, water or acidic solutions, it disproportionates.

(d) $KMnO_4$ does not act as oxidising agent in alkaline medium.

5. The species that undergoes disproportionation in an alkaline medium are:

(a) Cl_2 (b) MnO_4^{2-}

(c) NO_2 (d) ClO_4^-

6. Mercuric chloride is converted into mercury by:

(a) Placing copper metal in aqueous solution of $HgCl_2$.

(b) Treating aqueous solution of $HgCl_2$ with excess of stannous chloride.

(c) Treating aqueous solution of $HgCl_2$ with $PbCl_4$ solution.

(d) None of these.

7. Choose correct statement (s) regarding the following reaction:

$$Cr_2O^{2-}_{7(aq.)} + 3SO^{2-}_{3(aq.)} + 8H^+ \rightarrow 2Cr^{3+}_{(aq.)} + 3SO^{2-}_{4(aq.)} + 4H_2O$$

(a) $Cr_2O_7^{2-}$ is an oxidising agent.
(b) SO_3^{2-} is a reducing agent.
(c) The oxidation number of per S-atom in SO_3^{2-} is increased by two.
(d) The oxidation number of per Cr-atom in is $Cr_2O_{7(aq.)}^{2-}$ decreased by three.

8. Transition elements have greater tendency to form complexes because they have:
(a) vacant d-orbitals
(b) small size
(c) higher nuclear charge
(d) variable oxidation states

9. Which of the following ions give(s) coloured aqueous solution?
(a) Ni^{2+} (b) Fe^{2+}
(c) Cu^{2+} (d) Cu^{+}

10. What are the characteristics of products obtained when green vitriol is strongly heated?
(a) Basic oxide (b) Neutral oxide
(c) Acidic oxide (d) Reducing agent

11. Which of the following statements are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?
(a) Deep red vapours are liberated
(b) Deep red vapours dissolve in NaOH forming a yellow solution.
(c) Greenish yellow gas is liberated
(d) Deep red vapours dissolve in water forming yellow solution

PASSAGE-BASED QUESTIONS

Passage # 1 (Q. 12 and 13)

$$\text{Light green (Compound 'A')} \xrightarrow{\Delta} \text{White Residue (B)} \xrightarrow[\text{Temp.}]{\text{High}} C + D + E$$

(i) 'D' and 'E' are two acidic gas.
(ii) 'D' is passed through $HgCl_2$ solution to give yellow precipitate.
(iii) 'E' is passed through water first and then H_2S is passed, white turbidity is obtained.
(iv) A is water soluble and addition of $HgCl_2$ in it, white ppt is obtained but white ppt does not turn into grey on addition of excess solution of 'A'.

12. 'D' and 'E' are respectively.
(a) SO_2 and SO_3 (b) SO_3 and SO_2
(c) SO_2 and CO_2 (d) CO_2 and CO

13. Yellow ppt in the above observation is :
(a) Mercuric oxide
(b) Basic mercury (II) sulphite
(c) Basic mercury (II) sulphate
(d) Mercuric iodide

Passage # 2 (Q. 14 and 15)

MnO_2 is the most important oxide of maganese. It occurs naturally as the black coloured mineral pyrolusite. It is an oxidising agent, and decomposes to Mn_3O_4 on heating to 530°C. It is used in the preparation of potassium permanganate and in the production of Cl_2 gas. Over half a million tonnes per year of MnO_2 is used in dry batteries.

14. When MnO_2 is fused with KOH in the presence at air, the product formed is:
(a) purple colour $KMnO_4$
(b) green colour K_2MnO_4
(c) colourless MnO_4^-
(d) purple colour K_2MnO_4

15. In which of the following species, the colour is due to charge transfer.
(I) $[Mn(OH)_4]^{2-}$ (II) MnO_4^{2-}
(III) MnO_2 (IV) $KMnO_4$
(a) I, II, III (b) II, IV
(c) I, II (d) Only IV

Passage # 3 (Q. 16 and 17)

Iron forms iron halide salts by reacting the metal directly with halogen. FeI_3 does not exist. FeF_3 is white solid inspite of five unpaired electrons with d^5 configuration. $FeCl_3$ is soluble in water and is used as a mordant in dyeing industry.

16. FeI_3 does not exist because:
(a) of its large size.
(b) Fe^{3+} oxidises I^- to I_2.
(c) of low lattice energy.
(d) iodine is not highly electronegative enough to oxidise Fe to Fe^{3+}.

17. $FeCl_3$ solution added to $K_4[Fe(CN)_6]$ gives A while with KSCN gives B. A and B respectively are:
(a) $Fe_3[Fe(CN)_6]_2$, $Fe(CNS)_3$
(b) $Fe_4[Fe(CN)_6]_3$, $KFe(CNS)_3$
(c) $Fe_4[Fe(CN)_6]_3$, $K_3[Fe(CNS)_6]$
(d) $Fe_4[Fe(CN)_6]_3$, $K_3[Fe(SCN)_6]$

Passage # 4 (Q. 18 and 19)

Pyrolusite ore on oxidation with $KClO_3/KNO_3$ in basic medium produces dark green coloured compounds (A), which on electrolysis produces a purpule coloured compound (B). The purple coloured compound can be crystallisd to deep purple rhombic prisms. It shows different reactions in different mediums. Excess of compound (B) on heating with concentrated H_2SO_4 gives an explosive oil (C), which on heating decomposes to give another compound (D) along with oxygen.

18. The nature of compound (C) is:

(a) basic (b) acidic

(c) neutral (d) amphoteric

19. Identify (D)

(a) Mn_2O_7 (b) MnO_2

(c) $MnSO_4$ (d) Mn_2O_3

INTEGER VALUE TYPE QUESTIONS

20. Sum of highest stable oxidation states of following elements is:

Sc, Zn, Ti, Mn, Cr

21. Determine total number of unpaired electrons in following ions.

Ti^{3+}, V^{3+}, Cr^{3+}, Cr^{2+}, Mn^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}

22. $FeC_2O_4 \xrightarrow{\Delta}$ products

Number of dimagnetic products = x

Number of unpaired electrons in paramagnetic product = y

Report your answer as (x + y).

23. $KMnO_4 \xrightarrow[\text{R.A.}]{H^+} Mn^x$

$KMnO_4 \xrightarrow[\text{R.A.}]{OH^-} Mn^y$

$K_2Cr_2O_7 \xrightarrow{OH^-} Cr^z$

x + y + z is:

(here x, y and z are oxidation states)

COLUMN MATCHING TYPE QUESTIONS

24.

	Column I		Column II
(A)	Kipp's apparatus waste	(P)	$(NH_4)_2SO_4.FeSO_4.6H_2O$
(B)	Green coloured compound	(Q)	$Cu(OH)_2.\ CuCO_3$
(C)	Leave(s) brown residue on heating	(R)	$FeSO_4$
(D)	Leave(s) black residue on heating	(S)	$CuCl_2.2H_2O$

25.

	Column I		Column II
(A)	Cu(I) and Zn(II) complexes	(P)	Pair of compounds having similar colour and same but non- zero magnetic moment.
(B)	$KMnO_4$ and $K_2Cr_2O_7$	(Q)	Pair of compounds which are diamagnetic but coloured.
(C)	Cu_2O and HgI_2	(R)	Pair of compounds having metals in the highest stable oxidation states.
(D)	$VOCl_2$ and $CuCl_2$	(S)	Pair of compounds which show diamagnetism and are colourless.

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. Match the reactions in column-I with nature of the reaction/type of the products in column-II

	Column-I		Column-II
(A)	$O_2^- \rightarrow O_2 + O_2^{2-}$	(p)	Redox reaction
(B)	$CrO_4^{2-} + H^+ \rightarrow$	(q)	One of the products has trigonal planar structure
(C)	$MnO_4^- + NO_2^- + H^+ \rightarrow$	(r)	Dimeric bridged tetrahedral metal ion
(D)	$NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s)	(s) Disproportionation

[IIT-2007]

2. Among the following, the coloured compound is:

(a) CuCl (b) $K_3[Cu(CN)_4]$

(c) CuF_2 (d) $[Cu(CH_3CN)_4]BF_4$

[IIT-2008]

3. The oxidation number of Mn in the product of alkaline oxidation fusion of MnO_2 is:

[IIT-2009]

4. Reduction of the metal centre in aqueous permanganate ion involves :

(a) 3 electrons in neutral medium

(b) 5 electrons in neutral medium

(c) 3 electrons in alkaline medium

(d) 5 electrons in acidic medium

[IIT-2011]

5. The colour of light abosrbed by an aqueous solution of $CuSO_4$ is:

(a) orange-red (b) blue-green

(c) yellow (d) violet

[IIT-2012]

6. The correct statement(s) about Cr^{2+} and Mn^{3+} is/are:

[Atomic numbers of Cr = 24 and Mn = 25]

(a) Cr^{2+} is a reducing agent

(b) Mn^{3+} is an oxdizing agent

(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration

(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

[JEE (Advanced) 2015]

7. Fe^{3+} is reduced to Fe^{2+} by using

(a) H_2O_2 in presence of NaOH

(b) Na_2O_2 in water

(c) H_2O_2 in presence of H_2SO_4

(d) Na_2O_2 in presence of H_2SO_4

[JEE (Advanced) 2015]

8. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_s) of Ni^{2+} in aqueous solution would be (atomic number of Ni = 28)

(a) 2.84 (b) 4.90

(c) 0 (d) 1.73

[AIEEE-2006]

9. Lanthanoid contraction is caused due to:

(a) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge.

(b) the appreciable shielding on outer electrons by 5f electrons from the nuclear charge.

(c) the same effective nuclear charge from Ce to Lu.

(d) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge.

[AIEEE-2006]

10. Identify the incorrect statements among the following:

(a) The chemistry of various lanthanoids is very similar.

(b) 4f and 5f orbitals are equally shielded.

(c) d-block elements show irregular and erratic chemical properties among themselves.

(d) La and Lu have partially filled d orbitals and no other partially filled orbitals.

[AIEEE-2007]

11. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because:

(a) The actinoids are more reactive than the lanthanoids.

(b) The 5f orbitals extend farther from the nucleus than the 4f orbitals.

(c) The 5f orbitals are more buried than the 4f orbitals

(d) There is a similarity between 4f and 5f orbitals in their angular part of the wave function.

[AIEEE-2007]

12. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being:

(a) lesser energy difference between 5f and 6d than between 4f and 5d orbitals

(b) more energy difference between 5f and 6d than between 4f and 5d orbitals

(c) more reactive nature of the actinoids than the lanthanoids

(d) 4f orbitals more diffusion than the 5f orbitals.

[AIEEE-2008]

13. In context with transition elements, which of the following statements is incorrect?

(a) In the highest oxidation states, the transition metal show basic character and forms cationic complexes.

(b) In the highest oxidation states, of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.

(c) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

(d) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

[AIEEE-2009]

14. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?

(a) The ionic sizes of Ln(III) decreases in general with increasing atomic number.

(b) Ln(III) compounds are generally colourless.

(c) Ln(III) hydroxides are mainly basic in character.

(d) Because of the large size of the Ln(III) ions the bonding in its compounds is predominently ionic character.

[AIEEE-2009]

15. In context of the lanthanoids, which of the following statement is not correct?

(a) There is a gradual decreases in the radii of the members with increasing atomic number in the series.

(b) All the member exhibit +3 oxidation state.

(c) Because of similar properties the separation of lanthanoids is not easy.

(d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

[AIEEE-2011]

16. The outer electron configuration of Lu (Atomic number : 71) is:

(a) $4f^3\ 5d^5\ 6s^2$ (b) $4f^8\ 5d^{10}\ 6s^2$

(c) $4f^4\ 5d^4\ 6s^2$ (d) $4f^{14}\ 5d^1\ 6s^2$

[AIEEE-2011]

17. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect?

(a) Ferrous oxide is more basic in nature than the ferric oxide.

(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds

(c) Ferrous compounds are less volatile than the corresponding ferric compounds.

(d) Ferrous compouds are more easily hydrolysed than the corresponding ferric compounds.

[AIEEE-2012]

18. Which of the following arrangements does not represent the correct order of the property stated against it?

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$; paramagnetic behaviour

(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution

(d) Sc < Ti < Cr < Mn: number of oxidation states

[JEE-Main - 2014]

19. Which series of reactions correctly represents chemical relations related to iron and its compound?

(a) $Fe \xrightarrow{\text{dil } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$

(b) $Fe \xrightarrow{O_2,\ \text{heat}} FeO \xrightarrow{\text{dil } H_2\ SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$

(c) $Fe \xrightarrow{Cl_2\ ,\text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2,\text{heat}} Fe_3O_4 \xrightarrow{CO,\ 600°C} FeO \xrightarrow{CO,\ 700°C} Fe$

[JEE-Main - 2014]

20. The colour of $KMnO_4$ is due to:

(a) M → L charge transfer transition

(b) d → d transition

(c) L → M charge transfer transition

(d) $\sigma \rightarrow \sigma$ transition

[JEE-Main - 2015]

Answer Key

LEVEL I

1. (d) 2. (d) 3. (b) 4. (b) 5. (c) 6. (b) 7. (c) 8. (d) 9. (a) 10. (d)
11. (b) 12. (d) 13. (c) 14. (a) 15. (b) 16. (d) 17. (d) 18. (a) 19. (c) 20. (a)
21. (b) 22. (b) 23. (c) 24. (d) 25. (c) 26. (d) 27. (b) 28. (d) 29. (d) 30. (d)

LEVEL II

1. (c) 2. (b) 3. (a) 4. (a) 5. (d) 6. (a) 7. (a) 8. (d) 9. (c) 10. (b)
11. (d) 12. (a) 13. (d) 14. (c) 15. (d) 16. (c) 17. (b) 18. (c) 19. (a) 20. (a)
21. (a) 22. (c) 23. (c) 24. (b) 25. (c) 26. (a) 27. (d) 28. (d) 29. (d) 30. (d)

LEVEL III

1. (c, d) 2. (a, c, d) 3. (a, c, d) 4. (a, c) 5. (a, b, c) 6. (a, b) 7. (a, b, c, d) 8. (a, b, c)
9. (a,b,c) 10. (a,b,c,d) 11. (a, b, d) 12. (b) 13. (c) 14. (b) 15. (b) 16. (b)
17. (d) 18. (b) 19. (b) 20. (6) 21. (29) 22. (6) 23. (12)
24. A → R; B → P, Q,R,S; C → P, R; D → Q
25. A → S; B → Q, R; C → Q; D → P

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. A → p. s; B → r; C → p, q; D → p
2. (c) 3. (6) 4. (a, c, d) 5. (a) 6. (a, b, c) 7. (a, b) 8. (a) 9. (d) 10. (b)
11. (b) 12. (a) 13. (a) 14. (b) 15. (d) 16. (d) 17. (d) 18. (a) 19. (d) 20. (c)

Hints and Solutions

LEVEL I

1. **(d)** Unlike p-block elements, the various oxidation states of d-block elements differ by one unit.

2. **(d)** $M_{(s)} \rightarrow M^{+n}_{(aq)} + ne^-$

The above change involves sublimation, ionization and hydration.

3. **(b)** Sc^{3+} ([Ar] $4s^0\ 3d^0$) has no electrons in d-sub shell and hence, d-d transitions are not possible.

4. **(b)** Brass (Cu and Zn)

5. **(c)** Due to lanthanide contraction, elements in 5d-series have almost equal atomic and ionic radii with 4d- series elements.

6. **(b)** CuF_2 (Cu^{+2} = [Ar] $4s^0\ 3d^9$)

Due to d-d transitions, this compound is coloured.

7. **(c)** Stainless steel (Fe + Cr + Ni)

8. **(d)** Transition metals and their compound show catalytic activity because they can show variable oxidation state and they have tendency to form complex.

9. **(a)** $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$

10. **(d)** B_4C is a covalent network carbide.

11. **(b)** Interstitial compound do not have high chemical reactivity.

12. **(d)** K_2MnO_4 can be converted into $KMnO_4$ by passing Cl_2 (oxidizing agent) or by electrolytic oxidation or by disproportionation in acidic or in neutral medium.

13. **(c)** Sc and Zn show fixed oxidation state +3 and +2 respectively.

14. **(a)** Zn and Co are present in insulin and vitamin B_{12} respectively.

15. **(b)** $CrO_4^{2-} \underset{pH>7}{\overset{pH<7}{\rightleftharpoons}} Cr_2O_7^{2-}$

X will be less than 7 and Y will be more than 7.

16. **(d)**

$\overset{+7}{Mn}O_4^-$ (VII group)

$\overset{+6}{Cr_2}O_7^{2-}$ (VI group)

$\overset{+5}{V}O_4^{3-}$ (V group)

$\overset{+6}{Fe}O_4^{2-}$ (VIII group)

17. **(d)** S-block elements (Ca) are not formed interstitial compounds.

18. **(a)** MnF_6 does not exist.

19. **(c)** Mn_2O_7 and CrO_3 are acidic oxides.

20. **(a)** Solder (Pb + Sn)

21. **(b)** Chromium (+3, +6)

22. **(b)** Co^{+3} = [Ar] $4s^0\ 3d^6$ (4 unpaired e-)

Fe^{+2} = [Ar] $4s^0\ 3d^6$ (4 unpaired e-)

23. **(c)** SO_2 can decolorize acidified $KMnO_4$ but CO_2 cannot decolorize acidified $KMnO_4$.

24. **(d)** $Fe_2(SO_4)_3$ [Ferric sulphate] does not behave as reducing agent.

25. **(c)** In $Cr_2O_7^{-2}$, Six Cr-O bonds are identical while other two Cr-O bonds are identical but all eight Cr-O bonds are not identical.

26. **(d)** Sulphate (SO_4^{2-}) and chromate (CrO_4^{2-}) do not have same colour.

27. **(b)** $2Cu^{+2} + K_4[Fe(CN)_6] \rightarrow \underset{\text{Reddish-brown}}{Cu_2[Fe(CN)_6]}\downarrow + 4K^+$

28. **(d)** $Ce^{+4} = [Xe]\ 6s^0\ 5d^0$ (No unpaired e^-)

Hence, CeO_2 is colourless and diamagnetic in nature. The more common oxidation state of Ce is +3 hence, CeO_2 acts as a good oxidizing agent.

29. **(d)** Cl, Mn and Np all can show +7 oxidation state.

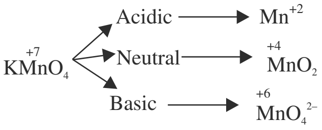
30. **(d)** Order of complex forming tendency:

$La^{+3} < Ce^{+3} < Eu^{+3} < Lu^{+3}$

LEVEL II

1. **(c)** Total number of Cr-O bonds in dichromate ion is 8.

2. **(b)**



3. **(a)** $\overset{+4}{Ti}F_6^{2-}$

$Ti^{+4} = [Ar]\ 4s^0\ 3d^0$ (No unpaired e- hence, no d-d transition)

$\overset{+1}{Cu_2}Cl_2$

$Cu^+ = [Ar]\ 4s^0\ 3d^{10}$ (No unpaired e- hence, no d-d transition)

4. **(a)** $\underset{\text{acid}}{CrO_3} + \underset{\text{base}}{2NaOH} \rightarrow \underset{\text{salt}}{Na_2CrO_4} + H_2O$

5. **(d)** 'Spin only' magnetic moment (μ_s) = $\sqrt{15}$ BM

$\mu_s = \sqrt{n(n+2)} = \sqrt{15}$

Here, n = 3 (unpaired e^-)

$M = [Ar]\ 4s^1\ 3d^5$

$M^{+3} = [Ar]\ 4s^0\ 3d^3$ (3 unpaired e^-)

6. **(a)** As atomic number increases, basic strength of hydroxides of lanthanides decreases.

7. **(a)** In $KMnO_4$, oxidation state of Mn is +7.

$Mn^{+7} = [Ar]\ 4s^0\ 3d^0$ (No unpaired e^-)

Colour in $KMnO_4$ is due to L → M charge transfer.

8. **(d)** $Zn + HNO_3$ (conc.) $\rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

NO_3^- ion is reduced in preference to H^+ ion.

9. **(c)** In process vegetable oil to ghee, the catalyst used is finely divided Ni.

10. **(b)** The X is $K_2Cr_2O_7$.

$K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + Cr_2O_3 + O_2\uparrow$

11. **(d)** X^- ion is I^-

$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2\downarrow + I_2$

12. **(a)** CO_2 does not react with $K_2Cr_2O_7$.

13. **(d)** As we move from Sc to Zn, number of unpaired e- increases upto Cr and then decreases.

14. **(c)** MnO_4^{-2} is green coloured due to L → M charge transfer. Oxidation state of Mn^{+6}.

$Mn^{+6} = [Ar]\ 4s^0\ 3d^1$ (1 unpaired e^-)

15. **(d)** $\underbrace{3HCl+HNO_3}_{\text{Aqura regia}} \rightarrow NOCl + 2H_2O + 2[Cl]$

$Au \xrightarrow{3[Cl]} AuCl_3 \xrightarrow{HCl} HAuCl_4$

16. **(c)** $KMnO_4 \xrightarrow{\text{Slightly alkaline}} MnO_2$

$KMnO_4 \xrightarrow{\text{Acidic}} Mn^{+2}$

17. **(b)** $K_2CrO_7 + H_2SO_4$ (Cold and Conc.) $\rightarrow CrO_3$

18. **(c)** $\underset{(X)}{MnO_2} + K_2CO_3 + \text{Air} \xrightarrow{\text{Heat}} \underset{(Y)}{K_2MnO_4}$

$K_2MnO_4 + Cl_2 \longrightarrow \underset{(Z)}{KMnO_4}$

19. **(a)** When acidified $KMnO_4$ reacts with oxalic acid then reaction is slow in the beginning but becomes very rapid because Mn^{+2} acts as autocatalyst.

20. **(a)** $NaCl + K_2Cr_2O_7 + H_2SO_{4(Conc)} \rightarrow NaHSO_4 + KHSO_4 + H_2O + \underset{\text{deep-red}}{CrO_2Cl_2}\uparrow$

$CrO_2Cl_2 + NaOH \rightarrow \underset{\text{Yellow}}{Na_2CrO_4} + NaCl + H_2O$

21. **(a)** $HgCl_2 + NH_3 \rightarrow Hg(NH_2)Cl.\ HgO$

22. **(c)** $AgNO_3 \rightarrow \underset{(W)}{Ag} + \underset{(X)}{NO_2} + O_2$

$NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

$HNO_3 + Ag \rightarrow AgNO_3 + NO + H_2O$

$AgNO_3 + Na_2S_2O_3$ (excess) $\rightarrow \underset{(Z)}{Na_3[Ag(S_2O_3)_2]}$

23. **(c)** $Mn = [Ar]\ 3d^5\ 4s^2$

Mn shows +7 oxidation state.

24. **(b)** $AgCl + NH_3 \rightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl}$

$AgCl + Na_2S_2O_3 \rightarrow \underset{\text{soluble}}{Na_3[Ag(S_2O_3)_2]}$

$AgCl + NaCN \rightarrow \underset{\text{soluble}}{Na[Ag(CN)_2]}$

25. **(c)** $Zn^{+2} + NaOH \rightarrow Zn(OH)_2\downarrow$

$Zn(OH)_2 + NaOH(excess) \rightarrow \underset{\text{soluble}}{Na_2[Zn(OH)_4]}$

26. **(a)** $HNO_{3(dil)} + Ag \rightarrow AgNO_3 + NO + H_2O$

27. **(d)** $C_2O_4^{2-}$, NO_2^- and S^{2-} can behave as reducing agent while F^- ion cannot behave as reducing agent.

28. **(d)** Actinoids are radioactive while lanthanoids are not radioactive.

29. **(d)** Nb is a d-block element.

30. **(d)** No lanthanoids have electron in 6d-subshell.

LEVEL III

1. **(c, d)** $2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$

$2HgO \xrightarrow{\Delta} 2Hg + O_2$

2. **(a, c, d)**

$Cu + HNO_3\,(dil) \longrightarrow Cu(NO_3)_2 + NO + H_2O$

$Cu + H_2SO_4\,(conc.) \longrightarrow CuSO_4 + SO_2 + H_2O$

$Cu + \text{Aqua regia}\,(3HCl + HNO_3) \longrightarrow CuCl_2$

3. **(a, c, d)**

$$\underset{\text{Oxidizing agent}}{\overset{+2}{CuSO_4}} + NaOH + \underset{\text{reducing agent}}{Glucose} \rightarrow \underset{\text{red}}{\overset{+1}{Cu_2O}}$$

4. **(a, c)**

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Decomposition of acidic $KMnO_4$ is catalysed by sunlight.

$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3O_2$

$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

($KMnO_4$ also acts as oxidizing agent in alkaline medium).

5. **(a, b, c)**

$Cl_2 + OH^- \rightarrow Cl^- + ClO_3^- + H_2O$

$MnO_4^{2-} + OH^- \rightarrow MnO_4^- + MnO_2 + H_2O$

$NO_2 + OH^- \rightarrow NO_2^- + NO_3^- + H_2O$

6. **(a, b)**

$Cu + HgCl_2 \rightarrow CuCl_2 + Hg$

$SnCl_2 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

7. **(a, b, c, d)**

$$\underset{\text{Oxidizing agent}}{\overset{+6}{Cr_2O_7^{-2}}} + \underset{\text{Reducing agent}}{\overset{+4}{3SO_3^{2-}}} + 8H^+ \rightarrow 2\overset{3+}{Cr} + \overset{+6}{3SO_4^{2-}} + 4H_2O$$

8 **(a, b, c)**

Conditions required to form complexes are:

(a) Metal ion must have vacant orbitals.

(b) Metal ion must have small size or high charge density or higher nuclear charge.

9 **(a, b, c)**

$Ni^{+2} = [Ar]\,4s^0 3d^8$

$Fe^{+2} = [Ar]\,4s^0 3d^6$

$Cu^{+2} = [Ar]\,4s^0 3d^9$

$Cu^{+} = [Ar]\,4s^0 3d^{10}$

Conditions required for d-d transition is electronic configuration of central metal from d^1 to d^9 hence, aqueous solution of Cu^+ is colourless.

10. **(a, b, c, d)**

$$\underset{\text{(green vitriol)}}{FeSO_4.7H_2O} \xrightarrow{\text{Strongly heated}} Fe_2O_3 + SO_2 + SO_3 + H_2O$$

Fe_2O_3 is basic oxide

H_2O is neutral oxide

SO_2 and SO_3 are acidic oxide

SO_2 is a reducing agent

11. **(a, b, d)**

$NaCl + K_2Cr_2O_7 + H_2SO_{4\,(conc.)} \longrightarrow \underset{\text{(Deep red)}}{CrO_2Cl_2}\uparrow$

$CrO_2Cl_2 + NaOH \longrightarrow \underset{\text{Yellow}}{Na_2CrO_4} + NaCl + H_2O$

$CrO_2Cl_2 + H_2O \longrightarrow \underset{\text{Yellow}}{H_2CrO_4} + HCl$

12. **(b)** $\underset{(A)}{FeSO_4.7H_2O} \xrightarrow{\Delta} \underset{(B)}{FeSO_4} \xrightarrow{\Delta} \underset{(C)}{Fe_2O_3} + \underset{(D)}{SO_3} + \underset{(E)}{SO_2}$

$SO_3 + HgCl_2 \longrightarrow HgO.HgSO_4\downarrow$

(Basic yellow mercury (II) sulphate)

$SO_2 + 2H_2S \longrightarrow \underset{\text{(turbidity)}}{3S} + 2H_2O$

13. **(c)** $SO_3 + HgCl_2 \longrightarrow HgO.\,HgSO_4\downarrow$

14. **(b)** $MnO_2 + KOH + O_2 \longrightarrow \underset{\text{green}}{K_2MnO_4} + H_2O$

15. **(b)** Cause of colour in MnO_4^{2-} and $KMnO_4$ is L → M charge transfer.

16. **(b)** I^- is very good reducing agent. It oxidizes into I_2 and reduces Fe^{3+} into Fe^{2+}.

17. **(d)** $FeCl_3 + K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3$

$FeCl_3 + KSCN \rightarrow K_3[Fe(SCN)_6]$

18. **(b)** $\underset{(A)}{MnO_4^{2-}} \xrightarrow{\text{electrolysis}} \underset{(B)}{MnO_4^-}$

$\underset{(A)}{MnO_4^-} + H_2SO_{4\,(\text{conc.})} \xrightarrow{\Delta} \underset{(C)}{Mn_2O_7}$

Mn_2O_7 is an acidic oxide.

19. **(b)** $Mn_2O_7 \xrightarrow{\Delta} \underset{(D)}{MnO_2} + O_2\uparrow$

20. **(22)**

Element	Higher stable oxidation state
Sc	+3
Zn	+2
Ti	+4
Mn	+7
Cr	+6

21. **(29)**

Element	No. of unpaired e^-
Ti^{3+}	1
V^{3+}	2
Cr^{3+}	3
Cr^{2+}	4
Mn^{3+}	4
Fe^{3+}	5
Fe^{2+}	4
Co^{2+}	3
Ni^{2+}	2
Cu^{2+}	1

22. $$FeC_2O_4 \xrightarrow{\Delta} \underset{\text{(Paramagnetic)}}{FeO} + \underbrace{CO + CO_2}_{\text{diamagnetic}}$$

Number of diamagnetic products (x) = 2

Number of unpaired e^- in FeO (y) = 4

x + y = 6

23. $KMnO_4 \xrightarrow[\text{R.A.}]{H^+} Mn^{+2}$

$KMnO_4 \xrightarrow[\text{R.A.}]{OH-} Mn^{+4}$

$K_2Cr_2O_7 \xrightarrow{OH^-} Cr^{+6}$

x + y + z = 12

24. (A → R ; B → P, Q, R, S ; C → P, R ; D → Q)

25. (A → S ; B → Q, R ; C → Q ; D → P)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (A → p, s ; B → r ; C → p, q ; D → p]

2. **(c)** $\overset{+2}{Cu}F_2$

$\overset{+2}{Cu} = [Ar]\ 4s°3d^9$

(due to d-d transition, CuF_2 is coloured)

3. $$MnO_2 + KOH + O_2 \xrightarrow{\Delta} K_2\overset{+6}{Mn}O_4 + H_2O$$

4. **(a, c, d)** $\overset{+7}{MnO_4^-} \xrightarrow{\text{acidic}} Mn^{+2}$

$MnO_4^- \xrightarrow{\text{neutral}} \overset{+4}{Mn}O_2$

$MnO_4^- \xrightarrow{\text{alkaline}} \overset{+4}{Mn}O_2$

5. **(a)** Colour of aqueous solution of $CuSO_4$ is blue green. It absorbs orange-red colour.

6. **(a, b, c)** $\underset{\text{Reducing agent}}{Cr^{2+}} \xrightarrow{\text{Oxidation}} Cr^{3+}$

$\underset{\text{Oxidizing agent}}{Mn^{3+}} \xrightarrow{\text{Reduction}} Mn^{2+}$

$Cr^{2+} = [Ar]\ 4s^0 3d^4$

$Mn^{3+} = [Ar]\ 4s^0 3d^4$

7. **(a, b)**

H_2O_2 in alkaline medium acts as reducing agent, reduces Fe^{3+} to Fe^{2+}.

8. **(a)** $Ni^{2+} = [Ar]\ 4s^0\ 3d^8$ (2 unpaired e^-)

$\mu_S = \sqrt{2(2+2)} \approx 2.84$

9. **(d)** Cause of lanthanoid contraction is the imperfect shielding on outer electrons by 4f electrons from the nuclear charge.

10. **(b)** 4f and 5f are not equally shielded.

11. **(b)** The 5f orbitals of actinoids extend farther from the nucleus than the 4f orbitals of lanthanoids. Hence, removal of e^- from 5f-orbitals is easier than 4f-orbitals.

12. **(a)** Antinoids show larger number of oxidation states than lanthanoids. It is due to lesser energy difference between 5f and 6d than 4f and 5d orbitals.

13. **(a)** In the highest oxidation states, the transition metal show acidic character and form cationic complexes.

14. **(b)** In general, due to presence of partially filled f-orbitals, Ln(III) compounds are coloured.

15. **(d)** All the members of lanthanoids exhibit +3 oxidation state not + 4 oxidation state.

16. **(d)** The outer electronic configuration of Lu is $4f^{14}\ 5d^1\ 6s^2$

17. **(d)** As the positive oxidation state increases, tendency of hydrolysis increases.

Ferric salts (Fe^{+3}) are more easily hydrolysed than the corresponding ferrous salts (Fe^{+2}).

18 **(a)**

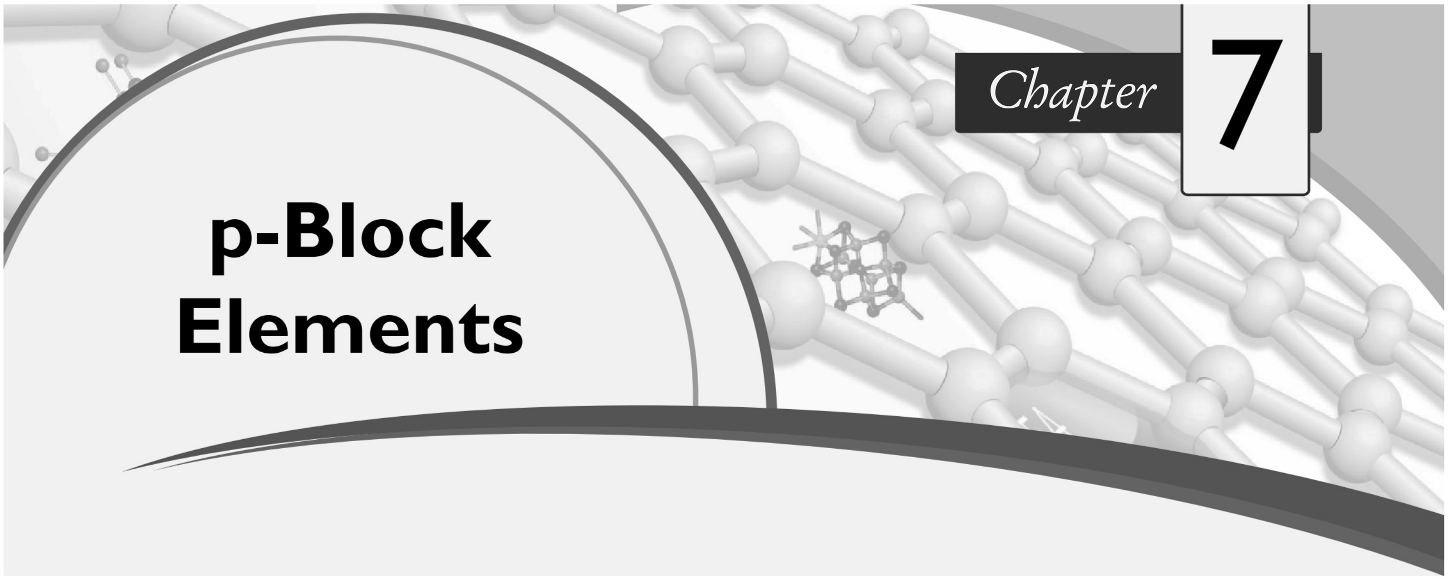
Ions	Number of unpaired e^-
V^{+2}	3
Cr^{+2}	4
Mn^{+2}	5
Fe^{+2}	4

Order of paramagnetic behaviour :

$V^{+2} < Fe^{+2} = Cr^{+2} < Mn^{+2}$

19. **(d)** CO acts as a reducing agent to reduce FeO into Fe.

20. **(c)** Cause of colour of $KMnO_4$ is L → M charge transfer.



Chapter 7

p-Block Elements

Key Concepts

GROUP 13 ELEMENTS – BORON FAMILY

Group 13 contains boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have outer electronic configuration $(ns)^2$ $(np)^1$, where n varies from 2 to 6. Boron is nonmetal while others are metals. The atomic radii of Ga, In and Tl are smaller than expected values due to d-block contraction. The atomic radius of Tl is a little larger than In due to lanthanide contraction. On descending the group, +1 oxidation state becomes more stable than +3 state due to the inert pair effect.

The very high melting point of boron is due to its covalent network structure. In boron family, gallium has the lowest melting point. The ionization energies do not follow the expected trend of decreasing values on descending the group. All elements burns in oxygen at high temperatures forming M_2O_3. The reaction of aluminium with oxygen (known as thermite reaction) is strongly exothermic.

Aluminium is amphoteric. It dissolves in dilute minerals acids and in aqueous sodium hydroxide.

The acidic character of hydroxides decreases on descending the group.

Boric acid is a very weak monobasic acid. It does not liberate hydrogen ion but accepts a hydroxyl ion. In the presence of cis-diol (glycerol, mannitol or sugars), boric acid behaves as a strong acid and can be titrated with NaOH in the presence of phenolphthalein indicator.

BF_3 is hydrolysed as follows:-

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$

$$\underline{12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O}$$

$$\underline{4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-}$$

The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Du to back bonding, the electron density on boron in increased. The tendency to form $p\pi$-$p\pi$ bond is maximum is BF_3 and falls rapidly on passing to BCl_3 to BBr_3. The increasing order of acid strength follows the order $BF_3 < BCl_3 < BBr_3$.

COMMON ELEMENTS AND THEIR COMPOUNDS

Boron

Boron belongs to Group 13 of the periodic table. The chief minerals of boron are borax ($Na_2[B_4O_5(OH)_4].8H_2O$), i.e., $Na_2B_4O_7$. $10H_2O$, colemanite ($Ca_2[B_3O_4(OH)_3]_2.2H_2O$) i.e., $Ca_2B_6O_{11}.5H_2O$ and kernite ($Na_2[B_4O_5(OH)_4].2H_2O$) i.e., $Na_2B_4O_7.4H_2O$.

Boron is isolated by converting its mineral into boron trioxide followed by its reduction with magnesium.

$$\underset{\text{borax}}{Na_2(B_4O_5(OH)_4).8H_2O} + 2HCl \longrightarrow 2NaCl + 5H_2O + \underset{\text{orthoboric acid}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow{\text{red heat}} B_2O_3 + 3H_2O$$

$$B_2O_3 + Mg \longrightarrow 2B + 3MgO$$

Crystalline boron is obtained by the reduction of boron trichloride with zinc or dihydrogen at the high temperatures.

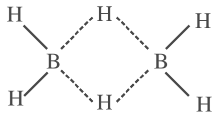
$$2BCl_3 + 3Zn \xrightarrow{1200\,K} 3ZnCl_2 + 2B$$

$$2BCl_3 + 3H_2 \xrightarrow{1200\,K} 2B + 6HCl$$

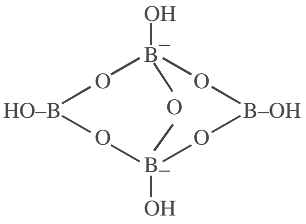
Boron is an extremely hard refractory solid of high melting point, low density and very low electrical conductivity. Boron is quite inert to chemical attack at ordinary temperature. It reacts with strong oxidising agents such as fluorine and concentrated HNO_3 at room temperature. At elevated temperatures, it combines with metals (forming borides) and nonmetals.

Diborane is B_2H_6. It has two coplanar BH_2 groups and the remaining two hydrogen atoms lie centrally between BH_2 groups in a plane perpenticular to the plane containing BH_2 groups.

In borax two boron atoms are in a trianglular geometry and two boron atoms are in tetrahedral geometry.



B_2H_6



$[B_4O_5(OH)_4]^{2-}$ ion in borax

Boric acid (H_3BO_3) is obtained by treating borax with minerals acids.

$$Na_2[B_4O_5(OH)_4].8H_2O + 2H^+ \longrightarrow 4H_3BO_3 + 5H_2O + 2Na^+$$

Boric acid is a white crystalline substance, soft and soapy to touch. It is moderately soluble in cold water. On heating it decomposes as follows:

$$H_3BO_3 \xrightarrow[-H_2O]{375\,K} \underset{\text{Metaboric acid}}{HBO_2}$$

$$4HBO_2 \xrightarrow[-H_2O]{435\,K} \underset{\text{Tetraboric acid}}{H_2B_4O_7}$$

$$H_2B_4O_7 \xrightarrow[-H_2O]{\text{red heat}} \underset{\text{Boric oxide}}{2B_2O_3}$$

Boric acid is a very weak monobasic acid. It does liberate hydrogen but accepts a hydroxyl ion, i.e., it behaves as a Lewis acid.

GROUP 14 ELEMENTS – CARBON FAMILY

Group 14 contains carbon (C), silicon (Si), germination (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is $(ns)^2\,(np)^2$, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is nonmetal but also has some metallic characterstics, and Sn and Pb are metals. The melting points decreases on descending the group, with the exception of Pb whose melting point is slightly higher than that of Sn. Carbon has extremely high melting point. This is due to the stronger C–C bonds in the network of carbon atoms. The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling d and f sub-shells.

Carbon forms single, double and triple bonds with carbon itself and with other elements. The tendency to form multiple bond by other elements is rare. However, silicon can form double bond due to back bonding in which the lone pair in p orbitals of an atom is extended to an empty orbital of Si. One of the examples of back bonding is trsilylamine, $N(SiH_3)_3$.

The chemical reactivity of elements decreases down the group. The inert effect becomes increasingly effective on descending the group.

The stability of +4 oxidation state decreases while that of the +2 oxidation state increases on descending the group.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$3Pb + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannate $[Sn(OH)_6]^{2-}$, and plumbate $[Pb(OH)_6]^{-2}$, respectively.

All the elements of Group 14 from tetrahalides with the exception of PbI_4 which is not known. The stability of halides decreases down the group. CCl_4 is stable while other halides are hydrolysed. The hydrolysed. The hydrolysis of $SiCl_4$ produces SiO_2 while SiF_4 produces SiO_2 as well as $(SiF_6)^{-2}$.

The acidic nature of the dioxdes of carbon family decreases down the group; CO_2 and SiO_2 are acidic, GeO_2 is weakly acidic and SnO_2 and PbO_2 are amphoteric.

Silicones are organosilicon polymers with general formula $(R_2SiO)_n$, where R may be methyl, ethyl or phenyl group.

COMMON ELEMENTS AND THEIR COMPOUNDS

Carbon Monoxide

The burning of carbon in a limited supply of air or in a deficiency of oxygen produces carbon monoxide. A few reactions producing carbon monoxide are as follows:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$\begin{array}{l}\text{COOH}\\ | \\ \text{COOH}\end{array} \xrightarrow{\text{concentrated } H_2SO_4} CO + CO_2 + H_2O$$

$$HCOOH \xrightarrow{\text{concentrated } H_2SO_4} CO + H_2O$$

$$CO_2 + Zn \xrightarrow[\text{heat}]{} CO + ZnO$$

$$K_4Fe(CN)_6 + \underset{\text{concentrated}}{6H_2SO_4} \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Carbon monoxide is an extremely poisonous gas. A concentration of one in 800 volume of air will lead to death in 30 minutes. It combines with haemoglobin of the blood to give more stable carboxyhaemoglobin and thus render it useless as an oxygen carrier. In air, it burns with a blue flame to give carbon dioxide. The gas readily dissolves in ammonical or acidic solution of cuprous chloride giving the additional product CuCl. CO. $2H_2O$. Some the reactions shown by carbon monoxide are given below.

$$CO + NaOH \xrightarrow[\text{heat}]{\text{pressure}} \underset{\text{sodium formate}}{HCOONa}$$

$$CO + Cl_2 \xrightarrow{hv} COCl_2$$

$$CO + 2H_2 \xrightarrow[425-675\,K]{ZnO + Cu\text{ powder}} CH_3OH$$

$$Fe_2O_3 + 3CO \xrightarrow{875-1175\,K} 2Fe + 3CO_2$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

The structure of carbon monoxide may be represented as

$$:\overset{-}{C}::\overset{+}{\ddot{O}}: \qquad \text{or} \qquad :C\equiv O:$$

Carbon atom is considered to be sp hybridized. One sp orbital used to form a single bond with oxygen atom while the other sp orbital which points away from the C–O bond contains a lone pair of electrons. The sideways overlap of singly filled 2p orbitals on carbon and oxygen atoms produces a π bond. The second π bond is formed by the overlap of doubly filled 2p orbitals on carbon and oxygen atoms produces a π bond. The second π bond is formed by the overlap of doubly filled 2p orbital on oxygen with the vacant 2p orbital on carbon. But once the bond is formed, it is not possible two distinguish the two π bonds.

Because of the directed lone pair of electrons on carbon, the molecule forms carbonyls with a number of metal in which the coordinate bond is formed through carbon atom and not through oxygen atom. With nickel, it forms tetracarbonyl which decomposes at higher temperature.

$$Ni + 4CO \underset{450\,K}{\overset{325-345\,K}{\rightleftharpoons}} [Ni(CO)_4]$$

The poisonous nature of carbon monoxide is due to its ability to form a bond with iron atom in the haemoglobin of blood. In the form of producer gas ($CO + N_2$), water gas ($CO + H_2$) or semiwater gas (mixture of producer and water gases), is used as fuel.

Carbon Dioxide

Carbon dioxide can be prepared by any of the following reactions.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

$$2NaHCO_3 \xrightarrow[\text{heat}]{} Na_2CO_3 + H_2O + CO_2$$

$$MgCO_3 \xrightarrow[\text{heat}]{} MgO + CO_2$$

Solid carbon dioxide is known as dry ice and is used as a refrigerant.

Carbon dioxide is an acidic oxide.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

With reactive metals, it is reduced to CO.

$$2Na + 2CO_2 \longrightarrow Na_2CO_3 + CO$$

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

Carbon dioxide is absorbed by green plants in the presence of sunlight and is ultimately transformed into starch and cellulose in the chloroplast. This process is known as photosynthesis.

Carbon dioxide is a linear molecule with carbon-oxygen ond equal to 115 pm, which is intermediate between those calculated for carbon-oxygen double and triple bond. It is thus cosidered to the resonance hybrid of the following structures.

$$:\ddot{O}::C::\ddot{O}: \longleftrightarrow :\overset{+}{O}:::C::\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}: \longleftrightarrow :\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}::C:::\overset{+}{O}:$$

Carbon in CO_2 is sp hybridized. The two sp orbitals form two bonds wiith two oxygen atoms. The two π orbital not included in hybridization give rise two π bonds.

Carbides

The are prepared by direct combination of metals with carbon at elevated temperature or indirectly, the heating of metallic oxide with carbon. The carbides may be classified into three groups, namely, ionic, covalent and interstitial. Ionic carbides are formed by metals of Group 1, 2 and 3.

These compounds, in general, occur as transparent crystals and in the solid state they are nonconductors of electric current. They give hydrocarbons when treated with water or acids. On the basis of anions, these have been classified as methanides (C^{4-}), acetylides (C_2^{2-}) and allylides. (C_3^{4-}).

The examples are:

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow Al(OH)_3 + 3CH_4$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_2C_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C_2H_2$$

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3C{\equiv}CH$$

Silicon

Silicon belongs to Group 14 and is classified as metalloid. It exists in two allotropic forms; the amorphous silicon and the crystalline or admantine silicon. Silicon does not occur freely in nature. It occurs as silica (SiO_2) or as silicates like feldspar, kaolinite, mica, etc. in rocks and clays.

Silicon is produced by the reduction of sand with coke in an electric arc furnace.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Silicon is a hard solid having melting point 1793 K and boiling point 3550 K. It reacts with fluorine at room temperature to form SiF_4. With other elements, it reacts at elevated temperatures.

Silicates and silica contains SiO_4^{4-} tetrahedra differing in the way the tetrahedra are linked together as described in the following.

Orthosilicates

These contain individual discrete SiO_4^{4-} tetrahedra. Examples are phenacite (Be_2SiO_4) and zircon ($ZrSiO_4$).

Pyrosilicates

These contain discrete $Si_2O_7^{6-}$ ions and are formed when one oxygen atom of two SiO_4 tetrahedra is shared. Example is thorteveitite ($Sc_2Si_2O_7$).

Chain and Cyclic Silicates

In these silicates two oxygen atoms per tetrahedron are shared.

Sheet Silicates

These are formed by the sharing of three oxygen atoms by each tetrahedron giving an infinite two-dimensional sheet of the empirical formula $(Si_2O_5)_n^{-2n}$

Three-Dimensional Silicates

In these silicates, all the four oxygen atom of a tetrahedron are shared with other tetrahedra resulting in a three-dimensional lattice. The formula of such silicates is SiO_2.

Silicones

Silicones are polymeric organosilicon compounds containing individual or cross-linked Si–O chains or rings in which some of the oxygens of SiO_4 tetrahedron are replaced by $-OH$, $-CH_3$, $-C_2H_5$ groups. For example, dialkyldichlorosilane (R_2SiCl_2), which is produced by the reaction

$$2RCl + Si(Cu) \longrightarrow R_2SiCl_2$$

reacts with water producing dialkyldihydrosilane. This, in turn, may be dehydrated to give a linear polymer.

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$

$$nR_2Si(OH)_2 \xrightarrow[-H_2O]{} \underset{\text{Silicone}}{(R_2SiO)_n}$$

Silicones have good thermal and oxidative stability. These are excellent water repellants and chemically inert substances. Silicon rubber is not attacked by ozone. Liquid silicones are used as excellent lubricants. These are mixed with paints and enamels to increase the resistance to the effects of high temperatures, sunlight and chemicals.

GROUP 15 ELEMENTS– NITROGEN FAMILY

Group 15 contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Their outer electronic configuration is $(ns)^2\,(np)^3$, where n varies from 2 to 6. The metallic character of these elements increases on descending the group; N and P are nonmetals, As and Sb are metalloids and Bi is a metal. The melting and boiling points follows the order

melting point	$N < P < As > Sb > Bi$
boiling point	$N < P < As < Sb > Bi$

Phosphorus has two common allotropic forms; white and red. White phosphorus is more reactive than red form due to highly strained structure (P–P–P angle is 60°).

Black phosphorus is a highly polymerised form and is most stable.

Nitrogen form triple bond in dinitrogen because bond enthalpy ε(N≡N) is greater than three times bond enthalpy ε(N–N). In phosphorus, the reverse is true, hence, it involves single bonds.

The melting points of hydrides follow the order

$$NH_3 > PH_3 < AsH_3 < SbH_3.$$

All the five elements of Group 15 form trihalides. Of these nitrogen halides are least stable. All the trihalides with the exception of NF_3 hydrolyse in aqueous solution.

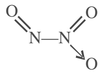
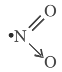
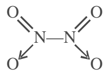
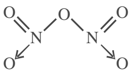
$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \longrightarrow SbO^+ + 2H^+ + 3Cl^-$$
$$BiCl_3 + H_2O \longrightarrow BiO^+ + 2H^+ + 3Cl^-$$

Nitrogen forms many oxides; N_2O, NO, N_2O_3, NO_2 and N_2O_5. The most common oxides of phosphorus are P_4O_6 and P_4O_{10}. Phosphorous trioxide is an acidic oxide and is anhydride of orthophosphorus acid (H_3PO_3). Phosphorus pentoxide in anhydride of phosphoric acid (H_3PO_4).

Nitrogen forms two acids; nitrous acid (HNO_2) and nitric acid (HNO_3). Phosphorus forms two series of oxoacids. These are phosphorous and phosphoric series. In phosphorous series, the acids include pyrophosphorous acid ($H_4P_2O_5$), orthophosphorous acid (H_3PO_3), metaphosphorous acid (HPO_2) and hypophosphorous acid (H_3PO_2). The acids $H_4P_2O_5$ and H_3PO_3 are reducing agents as they involve P–H bond.

In phosphoric series, the acids include orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and polymetaphosphoric acid, $(HPO_3)_n$.

Oxides of Nitrogen:

Name	Structure	Magnetic property	Nature	Physical appearance
1. Nitrous oxide, N_2O	$\dot{N}\equiv N\rightarrow \underset{\cdot\cdot}{\ddot{O}}:$	Diamagnetic	Neutral	Colourless gas
2. Nitric oxide, NO	$:\dot{N}=\ddot{O}:$ or $:N\overset{\cdot\cdot}{\equiv}O:$	Paramagnetic	Neutral	Colourless gas
3. Dinitrogen trioxide, N_2O_3		Diamagnetic	Acidic	Blue solid
4. Nitrogen dioxide, NO_2		Paramagnetic	Acidic	Reddish brown gas
5. Dinitrogen tetraoxide, N_2O_4		Diamagnetic	Acidic	Colourless solid
6. Dinitrogen pentaoxide, N_2O_5		Diamagnetic	Acidic	Colourless solid

Oxoacid of Nitrogen

Two oxacids of nitrogen are nitrous acid and nitric acid. Nitrous acid is unstable except in dilute solution. Pure nitric acid is a colourless liquid but on exposure to light it turns slightly brown because of slight decomposition into NO_2 and O_2. Nitric acid can be prepared by Brikeland-Eyde method in which N_2 and O_2 are sparked together in an electric furnace. The nitric oxide formed is converted to nitrogen dioxide when exposed to air. The dissolution of NO_2 in water gives nitric acid.

$$N_2 + O_2 \xrightarrow{\text{spark}} NO \xrightarrow{+O_2} NO_2 \xrightarrow{\text{water}} HNO_3.$$

Phosphorus Trioxide

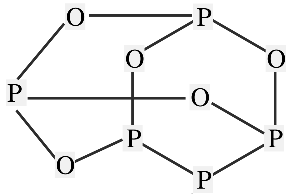
Burning of phosphorus in a limited supply of air gives phosphorus trioxide. It is a colourless crystalline solid with odour of garlic. It exists as dimer both in naphthalene and in the vapour phase.

It dissolves in cold water giving phosphorous acid (H_3PO_3) whereas in hot water it gives phosphoric acid (H_3PO_4) and phosphine (PH_3).

$$\underset{\text{Cold}}{P_4O_6 + 6H_2O} \longrightarrow 4H_3PO_3$$

$$\underset{\text{hot}}{P_4O_6 + 6H_2O} \longrightarrow 3H_3PO_4 + PH_3$$

In its structure, four P atoms lie at the corners of a tetrahedron and six oxygen atoms along the edges. The P–O bond distance is 165.6 pm which is shorter than the expected single bond distance (184 pm). This suggests that there exists a considerable double bond characcter in the P–O bonds because of the formation of a $p\pi$–$d\pi$ bond with oxygen donor.



Structuure of P_4O_6

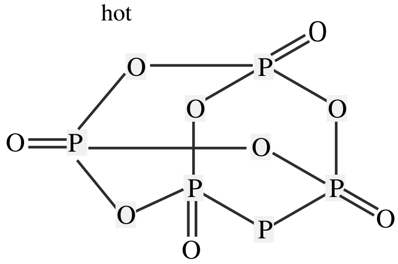
Phosphorus Pentoxide

Burning of phosphorus in an excess of dried air or oxygen gives phosphorus pentoxide. It is a white solid which sublimes on heating. It is odourless when pure. It dissolves in cold water giving metaphosphoric acid.

$$\underset{\text{cold}}{P_4O_{10} + 2H_2O} \longrightarrow 4HPO_3$$

With hot water, orthophophoric acid is formd.

$$\underset{\text{hot}}{P_4O_{10} + 6H_2O} \longrightarrow 4H_3PO_4$$



Structure of P_4O_{10}

It is a strong dehydrating agent. For example, H_2SO_4 and HNO_3 are converted into corresponding anhydride.

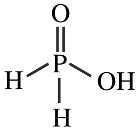
$$2H_2SO_4 + P_4O_{10} \longrightarrow 2SO_3 + 4HPO_3$$

$$4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$$

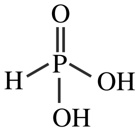
In the structure of P_4O_{10}, each P atom forms three bonds to oxygen atoms and also an additional coordinate bond with an oxygen atom. Terminal coordinate P–O bond is 143 pm which is much shorter than the expected bond length of 162 pm. The shows the presence of considerable pπ-dπ back bonding because of the leteral overlap of full p orbitals on oxygen with empty d orbitals on phosphorus.

Oxoacids of Phosphorus :-

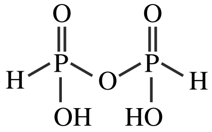
Hypophosphorus acid, H_3PO_2



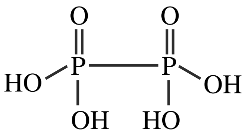
Phosphosrus acid, H_3PO_3



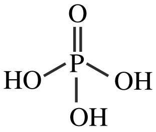
Pyrophosphorus acid, $H_4P_2O_5$



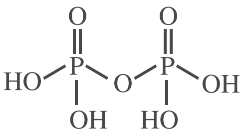
Hypophosphoric acid, $H_4P_2O_6$



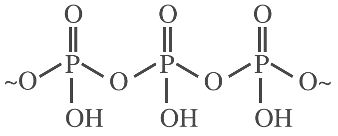
Phosphoric acid, H_3PO_4



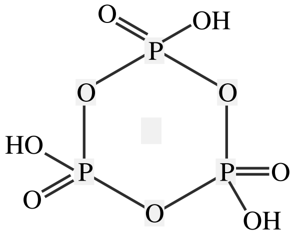
Pyrophosphoric acid, $H_4P_2O_7$



Metaphosphoric acid, HPO_3 or $(HPO_3)_n$



Cyclictrimetaphosphoric acid, $(HPO_3)_3$ or $H_3P_3O_9$



GROUP 16 ELEMENTS – OXYGEN FAMILY

Group 16 contains oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their electronic configuration is $(ns)^2$ $(np)^4$, where n varies from 2 to 6.

The metallic character of these elements increases on descending the group; O and S are nonmetallic, Se and Te are weaker nonmetallic and Po is metallic.

Electron affinity of sulphur is larger than that of oxygen, this due to the more repulsion experienced by the incoming electron from the smaller, more compact electronic cloud of oxygen atom.

Oxygen is diatomic with the unpaired electrons. Sulphur exists in two allotropic forms – rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature while monoclinic sulphur is stable above 369 K. Selenium exists in six allotropic forms. Tellurium has only one crystalline form and polonium has two allotropic forms (cubic and rhombohedral).

Ozone is another allotropic form of oxygen. It is very reactive. It is formed in the upper layer of atmosphere (about 20 km from the earth) by the action of ultraviolet radiation on oxygen. Ozone is a strong oxidizing agent. In organic chemistry, ozone is used to locate the carbon double and triple bonds. The ozone molecule is angular with bond angle about 117° and bond length 127.8 pm.

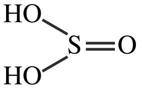
The melting and boiling point of hydrogen compounds of elements of Group 16 follow the order $H_2O > H_2S < H_2Se < H_2Te$. The exceptional high values of H_2O is due to hydrogen bondings.

H_2O_2 is a strong oxidizing agent. With stronger oxidizing agents such as $KMnO_4$, KIO_3, and O_2, hydrogen peroxide acts as a reducing agent.

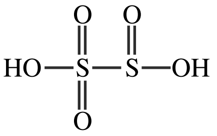
Oxoacids of sulphur may be classified into four series.

Sulphurous Acid Series

Sulphurous acid (H_2SO_3)

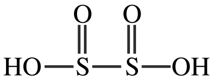


Di-or pyrosulphurous acid ($H_2S_2O_5$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{S}-OH}$$

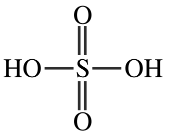
Dithionous acid ($H_2S_2O_4$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH}$$

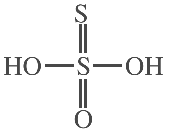
Sulphuric Acid Series

Sulphuric acid (H_2SO_4)



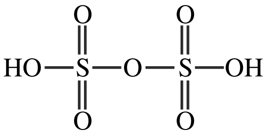
$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

Thiosulphuric acid ($H_2S_2O_3$)



$$\mathrm{HO-\overset{\overset{S}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

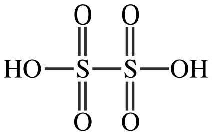
Di-or pyrosulphuric acid ($H_2S_2O_7$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

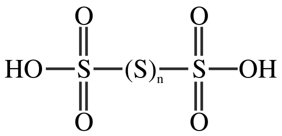
Thionic Acid Series

Dithionic acid ($H_2S_2O_6$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

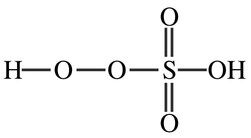
Polythionic acid ($H_2S_{n+2}O_6$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(S)_n-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

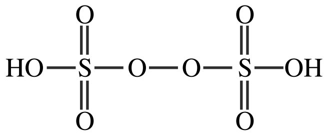
Peroxoacid Series

Peroxomonosulphuric acid (H_2SO_5)



$$\mathrm{H-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

Peroxodisulphuric acid ($H_2S_2O_8$)



$$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$$

GROUP 17 ELEMENTS–HALOGEN FAMILY

Group 17 contains fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Their outer electronic configuration is $(ns)^2(np)^5$, where n varies from 2 to 6. The trends in this group are as follows.

Covalent and ionic radii – *increases down the group.*

Electronegativity and ionization energy – *decreases down the group.*

Electron affiinity – Cl > F > Br > I

Melting and boiling points – *increases down the group.*

Bond enthalpy (X–X)– $Cl_2 > Br > F_2 > I_2$

Oxidizing ability – *decreases down the group.*

Halogens are very reactive and do not occur in free state. Fluorine is most electronegative atom, there exists hydrogen bondings in gaseous HF.

HF is a weak acid and HCl, HBr and HI behave as strong acids. In the glacial acetic acid medium, the acid strength follows the order HI > HBr > HCl > HF.

Halogens with the exception of F form a number of oxoacids– hypohalous acids (HOX), halous acids (HXO_2), halic acid (HXO_3) and perhalic acid (HXO_4). The acid strength follows the order $HXO_4 > HXO_3 > HXO_2 > HXO$. Fluorine forms only hypofluorous acid (HOF).

Halogens also form interhalogen compounds AX, AX_3, AX_5 and AX_7. The compounds AX and AX_3 are formed where the electronegativity is not very large. The compounds AX_5 and AX_7 are formed by large Br and I atoms surrounded by small atom F. The molecule AX_3 is T-shaped with two lone pair of electrons at the equilateral positions. The orientations of five pair of electrons around the atom A is trigonal bipyramidal. Interhalogens are more reactive than elemental halogens except fluorine.

The six pairs of electrons around atom A in AX_5 acquire octahedral orientation. The seven pairs of electrons around atom A in AX_7 acquire pentagonal bipyramidal orientation.

Halogens are nonmetallic and have high electron affinity. The nonmetallic character decreases down the group and iodine shows some metallic character. With metals, they form ionic compounds by accepting one electron and with nonmetals covalent compounds are formed by sharing an electron.

All halogens exhibit-1 oxidation state. Except fluorine, rest of the halogens also exhibit +1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative and thus there exists hydrogen bonding in HF with the result that it has exceptionally high melting and boiling points as compared to those of HCl, HBr and HI.

Because of high reactivity, halogens do not exist in the free state. The chief ore of flurine are fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluoroapatite ($Ca_2(PO_4)F$). Other halogens mainly occur in seawater as salt. Some sea weeds and sponges contain iodine as iodides. Chile slatpeter ($NaNO_3$) contains 0.02 – 1% iodide in the form of sodium iodate.

Fluorine was obtained by electrolysis of KF dissolved in anhydrous HF. The products H_2 and F_2 are collected separately so as to avoid explosion caused by combination of these two gases.

Chlorine, in the laboratory, can be prepared by the following methods:

1. Action of concentrated hydrochloric acid on manganese dioxide.
2. Oxidation of HCl by strong oxidizing agents such as $KMnO_4$ and $K_2Cr_2O_7$.

Bromine can be obtained by the oxidation of bromide with chlorine gas or manganese dioxide in the presence of concentrated sulphuric acid. Iodine can also be obtained by the oxidation of iodide.

Halogens are oxidizing agents, oxidizing power decreases down the group. Flourine is the most oxidizing in nature and can oxidize water to oxygen and ozone. With dilute alkalis, fluorine forms oxygen difluoride (OF_2) and with hot concentrated alkaliis flouride and oxyen are formed. The other halogens reacts with cold and dilute alkali solution to give hypohalites

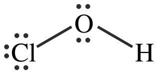
(XO^-) and with hot and concentrated alkali, halates (XO_3^-) are formed. Halogens react with metals and nonmetals to form halides, the reactivity decreases down the group.

All the halogens react with hydrogen to form hydrogen halides (HX). The reaction between flourine and hydrogen is violent while that between iodine and hydrogen is very slow at room temperature. The acidic character of hydrogen halides increases in the order, HF < HCl < HB_2 < HI.

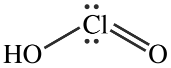
Oxoacids of Chlorine

Four oxoacids of chlorine are known. These are:

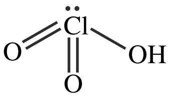
Hypochlorous acid, HOCl



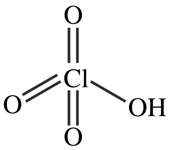
Chlorous acid, $HClO_2$



Chloric acid, $HClO_3$



Perchloric acid $HClO_4$



GROUP 18 ELEMENTS – NOBLE GASES

The Group 18 contains helium (He), neon (Ne), argon (Ar), krypton (Kr), xenone (Xe) and radon (Rn). Their outer electronic configurations is $(ns)^2(np)^6$ with the exception of the electronic configuration of He which is $1s^2$, all elements exist as monatomic gas.

Xenon forms a number of fluorides –XeF_2, XeF_4 and XeF_6. The other compounds are XeO_3, $XeOF_4$, XeO_2F_2, XeO_4 and $[XeO_6]^{4-}$

Solved Examples

1. Which species does not exist -

(a) $[BF_6]^{3-}$ (b) $[AlF_6]^{3-}$

(c) $[GaF_6]^{3-}$ (d) $[InF_6]^{3-}$

Sol.(a) $[BF_6]^{3-}$ does not exist because boron does not have vacant d-subshells.

2. Orthoboric acid when heated to red hot gives

(a) Metaboric acid (b) Pyroboric acid

(c) Boron and water (d) Boric anhydride

Sol.(d) $H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{160°C} H_2B_4O_7 + H_2O$

$$\downarrow$$

$$2B_2O_3 + H_2O$$

3. Alumnium vessels should not be washed with materials containing washing soda because -

(a) Washing soda is expensive.
(b) Washing soda is easily decomposed.
(c) Washing soda reacts with aluminium to form soluble aluminate.
(d) Washing soda reacts with aluminium to form insoluble aluminium oxide.

Sol.(c) $Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2O + CO_2$

$$2NaOH + 2Al + 2H_2O \longrightarrow \underset{\text{soluble}}{2NaAlO_2} + 3H_2.$$

4. When Al is added to KOH solution -

(a) No action takes place
(b) Oxygen gas is evolved
(c) Water is produced
(d) Hydrogen gas is evolved

Sol.(d) $2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$

5. Carbon forms carbon monoxide when burnt in -

(a) Absence of air or oxygen
(b) Excess of air or oxygen
(c) Limited supply of air or oxygen
(d) Moist air

Sol.(c) $C + \frac{1}{2} O_2 \text{ (limited)} \xrightarrow{\Delta} CO$

6. CCl_4 does not act as Lewis acid, while $SiCl_4$ and $SnCl_4$ acts as Lewis acid as well as their aqueous solution is acidic. Explain why?

Sol. $SiCl_4$ and $SnCl_4$ are hydrolysed to form acidic solution as well as they can act as Lewis acid because they can increase their co-ordination number greater than four due to availability of d-orbitals.

$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$
$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$
$SiCl_4 + 2Cl^- \longrightarrow (SiCl_6)^{-2}$

7. $PbCl_4$ exists while $PbBr_4$ and PbI_4 do not exist. Explain why?

Sol. Pb^{4+} is an oxidising agent and readily changes into Pb^{2+} (due to inert pair effect) while Br^- and I^- ions are reducing agents. Thus, redox reaction occurs indicating that $PbBr_4$ and PbI_4 are unstable compounds.

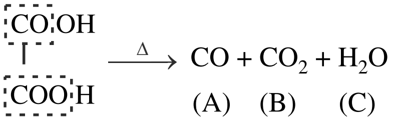
8. $\underset{\text{oxalic acid}}{H_2C_2O_4} \xrightarrow{\Delta} \text{gas(A)} + \text{gas(B)} + \text{liquid(C)}$

Gas (A) burns with blue flame and is oxidised to gas (B). Gas (B) turns lime water milky.

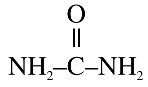
$\text{Gas(A)} + Cl_2 \longrightarrow \text{(D)} \xrightarrow{NH_3,\Delta} \text{(E)}$
$\text{(B)} \xrightarrow{NH_3,\Delta} \text{(E)}$

Identify (A) to (E) and explain the reactions.

Sol.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\Delta} \underset{(A)}{CO} + \underset{(B)}{CO_2} + \underset{(C)}{H_2O}$$



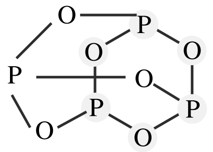
$$\underset{(A)}{CO} + Cl_2 \longrightarrow \underset{(D)}{COCl_2} \xrightarrow{NH_3,\Delta} \underset{\text{(E) Urea}}{NH_2\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}NH_2}$$

(A) is CO (B) is CO_2
(C) is H_2O (D) is $COCl_2$
(E) is NH_2CONH_2

9. In P_4O_6 the number of oxygen atoms bonded to each P atom is –

(a) 1.5 (b) 2
(c) 3 (d) 4

Sol.(c) Each P in P_4O_6 is bonded to 3 oxygen atoms.



10. Which trihalides is not hydrolysed by water -

(a) NF_3 (b) NCl_3
(c) PCl_3 (d) $AsCl_3$

Sol.(a) In the first stage of hydrolysis, an extra bond is formed by water molecule. While chlorine and the group 15 elements (except nitrogen) can expand their octet by using vacant d-orbitals of the valence shell, F and N cannot. As a result, NF_3 is extremely stable.

$NF_3 + H_2O \text{ (l)} \longrightarrow \text{No hydrolysis}$
$NCl_3 + 3H_2O \text{ (l)} \longrightarrow NH_3 + 3HOCl$
$PCl_3 + 3H_2O \text{ (l)} \longrightarrow H_3PO_3 + 3HCl$
$2AsCl_3 + 3H_2O \longrightarrow 6HCl + As_2O_3$

11. Derivatives of nitrogen (III) act as –

(a) Oxidizing agent only
(b) Reducing agent only
(c) Both Oxidizing and Reducing agent
(d) Nitrating agent

Sol.(c) Deriatives of nitrogen (III) have both oxidizing and reducing properties.

$$2Na^{+3}NO_2 + 2KI + 2H_2SO_4 \longrightarrow I_2 + 2\overset{+2}{N}O +$$

(Oxidant) $2K_2SO_4 + Na_2SO_4 + 2H_2O$

$$2KMnO_4 + \underset{\text{(Reductant)}}{5Na\overset{+3}{N}O_2} + 3H_2SO_4 \longrightarrow$$

$$2MnSO_4 + 5Na\overset{+5}{N}O_3 + K_2SO_4 + 3H_2O$$

12. In the compound of type POX_3, P atom show multiple bonding of the type –

(a) $p\pi - d\pi$ (b) $d\pi - d\pi$

(c) $p\pi - p\pi$ (d) No multiple bonding

Sol.(a) POX_3 has sp^3 hybridised P having vacant d-orbitals. p-orbital of O atom and d-orbitals of P undergoes $p\pi$-$d\pi$ bonding.

13. With the help of NH_3, O_2, Pt and H_2O, write equations for preparation of N_2O from these substances.

Sol. $4NH_3(g) + 5O_2(g) \xrightarrow{\text{Pt.}} 4NO(g) + 6H_2O(g)$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq.) + NO(g)$

$HNO_3(g) + NH_3(aq.) \longrightarrow NH_4NO_3(aq.)$

$NH_4NO_3(aq.) \xrightarrow{\Delta} NH_4NO_3(s)$

$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O\ (g)$

14. Which of the following is a laboratory method of preparation of oxygen?

(a) heating of $KClO_3$

(b) from liquid air

(c) by electrolysis of water

(d) by Brin's process

Sol.(a) The other three methods are employed for large production of O_2 for industrial applications.

Note: In Brin's process BaO is heated to get BaO_2 at 500ºC which is decomposed at 800ºC to give oxygen.

15. The catalyst used during decomposition of H_2O_2 is –

(a) Ni (b) Fe

(c) MnO_2 (d) Pt

Sol.(c) $2H_2O_2 \xrightarrow[\Delta]{MnO_2\ \text{Catalyst}} 2H_2O + O_2$

16. H_2O is liquid while H_2S is gas under given conditions. Explain why?

Sol. H_2O molecules have intermolecular H – bonding due to greater electronegativity of oxygen hence H_2O is liquid. H_2S lacks H – bonding. H_2S molecules are held by weak inter molecular vander waal's force of attraction.

17. O_3 is a powerful oxidising agent. Write equations to represent oxidation of –

(a) I^- to I_2 in acidic solutions.

(b) Sulphur to sulphuric acid in the presence of moisture

(c) $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in basic solution.

Sol. (a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$

(b) $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$

(c) $O_3 + 2[Fe(CN)_6]^{4-} + H_2O \longrightarrow$

$2[Fe(CN)_6]^{3-} + 2OH^- + O_2$

18. Explain why sugar turns black on addition of concentric H_2SO_4.

Sol. Concentric H_2SO_4 removes water molecules from sugar leaving behind black carbon because of its strong dehydrating nature.

$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11\ H_2O.$

19. The reaction of chlorine with CO in the presence of sunlight gives –

(a) $COCl_2$ (b) CO_2Cl_2

(c) HOCl (d) $H_2Cl_2O_2$

Sol.(a) $CO + Cl_2 \longrightarrow COCl_2$

20. Excess of Cl_2 reacts with ammonia, products formed are :

(a) NH_3 and N_2 (b) NCl_3 and HCl

(c) NCl_3 and N_2 (d) NH_4Cl and N_2

Sol.(b) $NH_3 + \underset{\text{(excess)}}{Cl_2} \longrightarrow NCl_3 + 3HCl$

21. Bromine is added to cold dilute aqueous solution of NaOH. The mixture is boiled. Which of the following statements is true?

(a) During the reaction bromine is present in four different oxidation states.

(b) The greatest difference between the various oxidation states of bromine is 5.

(c) on acidification of the final mixture, bromine is formed.

(d) Disproportionation of bromine occurs during the reaction.

Sol.(d) $6NaOH + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 +$

$3H_2O$ (disproportionation)

22. Which reaction cannot be used for the preparation of the halogen acid?

(a) $2KBr + H_2SO_{4\,(conc.)} \longrightarrow K_2SO_4 + 2HBr$
(b) $NaCl + H_2SO_{4\,(conc.)} \longrightarrow NaHSO_4 + HCl$
(c) $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$
(d) $CaF_2 + H_2SO_{4\,(conc.)} \longrightarrow CaSO_4 + 2HF$

Sol.(a) HBr is strong reducing agent and will be oxidised by H_2SO_4 an oxidant

23. Which of the following reactions will give bleaching powder?

(a) $CaCl_2 + H_2O$ (b) $CaO + HCl$
(c) $Ca(OH)_2 + Cl_2$ (d) $ClO_2 + Ca(OH)_2$

Sol.(c) $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$
Slaked lime Bleaching powder

24. I_3^- is formed when I_2 combines with I^-. Which of them is a Lewis base?

Sol. $I_2 + I_3^- \longrightarrow I_3^-$, I^- behaves as a Lewis base.

25. The statement, which prompted Neil Barlett to prepare the first noble gas compound was –
(a) Xe-F bond has high bond energy
(b) F_2 has exceptionally low bond energy
(c) PtF_6 is a strong oxidant
(d) O_2 molecule and Xe atom have very similar ionization energies.

Sol.(d) Both Xe and O_2 have comparable ionization energies.

$Xe \longrightarrow Xe^+ + e^-$;
Ionization energy = 1,170 kJ/mol
$O_2 \longrightarrow O_2^+ + e^-$;
Ionization energy = 1,175 kJ/mol

Exercise

LEVEL I

1. Amorphous boron is extracted from borax by following steps:

$$\text{Borax} \xrightarrow{(x)} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow{(Y)} \text{Boron}$$

Then X and Y are:

(a) H_2SO_4, Al (b) HCl, C
(c) HCl, Fe (d) H_2SO_4, Na

2. In which of the following compounds B atoms are in sp^2 and sp^3 hybridisation states?

(a) Borax (b) Diborane
(c) Borazole (d) All

3. Which of the following statement is not correct about CO ?
(a) Producer gas is the mixture of CO + N_2
(b) CO formes a volatile compound with Nickel.
(c) CO is absorbed by ammonical solution of Cu_2Cl_2
(d) CO and Cl_2 form phosphine gas in presence of sunlight.

4. $H_2C_2O_4 \xrightarrow[H_2SO_4]{Conc.} A + B$. A is neutral and B is acidic. Gases A and B are absorbed by conc.:

(a) $CuCl_2$, KOH (b) Cu_2Cl_2, KOH
(c) KOH, Cu_2Cl_2 (d) $CuCl_2$, H_2SO_4

5. Which of the following is covalent carbide?

(a) CaC_2 (b) Al_4C_3
(c) SiC (d) Be_2C

6. Product formed by catalytic oxidation of NH_3 by air is:

(a) N_2 (b) NO
(c) N_2O (d) N_2O_3

7. Which one of the following properties is not shown by NO?
(a) It combines with oxygen to from nitrogen dioxide.
(b) It's bond order is 2.5.
(c) It is diamagnetic in gaseous state.
(d) It is a neutral oxide.

8. $P_4 + Cl_2 \rightarrow A$
P_4 + Excess $Cl_2 \rightarrow B$.
Hydrolysis products of A and B are respectively:
(a) H_3PO_2, H_3PO_3 (b) H_3PO_4, H_3PO_3
(c) H_3PO_3, H_3PO_4 (d) H_3PO_2, H_3PO_4

9. Holme's signal can be given by using:
(a) $CaC_2 + CaCN_2$ (b) $CaC_2 + Ca_3P_2$
(c) $CaC_2 + CaCO_3$ (d) $Ca_3P_2 + CaCN_2$

10. Nitrogen cannot be obtained by heating:

(a) $Ba(N_3)_2$ (b) $Pb(NO_3)_2$
(c) $(NH_4)_2Cr_2O_7$ (d) NH_4NO_2(s)

11. Which of the following statements is wrong?

(a) Single N–N bond is stronger than the single P–P bond.

(b) PH_3 can act as a ligand in the formation of coordination compound with transition elements.

(c) NO_2 is paramagnetic in nature.

(d) Covalency of nitrogen in N_2O_5 is four.

12. The nitrogen oxide(s) that do(es) not contain(s) N–N bond(s) are:

(a) N_2O (b) N_2O_3

(c) N_2O_4 (d) N_2O_5

13. Impure phosphine is combustible due to presence of:

(a) P_2H_4 (b) N_2

(c) PH_5 (d) P_2O_5

14. Extra pure N_2 can be obtained by heating:

(a) NH_3 with CuO (b) NH_4NO_3

(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

15. Ammonia can be dried by:

(a) Conc. H_2SO_4 (b) P_4O_{10}

(c) CaO (d) Anhydrous $CaCl_2$

16. Which metal sticks on glass in contact with ozone?

(a) Ag (b) Au

(c) Pt (d) Hg

17. What is true about $H_2S_nO_6$(polythionic acid)?

(a) Total S-S bond = n

(b) Number of S with 'O' state = n – 1

(c) Number of S with +5 state = n – 2

(d) Number of $d\pi$-$p\pi$ bond = 4

18. In which of the following reactions, is there a change in the oxdiation number of nitrogen atoms?

(a) $2NO_2 \longrightarrow N_2O_4$

(b) $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

(c) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

(d) $N_2O_5 + H_2O \longrightarrow 2HNO_3$

19. Atom 'X' belong to group VII A and is not present in the second period. Choose incorrect statement regarding 'X':

(a) The most acidic oxyacid of X is HXO_3.

(b) Its highest oxidation state is +7.

(c) It can form compounds with other elements of its group.

(d) The pH of aqueous solution of its oxides is less than 7.

20. Which of the following speices is not a pseudohalide?

(a) CNO^- (b) $RCOO^-$

(c) CN^- (d) N_3^-

21. Which interhalogen compound exists in dimeric form?

(a) BrF_5 (b) IF_7

(c) ICl (d) ICl_3

22. Which of following halogen oxides is ionic?

(a) I_4O_9 (b) I_2O_5

(c) BrO_2 (d) ClO_3

23. Which of the following is not oxidised by MnO_2?

(a) F^- (b) Cl^-

(c) Br^- (d) I^-

24. Which pair of Halogen will not give disproportionation reaction with water?

(a) F_2, I_2 (b) Cl_2, Br_2

(c) Br_2, I_2 (d) Cl_2, F_2

25. F_2 being the strongest oxidising agent among halogen is due to:

(a) Highest hydration energy

(b) Low bond dissociation energy

(c) High electron affinity

(d) All of these

26. The state of hybridisation of Xe and Sb in the product, when XeF_4 react with SbF_5 respectively:

(a) sp^2d^2, sp^3d (b) sp^3d, sp^3d^2

(c) sp^3, sp^3d^2 (d) sp^3d^3, sp^3d

27. Which fluoride is isostructural with ICl_2^- ?

(a) XeF_4 (b) XeF_6

(c) XeF_2 (d) XeF_8^{2-}

28. Which of the following compound does not exist?

(a) KrF_2 (b) XeO_2F_2

(c) XeO_3 (d) NeF_2

29. The hybrid states of C in diamond and graphite are respectively:

(a) sp^3, sp^3 (b) sp^2, sp^2

(c) sp^2, sp^3 (d) sp^3, sp^2

30. The compound $H_2N—Hg—O—Hg—I$ is formed by the action of:

(a) NH_3 and HgO in the presence of iodine
(b) NI_3, HgO and H_2O
(c) $NH_3 + K_2HgI_4$
(d) $KI + NH_3 + Hg$

31. The part of the skin which comes in contact with nitric acid turns yellow because:

(a) proteins are converted into xanthoproteins.
(b) water is removed by the acid.
(c) skin gets burnt.
(d) nitrocellulose is formed.

32. Which halide of boron is a weakest Lewis acid?

(a) BCl_3 (b) BI_3
(c) BF_3 (d) BBr_3

33. Which of the following compounds of nitrogen is coloured?

(a) NO_2 (b) NH_3
(c) N_2O (d) N_2O_4

34. The number of lone pairs, and the number of S—S bonds in S_8 molecules are respectively:

(a) 8, 8 (b) 16, 8
(c) 8, 16 (d) 8, 4

35. Bond energy is highest for which of the following:

(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2

LEVEL II

1. Which of the following is an incorrect statement for Boric acid:

(a) It gives $B(OCH_3)_3$ when reacts with CH_3–OH.
(b) Hydrogen bonding in H_3BO_3 gives it a layered structure
(c) It is bronsted acid
(d) It can be prepared by reaction of borax with mineral acid.

2. $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} X + NaBO_2 + H_2O$

$X + Cr_2O_3 \xrightarrow{\Delta} Y$ (green coloured).

The X and Y are:

(a) Na_3BO_3 and $Cr(BO_2)_3$
(b) $Na_2B_4O_7$ and $Cr(BO_2)_3$
(c) B_2O_3 and $Cr(BO_2)_3$
(d) B_2O_3 and $CrBO_3$

3. $B_2H_6 + \underset{\text{(Lewis bases)}}{2} \longrightarrow 2BH_3L$ (L is a lewis base)

L would be:

(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

4. Which of the following is an incorrect statement about boric acid:

(a) Polymerises due to H-bonding
(b) Gives green flame with ethyl alcohol
(c) Act as strong acid with trans-1, 2-diol
(d) Weak, monobasic, lewis acid

5. CO_2 is gas, while SiO_2 is a solid but both are:

(a) Covalent containing π-bond
(b) Molecules having $p\pi$–$d\pi$ bonding
(c) Acidic
(d) Discrete molecules

6. If one mole P_4 completely reacts with NaOH solution then the incorrect statement among the following is:

(a) Products are NaH_2PO_2 and PH_3
(b) Total number of P–H bonds in products are 5
(c) It is a disproportination reaction
(d) None of the above

7. At 0°C, NO_2 is :

(a) Paramagnetic, Coloured gas
(b) Diamagnetic, Coloured gas
(c) Diamagnetic, Colourless solid
(d) Paramagnetic, Coloured solid

8. $Ca_3P_2 + H_2O \longrightarrow A + B_{(gas)}$

$B + HI \rightarrow C \xrightarrow[\Delta]{} B + KI + H_2O$

B, C, D are:

(a) P_2H_4, PH_4I, KNO_3 (b) PH_3, PH_4I, KOH
(c) H_3PO_2, I_2, KOH (d) PH_3, P_2H_4, $KClO_3$

9. NH_3 is not obtained by:

(a) Heating of NH_4NO_3 or NH_4NO_2
(b) Heating of NH_4Cl or $(NH_4)_2CO_3$
(c) Heating of NH_4NO_3 with NaOH
(d) Reaction of AlN or Mg_3N_2 or $CaCN_2$ with H_2O

10. Which of the following statements is wrong?

(a) The stability of hydrides increase from NH_3 to BiH_3 in group 15 of the periodic table.
(b) Nitrogen cannot form NCl_5.
(c) Single N–N bond is weaker than the single P–P bond.
(d) N_2O_4 has two resonance structure.

11. $(NH_4)_2Cr_2O_7$ on heating liberates a gas. The same gas will be obtained by:

(a) Heating NH_4NO_2
(b) Heating NH_4NO_3
(c) Treating H_2O_2 with $NaNO_2$
(d) Treating Mg_3N_2 with H_2O

12. When Cl_2 reacts with NH_3 of low concentration and of high concentration, then oxidised products obtained from NH_3 are ____ and _____ respectively:

(a) N_2, NH_2Cl (b) NCl_3, N_2
(c) N_2H_4, N_2 (d) N_2, NH_4Cl

13. The incorrect statement(s) about O_3 is (are):

(a) O–O bond lengths are equal.
(b) Thermal decomposition of O_3 is endothermic.
(c) O_3 is diamagnetic in nature.
(d) O_3 has a bent structure.

14. Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified dichromate paper green while Z turns lead acetate paper black. So, A and B compounds are respectively:

(a) Na_2SO_3, Na_2S
(b) NaCl, Na_2CO_3
(c) Na_2S, Na_2SO_3
(d) Na_2SO_4, K_2SO_3

15. When H_2SO_4 reacts with Cl_2 gas then X is produced. X is a good chlorinating agent and given H_2SO_4 after hydrolysis. Then [X] is:

(a) $SOCl_2$ (b) SO_2Cl_2
(c) SCl_2 (d) S_2Cl_2

16. Gaseous products formed when Zn react with dil. H_2SO_4 and conc. H_2SO_4 respectively:

(a) H_2S, SO_2 (b) H_2 and SO_2
(c) SO_2 and H_2 (d) SO_3, H_2S

17. Which of the following process is not feasible spontaneously?

(a) $F_2 + H_2O \rightarrow HF + O_2$
(b) $Cl_2 + H_2O \rightarrow HCl + HOCl$
(c) $Br_2 + H_2O \rightarrow HBr + HOBr$
(d) $I_2 + H_2O \rightarrow HI + HOI$

18. Molecular size of I-Cl and Br_2 is nearly same but boiling point of I-Cl is about 40°C higher than Br_2. This might be due to:

(a) I–Cl bond is stronger than Br–Br–bond
(b) Ionisation energy of I < ionisation energy of Br
(c) I-Cl is polar whereas Br_2 is non polar
(d) Size of I > size of Br

19. When chlorine is passed slow over dry slaked like $Ca(OH)_2$ at room temperature, the main product is:

(a) $CaCl_2$ only (b) $CaOCl_2$
(c) $Ca(ClO_2)_2$ (d) $Ca(OCl)_2$ only

20. Which of the following is not correct?

(a) Among halogens, radius ratio between iodine and fluorine is maximum
(b) All halogens have weak X–X bond than X–X' bond in interhalogens
(c) Among interhalogen compounds maximum number of atoms are present in iodine fluroide.
(d) Interhalogen compounds are more reactive than halogen compounds.

21. Which of the following order is not correct ?

(a) $F^- < Cl^- < Br^- < I^-$ reducing nature
(b) $F^- > Cl^- > Br^- > I^-$ hydration energy
(c) $Cl_2 > F_2 > Br_2 > I_2$ bond dissociation energy
(d) $F_2 > Cl_2 > Br_2 > I_2$ reactivity

22. What should be the correct statement with respect to XeF_5^-?

(a) Central atom Xe has sp^3d^2 hybridisation
(b) It is square planar
(c) There are two non bonding electron pairs, one above the plane and the other below the plane
(d) It is an odd electron species

23. XeF_4 act as fluoride acceptor with:

(a) PF_5 (b) SbF_5
(c) KF (d) All of these

24. What is not true for ozone?

(a) The two O—O bond lengths are not equal.
(b) O—O bond order is between 1 and 2.
(c) O—O—O angle is approximately 117°.
(d) It is light blue gas with pungent odour.

25. The formation of which of the substance is known as tailing of mercury?

(a) Hg_2O (b) HgO
(c) Hg_2O_3 (d) $Hg(NO_3)_2$

26. Heating of which of the following nitrate produces a gaseous substance which is used as anaesthetic in dental surgery?

(a) NH_4NO_2 (b) $Pb(NO_3)_2$

(c) NH_4NO_3 (d) $NaNO_3$

27. Which allotropic form of phosphorus is good conductor of electricity?

(a) Yellow phosphorus

(b) Red phosphorus

(c) Black phosphorus

(d) None of these

28. The inertness of nitrogen is due to:

(a) Its intermediate electronegativity.

(b) High bond dissociation energy of nitrogen-nitrogen bond.

(c) Stable configuration of N atom.

(d) Small atomic size.

29. Which is not true for phosphorus?

(a) Phosphorus exists in different allotropic forms.

(b) Black phosphorus has layer type structure.

(c) White phosphorus is less reactive than red phosphrous.

(d) White phosphorus exists in tetrahedral molecular solid.

30. What is not true about N_2O_5?

(a) It is anhydride of HNO_3.

(b) In solid stable it exists as $NO_2^+ NO_3^-$.

(c) It is structurally similar to P_2O_5.

(d) It can be prepared by heating HNO_3 over P_2O_5.

31. Sulphur does not exist as S_2 molecule because:

(a) it is less electronegative.

(b) it is not able to constitute $p\pi$-$p\pi$ bond.

(c) it has ability to exhibit catenation.

(d) of tendency to show variable oxidation states.

32. Among the oxo-acids of chlorine, the correct order of increasing acid strength is:

(a) $HClO_4 < HClO < HClO_2 < HClO_3$

(b) $HClO_3 < HClO_2 < HClO_4 < HClO$

(c) $HClO_4 > HClO_3 > HClO_2 > HClO$

(d) $HClO_4 < HClO_3 < HClO_2 < HClO$

33. The ease of liquification of noble gases decreases in the order

(a) Xe > Kr > Ar > Ne > He

(b) He > Ne > Ar > Kr > Xe

(c) Xe > Ar > Kr > Ne > He

(d) Xe > He > Kr > Ar > Ne

34. XeF_6 on complete hydrolysis gives:

(a) XeO_4 (b) $XeOF_2$

(c) $XeOF_4$ (d) XeO_3

35. XeF_6 on reaction with CsF gives:

(a) $[XeF_5]^+ [CsF_2]^-$

(b) XeF_8

(c) $[XeF_4]^{2+} [CsF_3]^{2-}$

(d) $Cs^+[XeF_7]^-$

LEVEL III

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Select the correct statement(s)

(a) Graphite is diamagnetic and diamond is paramagnetic in nature.

(b) Graphite acts as a metallic conductor along the layers of carbon atoms.

(c) Graphite is less denser than diamond.

(d) C_{60} is called as Buckminster fullerene.

2. Borax bead test is given by:

(a) An aluminium salt (b) A cobalt salt

(c) A copper (II) salt (d) A nickel salt

3. Which of the following species exists:

(a) $[BF_6]^{3-}$ (b) $[AlF_6]^{3-}$

(c) $[GaF_6]^{3-}$ (d) $[lnF_6]^{3-}$

4. A complex cross-linked polymer (silicone) is formed by:

(a) Hydrolysis of $(CH_3)_3SiCl$

(b) Hydrolysis of a mixture of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$

(c) Hydrolysis of CH_3SiCl_3

(d) Hydrolysis of $SiCl_4$

5. White phosphorus be removed from red phosphorus by:

(a) Sublimation under reduced pressure

(b) Dissolving in water

(c) Dissolving in CS_2

(d) Heating with an alkali solution

6. A gas is obtained on heating ammonium nitrate. Which of the following statements are incorrect about this gas?

(a) Causes laughter
(b) Brings tears to the eyes
(c) Is acidic in nature
(d) Is basic in nature

7. Which of the following represents correct dissociation of nitrate salts on heating?

(a) $2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2} O_2$
(b) $Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + \frac{1}{2} O_2$
(c) $NH_4NO_3 \longrightarrow N_2O + 2H_2O$
(d) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

8. Which of the following is/are correct regarding nitrogen family?

(a) Nitrogen is restricted to a maximum covalency of 4 as only four orbitals are available for bonding.
(b) The single N–N bond is weaker than the single P–P bond.
(c) The catenation tendency is weaker in nitrogen as compared to phosphorous.
(d) Nitrogen forms $p\pi$-$p\pi$ bond as well as $p\pi$-$d\pi$ bonds.

9. P_2O_5 can dehydrate:

(a) H_2SO_4 (b) HNO_3
(c) $HClO_4$ (d) HPO_3

10. Which statements are correct about halogen?

(a) They are all diatomic and form univalent ions.
(b) Halogen have the smallest atomic radii in there respective periods.
(c) They are all diatomic and form diatomic ions.
(d) They are all reducing agents.

11. In the reaction $2Br^- + X_2 \longrightarrow Br_2 + 2X^-$, X_2 is/are:

(a) Cl_2 (b) F_2
(c) I_2 (d) N_2

12 Among the following which reactions are possible

(a) $F_2 + H_2O \longrightarrow HF + O_2$
(b) $Cl_2 + H_2O \longrightarrow HCl + HClO$
(c) $Br_2 + H_2O \longrightarrow HBr + HBrO$
(d) $I_2 + H_2O \longrightarrow HI + HIO$

13. Which of the following inter-halogen compounds is/are possible?

(a) ClF_3 (b) IF_5
(c) FCl_3 (d) BrF_5

PASSAGE-BASED QUESTIONS

Passage # 1 (Q. 14 and 15)

Species having X—O—H linkage (X = non metal with positive oxidation state) are called oxy acids and parent acid of a non-metal may exist in two form (a) –ic form of parent oxy acid (b) -us form of parent oxy acid.

14. Which of the following parent oxy acid does not have its pyro-oxy acid?

(a) H_2SO_3 (b) HNO_3
(c) H_3PO_3 (d) H_4SiO_4

15. X—O—X bond (where X = central atom) is not present in species.

(a) Cl_2O_7 (b) $H_2N_2O_2$
(c) N_2O_5 (d) $H_2S_2O_7$

Passage # 2 (Q. 16 and 17)

The property of hydrides of p-block elements mostly depends on:

(i) electronegativity difference between central atom and hydrogen,
(ii) size of central atom, and
(iii) number of valence electrons in central atom.

Some undergo hydrolysis in which central atom is less electronegative, react with OH^- to give hydrogen. While acidic property of hydride in a period depends on electronegativity of central atoms, i.e. more electronegative the atom, more acidic is the hydride. In a group, acidic property is proportional to size of the central atom. Some electron deficient hydrides behave as Lewis acid while only one hydride of an element in p-block behaves as Lewis base with lone pair of electrons. Hydrides in which central atom's electronegativity is close to hydrogen has no reaction with water.

16. Which one is the weakest acid among the following?

(a) HF (b) HCl
(c) HBr (d) HI

17. Which one is strongest base?

(a) OH^- (b) HS^-
(c) HSe^- (d) HTe^-

Passage # 3 (Q. 18 and 19)

An orange solid (A) on heating gives a green residue (B), a colourless gas (C) and water vapours. The dry gas (C) on passing over heated Mg gave a white solid (D), (D) on reaction with water gave a gas (E) which formed black precipitate with mercurous nitrate solution.

18. Select the incorrect statement.

(a) The central atom of the anion of solid (A) has d^3s hybridisation.

(b) The orange solid (A) is diamagnetic in nature.

(c) The anion of orange solid (A) is oxidising in nature.

(d) All metal oxygen bond lengths are equal in anion of solid (A).

19. Which of the following is false for the gas (E)?

(a) It gives a deep blue colouration with $CuSO_4$ solution.

(b) It is oxidised to a colourless gas (neutral oxide) at 1200 K in presence of a catalyst Pt/Rh in air.

(c) It gives the same gas (C) with potassium permanganate solution.

(d) It gives black precipitate with $HgCl_2$.

INTEGER VALUE TYPE QUESTIONS

20. Consider a prototypical fullerence C_{60}.

Let, a = Number of 5-membered rings;

b = Number of 6-membered rings;

c = Number of π-bonds in C_{60}.

Find the value of (3a – 2b + c)

21. Central atom may exhibit sp^3 hybridisation in how many of the following species:

(a) CO_2	(b) Graphite
(c) Diamond	(d) CO
(e) H_3BO_3(aq)	(f) Zeolites (Si-central)
(g) Silicones (Si)	(h) Chlorosilane (Si)
(i) Borax (Boron)	(j) Al_2Cl_6
(k) B_2H_6	(l) SiO_2(solid)
(m) H_2CO_3	(n) $COCl_2$
(o) CH_4	(p) CCl_4

22. Which of the following compounds are amphoteric in nature?

PbO, PbO_2, SnO, SnO_2, Al_2O_3, ZnO, BeO, Ga_2O_3, B_2O_3.

23. What is the number of oxygen atoms which are shared between tetrahedrons in $Si_3O_9^{6-}$?

24. How many of the following properties increase down the group for nitrogen family?

(a) Atomic size

(b) Acidic character of oxides

(c) Boiling point of hydrides

(d) Reducing power of hydrides

(e) Extent of $p\pi$-$p\pi$ overlap

(f) Metallic character

25. Number of gaseous oxides among the following at room temperature is:

(a) N_2O	(b) NO
(c) N_2O_3	(d) NO_2
(e) N_2O_5	(f) P_4O_6
(g) P_4O_{10}	(h) SO_2
(i) SO_3	

26. The number of mixed anhydride among the following are:

Cl_2O; ClO_2; Cl_2O_6; Cl_2O_7; N_2O_5; NO_2; N_2O

27. How many ion in following behave like pseudohalide?

CN^-, SCN^-, I_3^-, O^{-2}, N_3^-, CNO^-, $S_2O_3^{-2}$, $C_2O_4^{-2}$

MATCH THE COLUMN TYPE QUESTIONS

28.

	Column I		Column II
(A)	Hypo phosphoric acid	(P)	All hydrogen are ionizable in water
(B)	Pyro phosphorus acid	(Q)	Lewis acid
(C)	Boric acid	(R)	Monobasic in water
(D)	Hypo phosphrous acid	(S)	sp^3 hybridized central atom

29.

	Column I	Column II	
	Silicates	Number of oxygen atoms shared per tetrahedron	
(A)	Ortho silicate	(P)	4
(B)	Pyro silicate	(Q)	1
(C)	Cyclic silicate	(R)	0
(D)	3-D silicate	(S)	2

30. Match the reactions island in column-I with characteristic(s) type of reactions listed in column-II.

	Column-I		**Column-II**
(A)	$PCl_5 \xrightarrow[\text{Air}]{\text{Moist}}$	(P)	Hydrolysis
(B)	$P_4 + NaOH(conc.) + H_2O \xrightarrow{\text{Warm}}$	(Q)	At least one of the products has tetrahedral geometry
(C)	$H_3PO_3 \xrightarrow{200°C}$	(R)	Disproportionation
(D)	$P_4O_6 + H_2O \xrightarrow{200°C}$	(S)	At least one of the products has $p\pi$-$d\pi$ bonding

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. KF combines with HF to form KHF_2. The compound contains the species:

(a) K^+, F^- and H^+ (b) K^+, F^- and HF

(c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

[IIT-1996]

2. The following acids have been arranged in the order of decreasing acidic strength. Identify the correct order.

ClOH (I), BrOH (II), IOH (III)

(a) I > II > III (b) II > I > III

(c) III > II >I (d) I > III > II

[IIT-1996]

3. Which one of the following species is not a pseudo halide?

(a) CNO^- (b) $RCOO^-$

(c) OCN^- (d) NNN^-

[IIT-1997]

4. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl — E — Cl for different E are in the order:

(a) B > P = As = Bi (b) B > P > As > Bi

(c) B < P = As = Bi (d) B < P < As < Bi

[IIT-1999]

5. Ammonia can be dried by:

(a) conc. H_2SO_4 (b) P_4O_{10}

(c) CaO (d) anhydrous $CaCl_2$

[IIT-2000]

6. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is:

(a) H_2O because of hydrogen bonding

(b) H_2O because of higher molecular weight

(c) H_2S because of hydrogen bonding

(d) H_2Se becuase of lower molecular weight

[IIT-2000]

7. The number of P—O—P bonds in cyclic metaphosphoric acid is:

(a) zero (b) two

(c) three (d) four

[IIT-2000]

8. The number of S—S bonds in sulphur trioxide trimer, (S_3O_9) is:

(a) three (b) two

(c) one (d) zero

[IIT-2001]

9. The set with correct order of acidic strength is:

(a) $HClO < HClO_2 < HClO_3 < HClO_4$

(b) $HClO_4 < HClO_3 < HClO_2 < HClO$

(c) $HClO < HClO_4 > HClO_3 > HClO_2$

(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

[IIT-2001]

ASSERTION AND REASON TYPE QUESTIONS (Q. 10 and 11)

Read the following questions and answer as per the direction given below:

(a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I.

(b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I.

(c) Statement I is correct; Statement II is incorrect.

(d) Statement I is incorrect; Statement II is correct.

10. **Statement I:** Pb^{4+} compounds are stronger oxidzing agents than Sn^{2+} compounds.

Statement II: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

[IIT-2008]

11. **Statement I:** Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.

Statement II: $SiCl_4$ is ionic and CCl_4 is covalent

[IIT-2001]

12. H_3BO_3 is:

(a) monobasic acid and weak Lewis acid
(b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid
(d) tribasic and weak Lewis acid

[IIT-2003]

13. Me_2SiCl_2 on hydrolysis will produce:

(a) $(Me)_2Si(OH)_2$
(b) $(Me)_2\ Si = O$
(c) $[—O—(Me)_2Si — O—]_n$
(d) $Me_2SiCl(OH)$

[IIT-2003]

14. For H_3PO_3 and H_3PO_4, the correct choice is:

(a) H_3PO_3 is dibasic and reducing
(b) H_3PO_3 is dibasic and non reducing
(c) H_3PO_4 is triabsic and reducing
(d) H_3PO_3 is tribasic and non reducing

[IIT-2003]

15. When I^- is oxidised by $KMnO_4$ in alkaline medium, I^- converts into:

(a) IO_3^- (b) I_2
(c) IO_4^- (d) IO^-

[IIT-2004]

16. Which of the following has —O—O— linkage?

(a) $H_2S_2O_6$ (b) $H_2S_2O_8$
(c) $H_2S_2O_3$ (d) $H_2S_4O_6$

[IIT-2004]

17. Name the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared:

(a) pyrosilicate
(b) sheet silicate
(c) linear chain silicate
(d) three-dimensional silicate

[IIT-2005]

18. Which of the following is not oxidised by O_3?

(a) KI (b) $FeSO_4$
(c) $KMnO_4$ (d) K_2MnO_4

[IIT - 2005]

19. Which gas is evolved when PbO_2 is treated with concentrated HNO_3?

(a) NO_2 (b) O_2
(c) N_2 (d) N_2O

[IIT - 2005]

20. A pale blue liquid obtained by equimolar mixture of two gases at –30°C is

(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5

[IIT - 2005]

21. Which of the following allotropes of phosphorus is thermodynamically most stable?

(a) Red (b) White
(c) Black (d) Yellow

[IIT-2005]

22. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$
How can this reaction be made to proceed in the forward direction?

(a) Addition of cis 1, 2-diol
(b) Addition of borax
(c) Addition of trans 1, 2-diol
(d) Addition of Na_2HPO_4

[IIT-2006]

ASSERTION AND REASON TYPE QUESTIONS (Q. 23 and 24)

Read the following questions and answer as per the direction given below:

(a) Statement I is correct; Statement II is correct. Statement II is the correct explanation of Statement I.
(b) Statement I is correct; Statement II is correct. Statement II is not the correct explanation of Statement I.
(c) Statement I is correct; Statement II is incorrect.
(d) Statement I is incorrect; Statement II is correct.

23. **Statement I :** Boron always forms covalent bond.

Statement II : The small size of B^{3+} favours formation of covalent bond.

[IIT-2007]

24. **Statement I :** In water, orthoboric acid behaves as a weak monobasic acid.
Statement II : In water, orthoboric acid acts as a proton donor.

[IIT-2007]

25. The percentage of p-character in the orbitals forming P—P bonds in P_4 is:

(a) 25 (b) 33
(c) 50 (d) 75

[IIT - 2007]

PASSAGE TYPE QUESTIONS

Passage # 1 (Q. 26 to 28)

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes to it easily. Ammonia forms large number of complexes with transition metal ions. Hybridisation easily explains the case of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus.

[IIT-2008]

26. Among the following, the correct statement is:
(a) Phosphates have no biological significance in humans.
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
(d) Oxidation of nitrates is possible in soil.

27. Among the following, the correct statement is:
(a) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's'-orbital and is less directional.
(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.
(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.
(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.

28. White phosphorous on reaction with NaOH gives PH_3 as one of the products. This is a:
(a) dimerisation reaction
(b) disproportination reaction
(c) condensation reaction
(d) precipitation reaction

29. The reaction of P_4 with X leads selectively to P_4O_6. The X, is:
(a) dry O_2
(b) a mixture of O_2 and N_2
(c) moist O_2
(d) O_2 in the presence of aqueous NaOH

[IIT - 2009]

30. Extra pure N_2 can be obtained by heating:
(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

[IIT - 2011]

31. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphrous containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are:
(a) redox reaction, –3 and –5
(b) redox reaction, +3 and +5
(c) disproportionation reaction, –3 and + 1
(d) disproportionation reaction, –3 and + 3

[IIT - 2012]

32. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
(a) HNO_3, NO, NH_4Cl, N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2

[IIT - 2012]

33. The shape of XeO_2F_2 molecule is:
(a) trigonal bipyramidal
(b) square planar
(c) tetrahedral
(d) see-saw

[IIT-2012]

Passage # 2 (Q. 34 - 35)

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The Cl_2 gas reacts with SO_2 gas in the presence of charcoal, to give a product R.R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus T.

34. P and Q respectively, are the sodium salts of:
(a) hypochlorous and chloric acids
(b) hypochlorous and chlorous acids
(c) chloric and perchloric acids
(d) chloric and hypochlorous acids

[JEE Advanced - 2013]

35. R, S and T, respectively, are:

(a) SO_2Cl_2, PCl_5 and H_3PO_4

(b) SO_2Cl_2, PCl_3 and H_3PO_3

(c) $SOCl_2$, PCl_3 and H_3PO_2

(d) $SOCl_2$, PCl_5 and H_3PO_4

36. The product formed in the reaction of $SOCl_2$ with white phosphorus is:

(a) PCl_3 (b) SO_2Cl_2

(c) SCl_2 (d) $POCl_2$

[JEE Advanced - 2014]

37. Concentrated nitric acid upon long standing, turns yellow-brown due to the formation of:

(a) NO (b) NO_2

(c) N_2O (d) N_2O_4

[JEE Advanced - 2014]

38. Which of the following is the wrong statement?

(a) ONCl and ONO^- are not isoelectronic

(b) O_3 molecule is bent

(c) Ozone is violet-black in solid state

(d) Ozone is diamagnetic gas

[JEE Main - 2013]

39. Which of the following properties in not shown by NO?

(a) It is paramagnetic in liquid state.

(b) It is neutral oxide.

(c) It combines with oxygen to form nitrogen dioxide.

(d) Its bond order is 2.5.

[JEE Main - 2014]

40. Among the following oxacids, the correct decreasing order of acidic strength is

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$

(b) $HClO_4 > HOCl > HClO_2 > HClO_3$

(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$

(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

[JEE-Main - 2014]

41. Which among the following is the most reactive?

(a) Cl_2 (b) Br_2

(c) I_2 (d) ICl

[JEE-Main - 2015]

42. Which one has highest boiling point?

(a) He (b) Ne

(c) Kr (d) Xe

[JEE-Main - 2015]

Answer Key

LEVEL I

1. (a) 2. (a) 3. (d) 4. (b) 5. (c) 6. (b) 7. (c) 8. (c) 9. (b) 10. (b)
11. (a) 12. (d) 13. (a) 14. (d) 15. (c) 16. (d) 17. (d) 18. (b) 19. (a) 20. (b)
21. (d) 22. (a) 23. (a) 24. (a) 25. (a) 26. (b) 27. (c) 28. (d) 29. (d) 30. (c)
31. (a) 32. (c) 33. (a) 34. (b) 35. (b)

LEVEL II

1. (c) 2. (c) 3. (d) 4. (c) 5. (c) 6. (b) 7. (c) 8. (b) 9. (a) 10. (a)
11. (a) 12. (b) 13. (b) 14. (a) 15. (b) 16. (b) 17. (d) 18. (c) 19. (b) 20. (b)
21. (c) 22. (c) 23. (c) 24. (a) 25. (a) 26. (c) 27. (c) 28. (b) 29. (c) 30. (c)
31. (b) 32. (c) 33. (a) 34. (d) 35. (d)

LEVEL III

1. (b, c, d) 2. (b, c, d) 3. (b, c, d) 4. (c) 5. (a, c, d) 6. (b, c, d) 7. (a, b, c, d) 8. (a, b, c)
9. (a, b, c) 10. (a, b) 11. (a, b) 12. (a, b, c) 13. (a, b, d) 14. (b) 15. (b) 16. (a)
17. (a) 18. (d) 19. (d) 20. (26) 21. (11) 22. (8) 23. (3) 24. (3)
25. (5) 26. (3) 27. (4)

28. A → P, S; B → S; C → Q, R; D → R,S

29. A → R; B → Q; C → S; D → P

30. A → P, Q, S; B → P, Q, R, S; C → Q, R, S; D → P, Q, R, S

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (c) 2. (a) 3. (b) 4. (b) 5. (c) 6. (a) 7. (c) 8. (d) 9. (a) 10. (c)
11. (c) 12. (a) 13. (c) 14. (a) 15. (a) 16. (b) 17. (b) 18. (c) 19. (b) 20. (b)
21. (c) 22. (a) 23. (a) 24. (a) 25. (d) 26. (c) 27. (c) 28. (b) 29. (b) 30. (d)
31. (c) 32. (b) 33. (d) 34. (a) 35. (a) 36. (a) 37. (b) 38. (*) 39. (a) 40. (c)
41. (d) 42. (d)

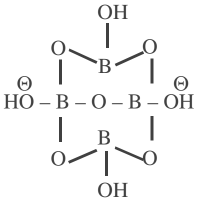
(*) No answer

Hints and Solutions

LEVEL I

1. **(a)** Borax $\xrightarrow{H_2SO_4} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow{Al} \underset{\text{(Boron)}}{B}$

2. **(a)** In borax, anion $[B_4O_5(OH)_4]^{-2}$ is present.



In this, hybridisation of B is sp^2 and sp^3.

3. **(d)** $CO + Cl_2 \xrightarrow{h\nu} \underset{\text{(phosgene)}}{COCl_2}$

4. **(b)** $\underset{\text{(Oxalic acid)}}{H_2C_2O_4} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(A)}}{CO} + \underset{\text{(B)}}{CO_2}$

CO is absorbed by ammonical cuprous chloride while CO_2 is absorbed by KOH.

5. **(c)** SiC is a covalent network solid.

6. **(b)** $NH_3 + O_2 \xrightarrow{pt} NO + H_2O$ (ostwald process)

7. **(c)** NO is paramagnetic in gaseous state.

8. **(c)** $P_4 + Cl_2 \rightarrow PCl_3(A)$

$PCl_3 + H_2O \rightarrow H_3PO_3 + HCl$

P_4 + excess $Cl_2 \rightarrow PCl_5$ (B)

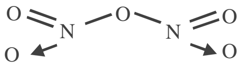
$PCl_5 + H_2O \rightarrow H_3PO_4 + HCl$

9. **(b)** Holme's signal can be given by using ($CaC_2 + Ca_3P_2$)

10. **(b)** $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2\uparrow + O_2\uparrow$

11. **(a)** Single N–N bond is weaker than the single P–P bond.

12. **(d)**



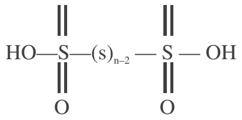
13. **(a)** Phosphine (PH_3) is combustible due to presence of P_2H_4.

14. **(d)** Extra pure N_2 can be obtained by heating metal azides $Ba(N_3)_2$.

15. **(c)** Ammoia can be dried by anhydrous CaO.

16. **(d)** $2Hg + O_3 \longrightarrow Hg_2O + O_2$

17. **(d)** Polythionic acid, $H_2S_nO_6$



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(s)_{n-2}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Total S–S bond = n – 1

Number of S with zero oxidation state = n – 2

Number of S with + 5 oxidation state = 2

Number of $d\pi - p\pi$ bond = 4

18. (b) $2\overset{+4}{NO_2} + H_2O \rightarrow H\overset{+3}{NO_2} + H\overset{+5}{NO_3}$

19. (a) Element ‘X’ may be Cl, Br or I.

The most acidic oxyacid of X is HXO_4.

20. (b) $RCOO^-$ is not a pseudohalide because it does not have N-atom.

21. (d) ICl_3 can form dimer I_2Cl_6.

22. (a) I_4O_9 is an ionic oxide.

I_4O_9 is $I(IO_3)_3$

23. (a) F^- ion does not behave as reducing agent.

24. (a) F_2 acts as oxidizing agent with water.

$5F_2 + 5H_2O \rightarrow 10HF + O_2 + O_3$

I_2 does not react with water.

25. (a) F_2 is the strongest oxidizing agent due to exceptionally high hydration energy of F^-.

26. (b) $XeF_4 + SbF_5 \rightarrow \underset{sp^3d}{[XeF_3]^+}\ \underset{sp^3d^2}{[SbF_6]^-}$

27. (c) Both ICl_2^- and XeF_2 are linear.

28. (d) No real compounds of He, Ne and Ar are known.

29. (d) Hybridisation of C in diamond and graphite is sp^3 and sp^2 respectively.

30. (c) $K_2HgI_4 + KOH + NH_3 \rightarrow H_2N{-}Hg{-}O{-}Hg{-}I\downarrow$

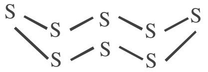
31. (a) The part of the skin which comes in contact with HNO_3 turns yellow because proteins of skin are converted into xanthoproteins.

32. (c) Order of lewis acidic strength:-

$BF_3 < BCl_3 < BBr_3 < BI_3$

33. (a) NO_2 is a reddish-brown gas.

34. (b)



Total number of lone pairs = 16

Total number of S–S bonds = 8

35. (b) Order of bond energy is :

$Cl_2 > Br_2 > F_2 > I_2$

LEVEL II

1. (c) Boric acid is not a bronsted acid because it is not a H^+ donor. It is an OH^- acceptor.

2. (c) $Na_2B_4O_7 . 10H_2O \xrightarrow{\Delta} \underset{(X)}{B_2O_3} + NaBO_2 + H_2O$

$B_2O_3 + Cr_2O_3 \xrightarrow{\Delta} \underset{(Y)}{Cr(BO_2)_3}$

3. (d) With large sized Lewis base like $(CH_3)_3N$, symmetrical deavage of B_2H_6 takes place.

4. (c) $H_3BO_3 + NaOH \rightleftharpoons Na[B(OH)_4] + NaBO_2 + H_2O$

This reaction can be shifted in forward direction by adding cis-1, 2-diol not by trans-1,2-diol.

5. (c) Both CO_2 and SiO_2 are acidic.

6. (b) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

In products total 9 P–H bonds are present.

7. (c) At 0°C, NO_2 diamerises into $N_2O_4(s)$ which is colourless.

8. (b) $Ca_3P_2 + H_2O \rightarrow \underset{(A)}{Ca(OH)_2} + \underset{(B)}{PH_3}$

$PH_3 + HI \rightarrow \underset{(C)}{PH_4I} \xrightarrow[(D)]{KOH} \underset{(B)}{PH_3} + KI + H_2O$

9 . (a) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

10. (a) Order of stability of hydrides:-

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

11. (a) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + Cr_2O_3 + H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$

12. (b) $NH_3 + Cl_{2(excess)} \rightarrow NCl_3 + HCl$

$NH_{3(excess)} + Cl_2 \rightarrow N_2 + NH_4Cl$

13. (b) Thermal decomposition of O_3 is exothermic.

14. (a) $\underset{(A)}{Na_2SO_3} + HCl_{(dil)} \rightarrow NaCl + \underset{(Y)}{SO_2}\uparrow + H_2O$

$\underset{(B)}{Na_2S} + HCl_{(dil)} \rightarrow NaCl + \underset{(Z)}{H_2S}$

15. (b) $H_2SO_4 + Cl_2 \longrightarrow \underset{(X)}{SO_2Cl_2}$

$SO_2Cl_2 + H_2O \longrightarrow H_2SO_4 + HCl$

16. (b) $Zn + H_2SO_4(dil) \longrightarrow ZnSO_4 + H_2$

$Zn + H_2SO_4(conc.) \longrightarrow ZnSO_4 + SO_2 + H_2O$

17. (d) $I_2 + H_2O \not\longrightarrow HI + HOI$

18. (c) I–Cl is polar and Br_2 is non-polar.

19. (b) $Cl_2 + Ca(OH)_2 \longrightarrow \underset{\text{bleaching powder}}{CaOCl_2} + H_2O$

20. (b) Interhalogen compounds are more reactive than halogen compounds because X–X' bond of interhalogen is polar while X–X bond of halogen is non-polar.

21. (c) Correct order of bond dissociation energy:-

$Cl_2 > Br_2 > F_2 > I_2$

22. (c) Shape of XeF_5^- is pentagonal planar. Hybridisation of Xe is sp^3d^3.

23. (c) XeF_4 acts as fluoride acceptor with KF.

24. (a) Due to resonance both O—O bond lengths are equal.

25. (a) $2Hg + O_3 \longrightarrow Hg_2O + O_2$

26. (c) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

N_2O acts as anaesthesia.

27. (c) Black phosphorus has layery structure. It behaves as conductor of electricity.

28. (b) N_2 is almost chemically inert. It is due to very high bond dissociation energy of $N\equiv N$.

29. (c) Order of reactivity :

White P > Red P > Black P

30. (c) N_2O_5 has different structure from P_2O_5.

$P_2O_5(P_4O_{10})$ has cage like structure.

31. (b) Third period elements can not form stable $3p\pi - 3p\pi$ bond.

32. (c) Correct order of acidic strength is:-

$HClO < HClO_2 < HClO_2 < HClO_4$

33. (a) The ease of liquification $\propto$ intermolecular bonding order of case of liquification :

Xe > Kr > Ar > Ne > He

34. (d) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

35. (d) $XeF_6 + CsF \longrightarrow Cs^+[XeF_7]^-$

Lewis acid   Lewis base

LEVEL III

1. (b, c, d)

Both graphite and diamond are diamagnetic in nature.

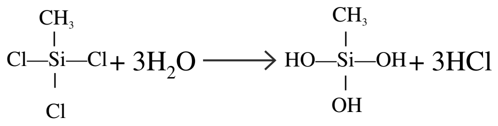
2. (b, c, d)

Co^{+3}, Cu^{+2} and Ni^{+2} give borax bead test.

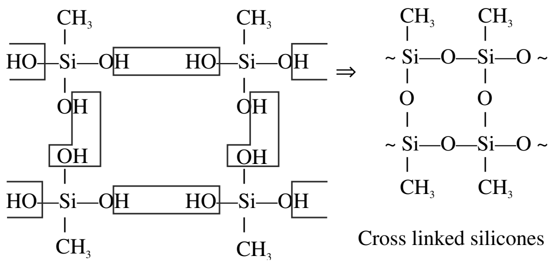
3. (b, c, d)

$[BF_6]^{-3}$ does not exist because due to unavailability of d-orbital B can not form more than 4 bonds.

4. (c)



$$CH_3SiCl_3 + 3H_2O \longrightarrow CH_3Si(OH)_3 + 3HCl$$



Cross linked silicones

5. (a, c, d) In white phosphorus P_4 molecules are attached with weak vander waal's force of attraction while red phosphorus is polymeric. White phosphorus is insoluble in water but soluble in organic solvents like CS_2. White phosphorus disproportionates in alkali solution.

6. (b, c, d) $NH_4NO_3 \xrightarrow{\Delta} N_2O\uparrow + 2H_2O$

N_2O is also called as laughing gas. N_2O is a neutral oxide. It does not bring tears to the eyes.

7. (a, b, c, d)

All decompositions are correct.

8. (a, b, c)

Nitrogen is restricted to a maximum covalency of 4 because in its valence shell only 4 orbitals are available for bonding. N–N bond is weaker than P—P bond hence, catenation tendency of P is stronger than N.

N can not form pπ-dπ bonding.

9. (a, b, c)

P_2O_5 (P_4O_{10}) is an acidic dehydrating agent. It dehydrate acidic substances.

10. (a, b)

They (halogens), all are diatomic, form univalent ions and are oxidizing agents.

11. (a, b) F_2 and Cl_2 can oxidize Br^- into Br_2

12. (a, b, c)

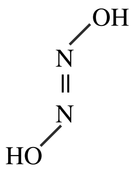
$I_2 + H_2O \not\longrightarrow HI + HIO$

13. (a, b, d)

F can not form 3 bonds. It can form only one bond.

14. (b) To form pyro-oxy acid atleast two OH groups must present in parent oxyacid.

15. (b) Structure of $H_2N_2O_2$



16. (a) Order of acidic strength:

$HF < HCl < HBr < HI$

17. (a)

Order of acidic strength:

$H_2O < H_2S < H_2Se < H_2Te$

Order of basic strength :

$OH^- > HS^- > HSe^- > HTe^-$

18. (d)

$\underset{(A)}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{(C)}{N_2} + \underset{(B)}{Cr_2O_3} + H_2O$

$Mg + N_2 \longrightarrow \underset{(D)}{Mg_3N_2}$

$Mg_3N_2 + H_2O \longrightarrow Mg(OH)_2 + \underset{(E)}{NH_3}$

Anion of (A) is $Cr_2O_7^{-2}$. In structure of dichromate ($Cr_2O_7^{-2}$) all metal-oxygen bond lengths are not equal.

19. (d)

Gas (E) is NH_3

$CuSO_4 + NH_3 \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]\ SO_4}$

$NH_3 + O_2 \xrightarrow{Pt/Rh} NO + H_2O$

$NH_3 + KMnO_4 \longrightarrow N_2$

NH_3 form black precipitate with Hg_2Cl_2.

20. In C_{60}, Number of 5-membered rings (a) = 12

Number of 6-memberd rings (b) = 20

Number of π-bonds in C_{60}(c) = 30

Value of $(3a - 2b + c) = 36 - 40 + 30 = 26$

21. Species having sp^3 hybridization:

Diamond, $H_3BO_{3(eq)}$, Zeolites (Si-central).

Silicones (Si), chlorosilane (Si), Borax (boron), Al_2Cl_6, B_2H_6, SiO_2, CH_4, CCl_4

22. Ampoteric oxixdes are:

PbO , PbO_2 , SnO , SnO_2 , Al_2O_3 , ZnO , BeO , Ga_2O_3

23. $Si_3O_9^{6-}$ is a cyclic trimer. In this , 3 oxygen atoms are shared between tetrahedrons.

24. Atomic size, reducing power of hydrides and metallic character increase down the group for nitrogen family.

25. Gaseous oxides are:

N_2O , NO , NO_2 , SO_2 , SO_3

26. Mixed anhydride are:

ClO_2 , Cl_2O_6 , NO_2

$$2\overset{+4}{Cl}O_2 + H_2O \longrightarrow H\overset{+3}{Cl}O_2 + H\overset{+5}{Cl}O_3$$

$$\overset{+6}{Cl_2}O_6 + H_2O \longrightarrow H\overset{+5}{Cl}O_3 + H\overset{+7}{Cl}O_4$$

$$2\overset{+4}{N}O_2 + H_2O \longrightarrow H\overset{+3}{N}O_2 + H\overset{+5}{N}O_3$$

27. Pseudohalides are:

CN^- , SCN^- , N_3^- , CNO^-

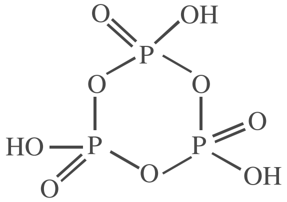
28. A ⟶ P, S ; B ⟶ S ; C ⟶ Q, R ; D ⟶ R, S

29. A ⟶ R ; B ⟶ Q ; C ⟶ S ; D ⟶ P

30. A ⟶ P, Q, S ; B ⟶ P, Q, R, S ; C ⟶ Q, R, S ; D ⟶ P, Q, R, S

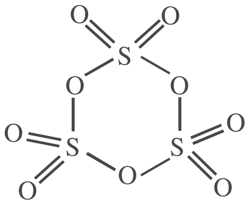
PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **(c)** $KHF_2 \longrightarrow K^+ + HF_2^-$
2. **(a)** Order of acidic strength: $ClOH > BrOH > IOH$
3. **(b)** $RCOO^-$ is not a pseudo halide because it does not contain any N-atom.
4. **(b)** Order of bond angle: $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$
5. **(c)** NH_3 can be dried by anhydrous CaO.
6. **(a)** Order of biling point: $H_2O > H_2Te > H_2Se > H_2S$
7. **(c)** Cyclic metaphosphoric acid, $(HPO_3)_3$



It has three P—O—P bonds.

8. **(d)**



It has zero S—S bonds

9. (a) Order of correct acidic strength:

$HClO < HClO_2 < HClO_3 < HClO_4$

10. (c) The lower oxidation states for the group 14 elements are more stable for the heavier members of the group due to inert pair effect.

11. (c) Both $SiCl_4$ and CCl_4 are covalent.

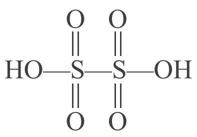
12. (a) H_3BO_3 is weak monobasic and Lewis acid.

13. (c) $Me_2SiCl_2 \xrightarrow{H_2O}$ linear silicones

14. (a) H_3PO_3 is dibasic and reducing agent because it can oxidize to +5 oxidation state.

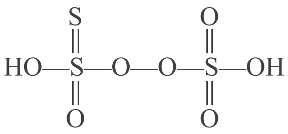
15. (a) $KMnO_4 + KOH + KI \longrightarrow K_2MnO_4 + KIO_3 + H_2O$

16. (b) $H_2S_2O_6$



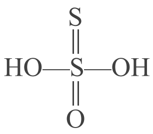
$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$

$H_2S_2O_8$



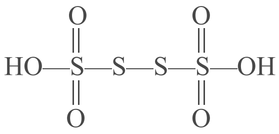
$HO-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$

$H_2S_2O_3$



$HO-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}-OH$

$H_2S_4O_6$



$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-S-S-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$

17. (b) In sheet silicates, three oxygen atoms are shared of $[SiO_4]^{4-}$.

18. (c) In $KMnO_4$, Mn is present in its highest oxidation state +7.

19. (b) $PbO_2 + HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + O_2$

20. (b) N_2O_3 is mixture of NO and NO_2.

21. (c) Order of stability:

Black > Red > White phosphorus

22. (a) Cis-1, 2-diol consumes $Na[B(OH)_4]$ hence, this reaction proceed in forward direction.

23. (a) Due to small size of B^{+3}, Boron always forms covalent bond.

24. (a) In water, orthoboric acid donates only one H^+.

$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$
or
$B(OH)_3$

25. (d) In P_4, hybridisation of P is sp^3.

26. (c) Due to greater solubility in water, nitrates are less abundant in earth's crust.

27. (c) Lone pair in N of NH_3 is present in sp^3-hybrid orbital which is more directional.

28. (b) White phosphorus (P_4) undergo disproportionation in alkaline medium.

29. (b) P_4 + (mixture of O_2 and N_2) $\longrightarrow P_4O_6$

Due to addition of N_2, rate of reaction decreases.

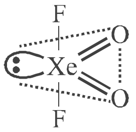
30. (d) Extra pure N_2 can be obtained by heating metallic azides, $Ba(N_3)_2$.

31. (c) $\overset{0}{P_4} + NaOH + H_2O \longrightarrow \overset{-3}{P}H_3 + NaH_2\overset{+1}{P}O_2$

(disproportionation)

32. (b) $\overset{+5}{HNO_3} \quad \overset{+2}{NO} \quad \overset{0}{N_2} \quad \overset{-3}{N}H_4Cl$

33. (d)



See - saw shape

34. (a) P is NaOCl (Salt of HOCl, hypochlorous acid)

Q is $NaClO_3$ (Salt of $HClO_3$, Chloric acid)

35. (a) R is SO_2Cl_2

S is PCl_5

T is H_3PO_4

36. (a) $P_4 + SOCl_2 \longrightarrow PCl_3$

37. (b) Due to release of NO_2 gas, upper layer of HNO_3 turns yellow.

38. No answer because all statements are correct.

39. (a) NO is diamagnetic in liquid state.

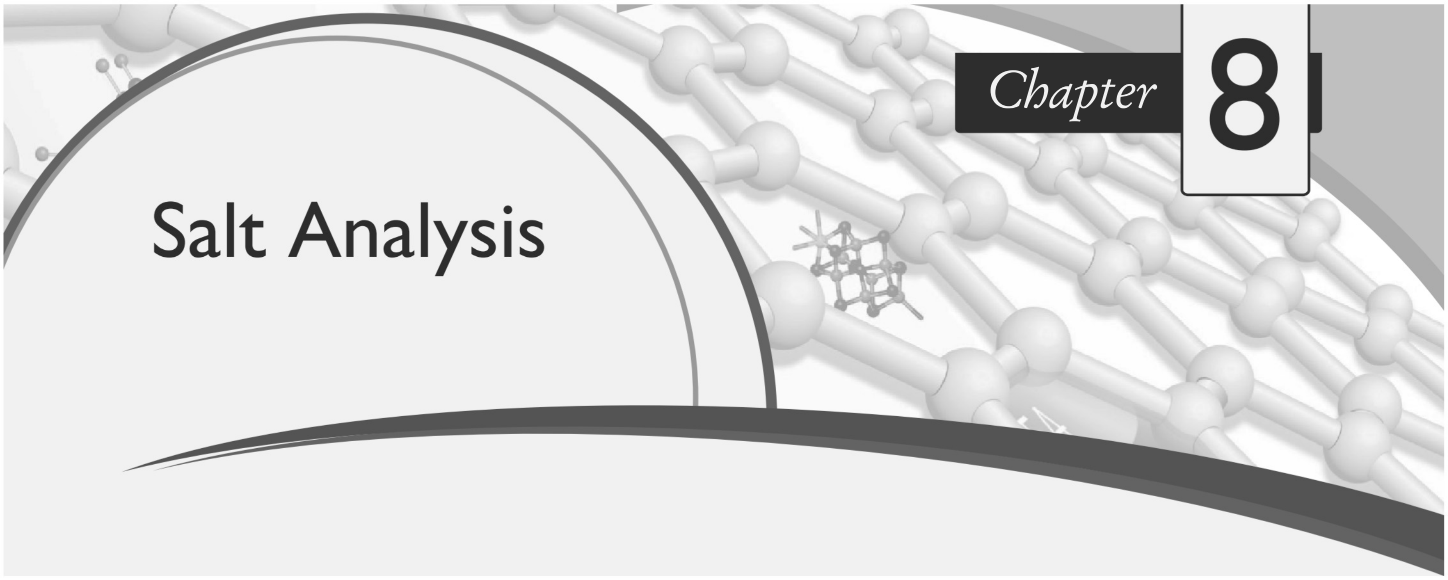
40. (c) Order of acidic strength:

$HClO < HClO_2 < HClO_3 < HClO_4$

41. (d) Interhalogen compound (ICl) is more reactive than pure halogen.

42. (d) Order of boiling point:

He < Ne < Kr < Xe



Chapter 8

Salt Analysis

Key Concepts

Qualitative analysis involves the detection of basic radicals (cations) and acidic radicals (anions) of a salt or a mixture of salts.

Acid + Base → Salt + H_2O + Heat of Neutralisation

HCl + NaOH → <u>NaCl</u> + H_2O + Heat

Na^+ (Basic radical because it comes from base)

Cl^- (Acidic radical because it comes from acid)

The systematic procedure for qualitative analysis is:

a. Preliminary tests:
  - → Physical appearance (Colour and smell)
  - → Dry heating test
  - → Flame test
  - → Borax bead test
  - → Charcoal cavity test
  - → Cobalt nitrate test

b. Wet tests for acidic radicals

c. Wet tests for basic radicals

Physical appearance (Smell):

Smell	Inference
Ammonical Smell	NH_4^+
Vinegar like Smell	CH_3COO^-
Smell like that of rotten eggs	S^{-2}
Chlorine gas smell	Hypochlorites (ClO^-)
Bitter almond smell	Cyanides

Physical appearance (Coloured substance):

Light pink	Hydrated salt of Mn
Reddish Pink	Hydrated salt of Co(II)
Red	HgO, HgI_2, Pb_3O_4
Orange – red	Sb_2S_3, Some dichromates and ferricyanides
Reddish brown	Fe_2O_3
Dark brown	PbO_2, Bi_2S_3, CdO, Ag_2O, $CuCrO_4$, SnS
Light yellow or brown	Chromates, As_2S_3, As_2S_5, AgBr, AgI, PbI_2, CdS, SnS_2, a few iodides and ferrocyanides.
Green	K_2MnO_4, Ni salts, hydrated ferrous salts, some Cu (II) Compound
Dark green	Salt of Cr(III)
Blue	Hydrated $CuSO_4$, anhydrous $CoSO_4$
Black	Sulphides of Ag^+, Cu^+, Cu^{+2}, Fe^{+2}, Ni^{+2}, Co^{+2}, Hg^{+2}, and Pb^{+2}. MnO_2, Fe_3O_4, FeO, CuO, Co_3O_4, Ni_2O_3

Physical appearance (Solution is coloured):

Green or blue	Ni^{+2}, Fe^{+2}, Cr^{+3} and Cu^{+2}
Pink	Co^{+2} and Mn^{+2}
Yellow	CrO_4^{2-}, Fe^{+3}, $[Fe(CN)_6]^{4-}$
Orange	Dichromates
Purple	Permanganates

Dry heating:

	Observation	Inference
1.	Substance decrepitates (Crackling noise)	NaCl, KI, $Pb(NO_3)_2$, $Ba(NO_3)_2$
2.	Substance Melts (or, fuses)	Alkali metal salts or salt containing water of crystallization
3.	Substance swells (due to loss of water of crystallization)	Alums, borates and Phosphates
4.	The substance Sublimes and the colour of sublimate is:-	
	a. White	Hg_2Cl_2, NH_4X, $AlCl_3$, $HgCl_2$, As_2O_3,Sb_2O_3
	b. Yellow	As_2S_3 and HgI_2 (turns red when rubbed with glass rod)
	c. Blue black and violet vapours	Iodides
5.	A residue (generally oxides) is left and its colour is:	
	a. White (Cold) and Yellow (Hot)	ZnO
	b. Reddish brown (Hot); Yellow (Cold)	PbO
	c. Black (Hot); Red (Cold)	HgO, Pb_3O_4
	d. Black (Hot); Red brown (Cold)	Fe_2O_3
	e. Original salt Blue becomes White on heating	Hydrated $CuSO_4$
6.	Gas is evolved:	Ammonium nitrate
	(i) Colourless and odourless	
	a. CO_2 (Turns lime water milky)	CO_3^{-2} $C_2O_4^{-2}$
	b. O_2 (Rekindles a glowing splinter)	Nitrates, permanganate, Dichromate, chlorate
	c. N_2	Amonium Nitrate
	(ii) Colourless gas with odour	
	a. NH_3 (Characteristic smell, turns nesseler's solution brown and turns red litmus blue)	NH_4^+
	b. H_2S (Smell of rotten eggs, turns lead acetate paper black)	S^{-2} or Hydrated S^{-2}
	c. SO_2 (suffocating or irritating smell of burning sulphur, turns acidified $K_2Cr_2O_7$ paper green)	SO_3^{2-}
	d. HCl (Pungent smell, white fumes with ammonia, white ppt with $AgNO_3$ Solution)	Hydrated Cl^-
	e. Acetic acid vapours (characteristic vinegar like smell)	CH_3COO^-
	(iii) Coloured gas	
	a. NO_2 (Reddish brown, turns ferrous sulphate solution brownish black)	NO_2^- or NO_3^-
	b. Br_2 (Reddish brown turns starch paper orange-red or yellow, turns starch iodide paper blue)	Br^-
	c. Cl_2 (Greenish yellow, turns starch iodide paper blue, bleaches moist litmus paper, bleaches indigo solution)	Cl^-
	d. I_2 (violet, turns starch paper blue)	I^-

Flame test: The chlorides of the metals are more volatile as compared to other salts and these are prepared by mixing the compounds with a little concentrated HCl. On heating in a non- luminous Bunsen flame, they are volatilized and impart a characteristic colour to the flame.

Metal	Colour of flame
Li	Crimson red
Na	Golden yellow
K	Violet/lilac
Rb	Red violet
Cs	Blue violet
Ca	Brick red
Sr	Crimson red
Ba	Apple green

Borax bead test:

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{Colourless transparent glassy bead}}$$

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidizing flame.

Colour of bead

Metal	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Cr	Yellow	Green	Green	Green
Mn	Violet (Amethyst)	Amethyst	Colourless	Colourless
Fe	Yellowish Brown	Yellow	Green	Green
Co	Blue	Blue	Blue	Blue
Ni	Violet	Reddish-Brown	Grey	Grey
Cu	Green	Blue	Colourless	Red opaque

Solubility rules:

Ions	Solubility	Exceptions
NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+	Soluble	None
NO_3^-, CH_3COO^-, ClO_4^-, ClO_3^-, MnO_4^-, HCO_3^-, HSO_3^-	Soluble	None
Cl^-,Br^-,I^-	Soluble	Ag^+, Pb^{+2}, Hg_2^{+2}, Cu^+
SO_4^{-2}	Soluble	Hg^{+2}, Pb^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}
OH^-	Insoluble	Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{+2}, Sr^{+2}, Ba^{+2}
PO_4^{-3}, S^{-2}, CO_3^{-2}, SO_3^{-2}	Insoluble	NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+

Classification of basic radicals:

Group	Group reagent	Basic radical	Precipitate and its colour
i.	Dil HCl	Pb^{2+}, Hg_2^{2+}, Ag^+	$AgCl$ (white) $PbCl_2$ (white) Hg_2Cl_2 (white)
ii	H_2S in presence of dilute HCl	ii (a) Hg^{2+}, Pb^{2+}, Bi^{3+} Cu^{2+}, Cd^{2+} (Copper group) Their sulphides are not soluble in YAS ($(NH_4)_2S_2$) as well as in colourless $(NH_4)_2S$	HgS $\left.\begin{array}{l}PbS\\CuS\\Bi_2S_3\end{array}\right\}$ Black CdS (Yellow)
		ii (b) As^{3+},As^{5+},Sb^{3+}, Sb^{5+},Sn^{2+},Sn^{4+} (Aresenic group). Their sulphides are soluble in YAS, also they are soluble in colourless $(NH_4)_2S$ except SnS	$\left.\begin{array}{l}As_2S_3\\As_2S_5\end{array}\right\}$ Yellow $\left.\begin{array}{l}Sb_2S_3\\Sb_2S_5\end{array}\right\}$ Orange Sb_2S_5 (Brown) SnS_2 (Yellow)
iii	NH_4Cl + NH_4OH	Fe^{3+}, Al^{3+}, Cr^{3+}	$Al(OH)_3$ (Gelatinous White) $Fe(OH)_3$ (Reddish Brown) $Cr(OH)_3$ (Green)
iv	NH_4Cl + NH_4OH + H_2S in warm solution (or, excess $(NH_4)_2S$)	Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}	ZnS (White) MnS (Buff or Pink) of flesh colour $\left.\begin{array}{l}CoS\\NiS\end{array}\right\}$ Black
v	NH_4Cl + $(NH_4)_2CO_3$	Ca^{2+}, Sr^{2+},Ba^{2+}	$\left.\begin{array}{l}CaCO_3\\SrCO_3\\BaCO_3\end{array}\right\}$ White
vi	NH_4Cl + NH_4OH+ $Na_2\,HPO_4$	Mg^{2+}	$Mg(NH_4)PO_4$ (White)
Zero	NaOH or $Ca(OH)_2$ (heat)	NH_4^+	NH_3 Gas

(a) From the filtrate of ii^nd group, H_2S gas is boiled off and then one or two drop of concentrated HNO_3 is added and again boil so that if Fe^{2+} is present, it will oxidize into Fe^{3+}.

(b) iii^rd group radicals are precipitated as hydroxides and the addition of NH_4Cl suppresses the ionization of NH_4OH so that only iii group radicals are precipitated as hydroxides because of their low solubility products.

(c) Excess of NH_4Cl should not be added, Mn^{2+} will precipitate as $MnO_2.H_2O$.

(d) $(NH_4)_2SO_4$ cannot be used in place of NH_4Cl because SO_4^{2-} will also give the precipitate of $BaSO_4$, $SrSO_4$ etc.

(e) In acidic medium, hydroxides do not precipitate.

(f) In place of NH_4OH, NaOH can't be used because in excess of it we get soluble complexes of Al^{3+} and Cr^{3+}.

(g) In iv^th group radicals NH_4OH increases the ionization of H_2S by removing H^+ from H_2S as unionized water. (Ksp values of these sulphides are very high)

(h) In v^th group radicals, $(NH_4)_2CO_3$ should be added in alkaline or neutral medium. In the absence of ammonia or NH_4^+ ions, Mg^{2+} will also be precipitated.

Zero group (NH_4^+ ion):

1. Sodium hydroxide solution:

$$\underset{(NH_4Cl)}{NH_4^+} + \underset{(NaOH)}{OH^-} \longrightarrow NH_3\uparrow + H_2O$$

Ammonia gas can be identified, if

a. By its characteristics smell.

b. By formation of white fumes of NH_4Cl with HCl.

$NH_3 + HCl \longrightarrow NH_4Cl\uparrow$ (white fumes)

c. By its turning moistened red litmus paper blue or turmeric paper brown.

d. By its ability to turn filter paper moistened with mercury (I) nitrate solution black.

$$Hg_2(NO_3)_2 + 2NH_3 \longrightarrow \underbrace{Hg(NH_2)NO_3 + Hg}_{\text{Black}} + NH_4NO_3$$

2. With Nessler's reagent:

$$\begin{array}{l} NH_4^+ \\ \text{or} \\ NH_3 \end{array} + \underbrace{2[HgI_4]^{2-} + 4OH^-}_{\text{Nessler's reagent}} \longrightarrow HgO.Hg(NH_2)I\downarrow + 7I^- + 3H_2O$$

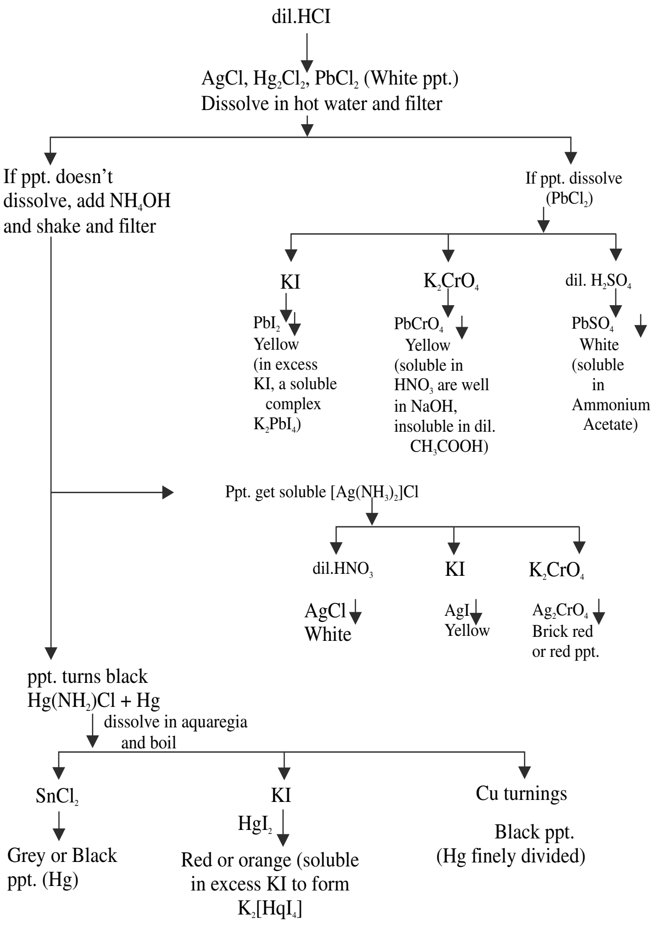
Brown ppt.

or

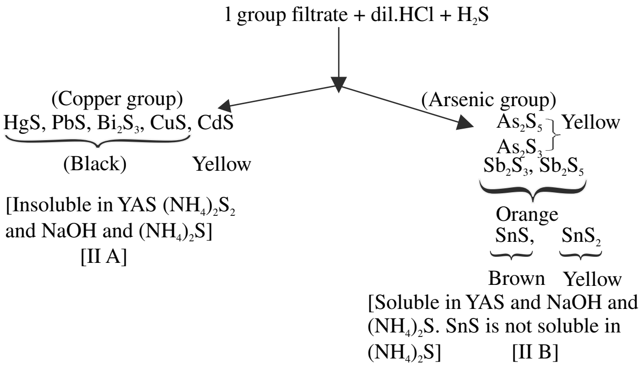
Brown or Yellow colouration

(Iodide of millon's base)

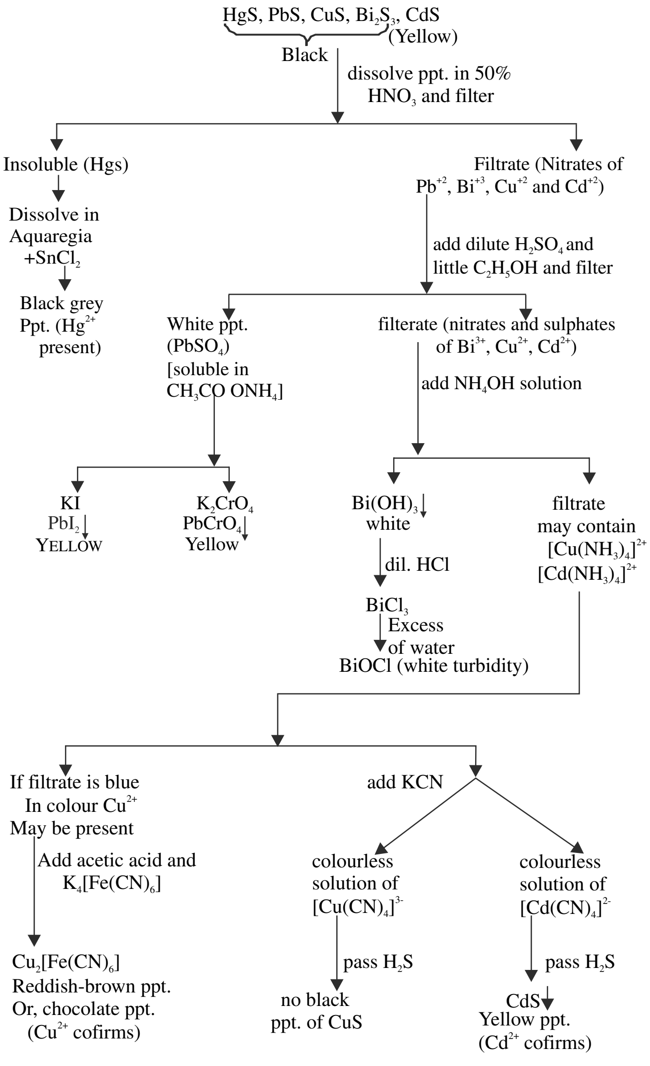
Group I



Group II



Group II (A)



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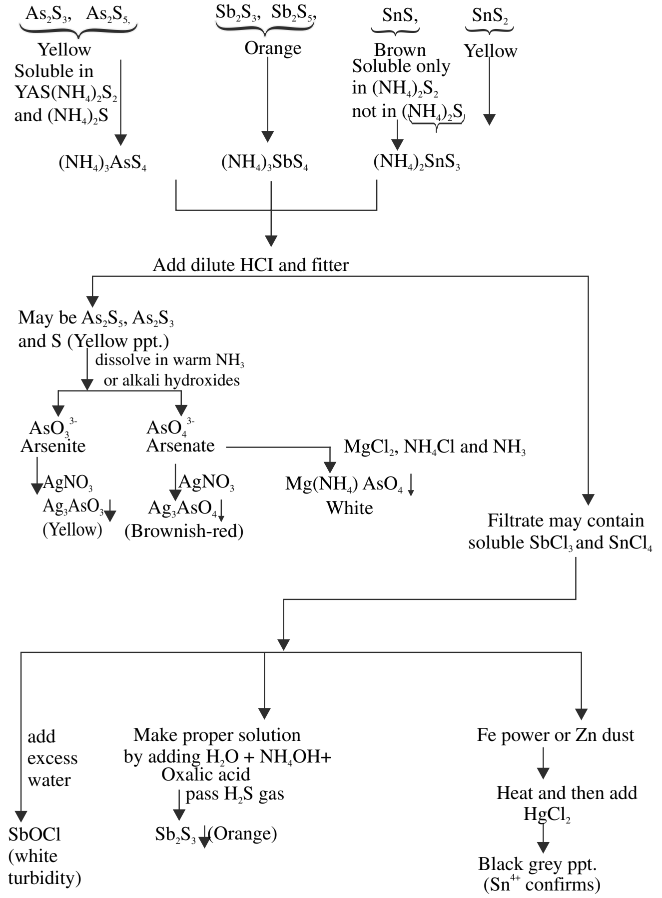

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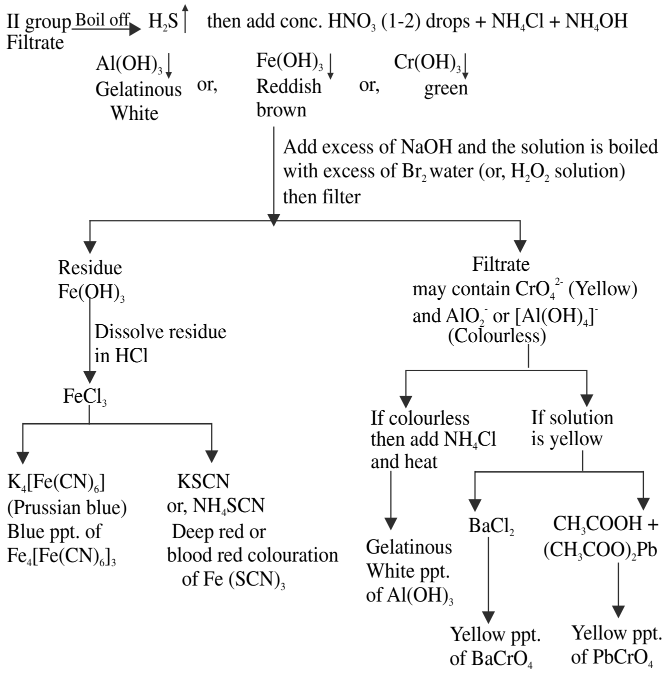

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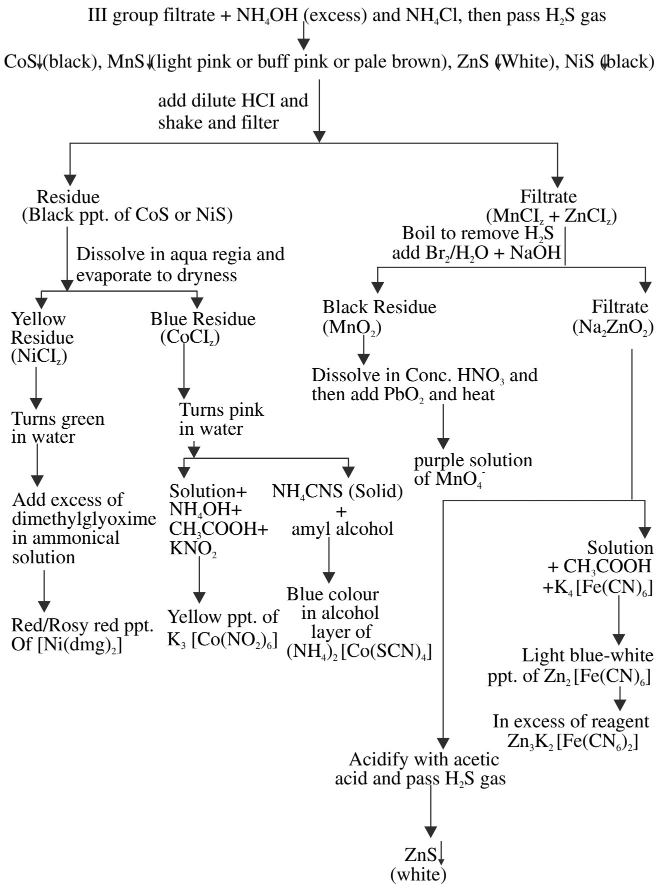
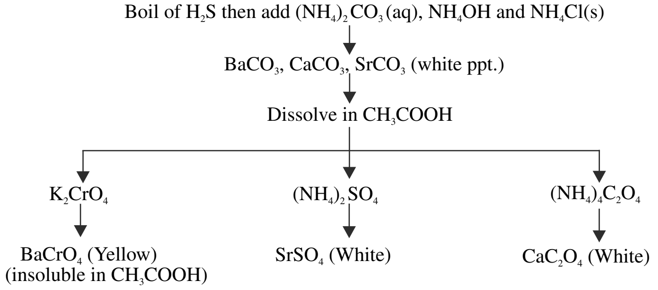


Group V



Group VI

Test of Mg^{2+}:

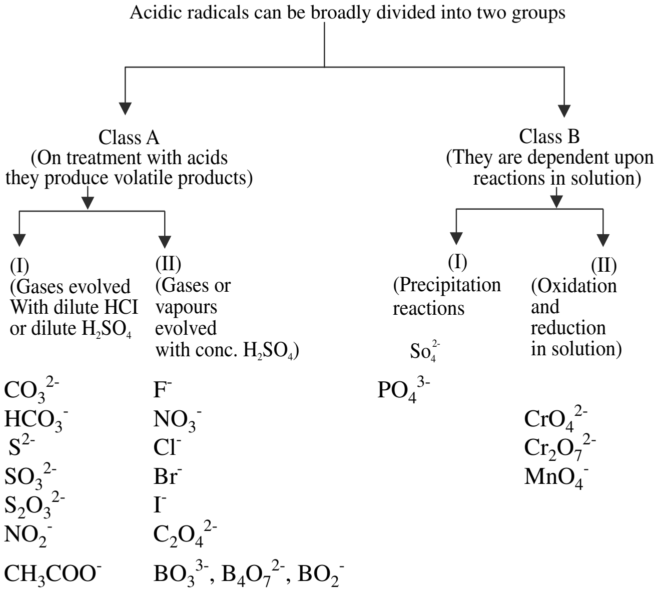
With Na_2HPO_4 solution:

White crystalline ppt. of $Mg(NH_4)PO_4.6H_2O$ in the presence of NH_4Cl (to prevent ppt. of $Mg(OH)_2$) and NH_3 solution.

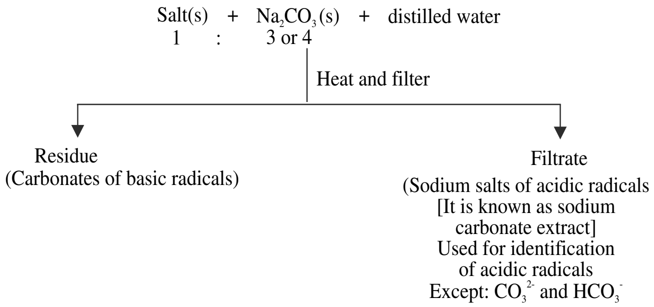
$$Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow \underset{\text{White}}{Mg(NH_4)PO_4\downarrow}$$

The ppt. is sparingly soluble in water, soluble in acetic acid and in mineral acids.

Classification of acidic radicals (anions):



Preparation sodium carbonate extract:-



$$BaCl_2 + Na_2CO_3 \longrightarrow \underset{\text{White}}{BaCO_3}\downarrow + 2NaCl\,(aq)$$

Sodium carbonate extract is used when:

a. Salt is only partially soluble in water or insoluble in water.
b. Cations interfere with the tests for acidic radicals or the coloured salt solution may be too intense in colour that the test results are not too clear.

Carbonte, CO_3^{2-}:

(i) The carbonates are decomposed with the effervescence of carbon dioxide gas.

$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2$

(ii) When this gas is passed through lime water, it turns milky with the formation of calcium carbonate.

$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{white ppt.}}{CaCO_3} + H_2O$

(iii) If the CO_2, gas is passed in excess, the milky solution becomes colourless due to the formation of soluble calcium bicarbonate.

$\underset{\text{White ppt.}}{CaCO_3} + H_2O + CO_2 \rightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$

Note: Sulphur dioxide evolved from sulphites also turns lime water milky.

$Ca(OH)_2 + SO_2 \rightarrow \underset{\text{White ppt.}}{CaSO_3} + H_2O$

However SO_2 can be identified by its pungent odour of burning sulphur.

Sulphite, SO_3^{2-}:

(i) The sulphite gives out sulphur dioxide gas, having suffocating smell of burning sulphur.

$CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + SO_2\uparrow$

(ii) When acidified potassium dichromate paper is exposed to the gas, it attains green colour due to the formation of chromic sulphate.

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

The sulphite also gives white precipitate with $BaCl_2$, soluble in dil. HCl

$Na_2SO_3 + BaCl_2 \rightarrow 2NaCl + BaSO_3\downarrow$

Sulphide, S^{-2}:

(i) The sulphide salts form H_2S which smells like rotten eggs.

$Na_2S + H_2SO_4 \rightarrow NaSO_4 + H_2S\uparrow$

(ii) On exposure to this gas, the lead acetate paper turns black due to the formation of lead sulphide.

$Pb(CH_3COO)_2 + H_2S \rightarrow \underset{\text{black ppt.}}{PbS}\downarrow + 2CH_3COOH$

(iii) The sulphides also turn sodium nitroprusside solution violet (use sodium carbonate extract for this test).

$Na_2S + Na_2[FeNO(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$

Sulphide of lead, calcium, nickel, cobalt, antimony and stannic are not decomposed with dilute H_2SO_4. Conc. HCl should be used for their test. However brisk evolution of H_2S takes place even by use of dilute H_2SO_4 if a pinch of zinc dust is added.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$

$HgS + 2H \rightarrow Hg + H_2S\uparrow$

Nitrite, NO_2^-:

(i) The nitrites yield a colourless nitric oxide gas which in contact with oxygen of the air becomes brown due to the formation of nitrogen dioxide.

$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_2$

Nitrous acid

$3HNO \rightarrow H_2O + 2NO + HNO_3$

$2NO + O_2 \rightarrow 2NO_2$

brown coloured gas

(ii) On passing the gas through dilute $FeSO_4$ solution, brown colored complex salt is formed.

$FeSO_4.7H_2O + NO \rightarrow [Fe(H_2O)_5NO]SO_4 + 2H_2O$

Brown ring complex

(iii) When a mixture of iodide and nitrite is treated with dilute H_2SO_4, the iodides are decomposed giving violet vapours of iodine, which turns starch iodide paper blue.

$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$

$2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$

$2HNO_2 + 2HI \rightarrow 2H_2O + I_2 + 2NO$

Violet vapours

I_2 + Starch → colour

Chloride Cl^-

(i) Colourless pungent fumes of hydrogen chloride are evolved.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

(ii) Yellowish green chlorine gas with suffocating odour is evolved on addition of MnO_2 to the above reaction mixture.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$MnO_4 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(iii) The gas evolved forms white fumes of ammonium chloride with NH_4OH.

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

(iv) The gas evolved or solution of chloride salt forms a curdy precipitate of silver chloride with silver nitrate solution.

$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$

Note:

(a) The curdy precipitate of AgCl dissolves in ammonium hydroxide forming a complex salt.

$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2Cl + 2H_2O$

(b) The solution having the silver complex on acidifying with dilute nitric acid gives again a white precipitate of silver chloride.

$Ag(NH_3)_2Cl + 2HNO_3 \rightarrow AgCl + 2NH_4NO_3$

(c) Chromyl chloride Test: When solid chloride is heated with conc. H_2SO_4 in presence of $K_2Cr_2O_7$, deep red vapours of chromyl chloride are evolved.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$K_2Cr_2O_7 + 2HCl \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$

Chromyl chloride

These vapours on passing through NaOH solution form the yellow solution due to the formation of sodium chromate.

$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

Yellow colour

The yellow solution neutralized with acetic acid gives a yellow precipitate of lead chromate with lead acetate.

$Na_2CrO_4 + Pb(CH_3COO)_2 \rightarrow PbCrO_4 + 2CH_3COONa$

Yellow ppt.

Note:

(a) This test is not given by the chloride of mercuric, tin, silver, lead and antimony.

(b) The chromyl chloride test is always to be performed in a dry test tube otherwise the chromyl chloride vapours will be hydrolysed in the test tube.

$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl$

(c) Bromides and iodides do not give this test.

Bromide, Br^-:

(a) Reddish-brown fumes of bromine are formed.

$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$

(b) More reddish brown fumes of bromine are evolved when MnO_2 is added.

$$2NaBr + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$$

(c) The aqueous solution of bromide or sodium carbonate extract gives pale yellow precipitate of silver bromide which partly dissolve in excess of NH_4OH forming a soluble complex.

$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$

Pale yellow ppt.

$AgBr + 2NH_4OH \rightarrow Ag(NH_3)_2\,Br + 2H_2O$

Iodide, I^-:

(a) Violet vapours of iodine are evolved.

$2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI$

$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

(b) Violet vapours with starch produce blue colour.

I_2 + starch → Blue colour

(c) More violet vapours are evolved when MnO_2 is added.

$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$

(d) Aqueous solution of the iodide or sodium carbonate extract gives yellow precipitate of Agl with silver nitrate solution which does not dissolve in NH_4OH.

$NaI + AgNO_3 \rightarrow \underset{\text{Yellow ppt.}}{AgI} + NaNO_3$

Nitrate, NO_3^-:

(a) Light brown fumes of nitrogen dioxide are evolved.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$4\,HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$

(b) These fumes intensify when copper turnings are added.

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(c) **Ring Test:** An aqueous solution of salt is mixed with freshly prepared $FeSO_4$ solution and conc. H_2SO_4 is poured in test tube from sides, a brown ring is formed on account of the formation of a complex at the junction of two liquids.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

$[Fe(H_2O)_6]SO_4.H_2O + NO \rightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + H_2O$

Oxalate, $C_2O_4^{-2}$:

A mixture of CO and CO_2 is given off. The CO burns with blue flame.

$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$

$H_2C_2O_4 + H_2SO_4 \rightarrow CO + CO_2 + H_2O + [H_2SO_4]$

$2CO + O_2 \rightarrow 2CO_2$

Sulphate, SO_4^{-2}:

Add conc. HNO_3 to a small amount of substance or take sodium carbonate extract and then add $BaCl_2$ solution. A white precipitate of $BaSO_4$ insoluble in conc. acid is obtained.

$NaSO_4 + BaCl_2 \rightarrow 2NaCl + \underset{\text{White ppt.}}{BaSO_4}$

Borate:

To a small quantity of the substance (salt or mixture), add few multilitres of ethyl alcohol and conc. H_2SO_4 and stir the contents with a glass rod. Heat the test tube and bring the mouth of the test tube near the flame. The formation of green edged flame indicates the presence of borate.

$2Na_3BO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 2H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Ethyl borate}}{(C_2H_5)_3BO_3} + 3H_2O$

Phosphate:

Add conc. HNO_3 to a small amount of substance or take sodium carbonate extract, heat and then add ammonium molybdate. A canary yellow precipitate of ammonium phosphomolybdate is formed.

$Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 3Ca\,(NO_3)_2 + 2H_3PO_4$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow \underset{\text{Canary yellow ppt.}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$

Solved Examples

1. Chemical volcano is produced on heating:

(a) $K_2Cr_2O_7$ (b) $(NH_4)_2Cr_2O_7$

(c) $ZnCr_2O_7$ (d) K_2CrO_4

Sol. (b) On heating $(NH_4)_2Cr_2O_7$, N_2 is given out with Cr_2O_3 powder at higher rate giving a look artificial volcano.

2. Which of the following ions forms(s) ppt. with KI:

(a) Mg^{2+} (b) Pb^{2+}

(c) Hg^{2+} (d) Cu^{2+}

Sol. (b, c, d)

$$Pb^{2+} + 2I^- \rightarrow \underset{\text{Yellow ppt.}}{PbI_2}$$

$$Hg^{2+} + 2I^- \rightarrow \underset{\text{Red ppt.}}{HgI_2}$$

$$Cu^{2+} + 2I^- \rightarrow CuI_2 \rightarrow \underset{\text{White ppt.}}{Cu_2I_2} + I_2$$

3. Name one common reagent that can form precipitate or react and differentiate the following pairs:

(a) Ag^+ and Ba^{2+} (b) Cu^{2+} and Pb^{2+}

(c) Fe^{3+} and Cu^{2+} (d) Co^{2+} and Cu^{2+}

Sol. (a) $K_2Cr_2O_4$

$$2Ag^+ + CrO_4^{2-} \rightarrow \underset{\text{Red}}{Ag_2CrO_4\downarrow}$$

$$Ba^{2+} + CrO_4^{2-} \rightarrow \underset{\text{Yellow}}{BaCrO_4\downarrow}$$

(b) K_2CrO_4

$$Cu^{2+} + CrO_4^{2-} \rightarrow \underset{\text{Chocolate}}{CuCrO_4\downarrow}$$

$$Pb^{2+} + CrO_4^{2-} \rightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow}$$

(c) NH_4SCN

$$Fe^{3+} + 3SCN^- \rightarrow \underset{\text{red colour}}{[Fe(SCN)_3]\downarrow}$$

$$2Cu^{2+} + 4SCN^- \rightarrow \underset{\text{white}}{Cu_2(SCN)_2\downarrow} + (SCN)_2$$

(d) NH_4SCN

$$Co^{2+} + 4SCN^- \rightarrow \underset{\text{blue colour}}{[Co(SCN)_4]^{2-}}$$

$$2Cu^{2+} + 4SCN^- \rightarrow \underset{\text{White}}{[Cu_2(SCN)_2]\downarrow} + (SCN)_2$$

4. In which of the following tests, Cl^- ion is tested by observing the colour of a precipitate which does not contain Cl^- ions at all:

(a) Chromyl chloride test

(b) Lassaigne's test

(c) Silver mirror test

(d) Fehling solution test

Sol. (a) $CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{Yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \rightarrow \underset{\text{Yellow ppt.}}{PbCrO_4} + 2CH_3COONa$$

5. When an inorganic mixture was treated with excess of dil. H_2SO_4, effervescence were produced. The solution was heated till effervescence ceased. After this a small pinch of MnO_2 were added, fresh effervescence were produced. Select the correct statements:

(a) Mixture contains CO_3^{2-} ions

(b) Mixture contains $C_2O_4^{2-}$ ions

(c) Mixture contains SO_3^{2-} ions

(d) Mixture contains CO_3^{2-} and $C_2O_4^{2-}$

Sol. (d) Effervescence on heating the mixture with dil. H_2SO_4, it is due to decomposition of carbonate.

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_3 + CO_2 + H_2O$$

When evolution of CO_2 occurs again after adding MnO_2, it is due to decomposition of oxalate.

$$Na_2C_2O_4 + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + 2CO_2$$

6. Few drops of a salt solution are shaken with chloroform, chlorine water. Chloroform layer becomes violet. The solution contains:

(a) F^- ion (b) Cl^- ion

(c) Br^- ion (d) I^- ion

Sol. (d) $2KI + Cl_2 \rightarrow 2KCl + I_2$;

$I_2 + CCl_4 \rightarrow$ violet solution

7. Name one common reagent that can precipitate or react and differentiate following pairs:

(a) I^- and Cl^-

(b) I^- and Br^-

(c) SO_3^{2-} and SO_4^{2-}

Sol. (a) $AgNO_3$

$$Ag^+ + I^- \rightarrow \underset{\text{yellow}}{Agl}$$

$$Ag^+ + Cl^- \rightarrow \underset{\text{white}}{AgCl^-}$$

(b) Cl_2 water + $CHCl_3$:

$$2I^- + Cl_2 \rightarrow \underset{\text{(violet in CHCl3 layer)}}{I_2 + 2Cl^-}$$

$$2Br^- + Cl_2 \rightarrow \underset{\text{(orange in CHCl3 layer)}}{Br_2 + 2Cl^-}$$

(c) $BaCl_2$

$$BaCl_2 + SO_3^{2-} \rightarrow \underset{\text{white ppt. soluble in conc. HCl}}{BaSO_3\downarrow + 2Cl^-}$$

$$BaCl_2 + SO_4^{2-} \rightarrow \underset{\text{white ppt. insoluble in conc. HCl}}{BaSO_4\downarrow + 2Cl^-}$$

8. During qualitative test of nitrate radical, a brown ring is formed. The ring formed is due to the formation of:

(a) $FeSO_4NO$

(b) $(FeSO_4)_2NO$

(c) $FeSO_4(NO)_2$

(d) $[Fe(H_2O)_5NO]SO_4$

Sol. (d) $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$$6FeSO_4 + 2HNO_3 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO + 5H_2O \rightarrow [Fe(H_2O)_5NO]SO_4$$

Nitrosyl ferrous sulphate

9. An inorganic compound gives a white ppt. with a solution of $AgNO_3$, a white ppt. with dil. H_2SO_4 and imparts green colour to flame.

The probable compound is:

(a) $CuCl_2$	(b) $BaCl_2$
(c) $Cu(NO_3)_2$	(d) $PbCl_2$

Sol. (b) $2AgNO_3 + BaCl_2 \rightarrow 2AgCl + Ba(NO_3)_2$

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{White ppt.}}{BaSO_4} + 2HCl$$

Barium imparts green colour to flame.

10. An inorganic salt in its a solution produced a white ppt. with NaOH which dissolves in excess of NaOH, Also its a solution produced light yellow ppt. with $AgNO_3$, sparingly soluble in NH_4OH the probable salt is:

Sol. (a) $AlBr_3 + 3NaOH \rightarrow \underset{\text{White ppt.}}{Al(OH)_3} + 3NaBr$

$$Al(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{NaAlO_2} + 3NaBr$$

$$3AgNO_3 + AlBr_3 \rightarrow \underset{\text{Light yellow ppt.}}{3AgBr} + Al(NO_3)_3$$

The salt is $AlBr_3$.

11. A compound (A) forms an unstable pale blue colour solution in water. The solution decolorizes Br_2 water and an acidified solution of $KMnO_4$. The possible compound (A) is:

(a) HNO_2	(b) HNO_3
(c) N_2O_5	(d) None of these

Sol. (a) HNO_2 is pale blue in colour due to dissolution of N_2O_3. In conc. solution it decomposes as:

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$

and in dilute solution as:

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

Reaction with:

(a) Br_2 water-

$$HNO_2 + H_2O + Br_2 \rightarrow HNO_3 + 2HBr$$

(b) $KMnO_4 + 3H_2SO_4 + 5HNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$

12.(a) If $CO_2(g)$ under pressure is passed into $Na_2CrO_{4(aq.)}$, $Na_2Cr_2O_{7(aq.)}$ is formed. What is the function of the $CO_2(g)$?

(b) When zinc is added to acidic solution of $Na_2Cr_2O_7$. What is the colour of the solution?

(c) In acidic solution silver (II) oxide first dissolves to produce Ag^{2+} (aq.) and then reduces to Ag^+ by H_2O which is oxidized to $O_2(g)$. Explain?

Sol. (a) CO_2 makes the solution acidic that can convert Na_2CrO_4 to $Na_2Cr_2O_7$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

(b) Zn reduces $Cr_2O_7^{2-}$ to Cr^{3+} (green) and then to Cr^{2+} (blue). Over a long time, Cr^{2+} is oxdised to Cr^{3+} by atmospheric O_2 and thus blue colour changes to green.

$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 14H^+ + 3Zn \rightarrow \underset{\text{green}}{2Cr^{3+}} + 7H_2O + 3Zn^{2+}$

$\underset{\text{Green}}{Cr^{3+}} + e^- \rightarrow \underset{\text{blue}}{Cr^{2+}}$

$\underset{\text{Blue}}{Cr^{2+}} \rightarrow \underset{\text{green}}{Cr^{3+}} + e^-$

(**Note:** These reactions are spontaneous based on the standard reduction electrons potential values.)

(c) $AgO + 2H^+ \rightarrow Ag^{2+} + H_2O$

$4Ag^{2+} + 2H_2O \rightarrow 4Ag^+ + 4H^+ + O_2$

13. Colourless salt (A), on heating with sodium hydroxide, give gas (B) that can also be obtained when Mg_3N_2 reacts with H_2O. When reaction of (A) with NaOH was complete, solution obtained on reaction with $FeSO_4$ gave a brown coloured ring (C) between two layers. (A) on heating strongly, forms (D) and (E). (D) and (E) reacting together forming a dibasic acid (F) that exists as cis and trans isomers. Identify (A) to (F) and explain reactions.

Sol. $(A) \xrightarrow{NaOH.\Delta} (B) \xleftarrow{H_2O} Mg_3N_2$

(A) has NH_4^+ ion and (B) is NH_3

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

$NH_4^+ + NaOH \rightarrow Na^+ + NH_3 + H_2O$

Resultant solution after NH_3 has escaped completely. It contains Na^+ and anion of (A) which also gives Ring Test of NO_3^- thus, (A) is NH_4NO_3

$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$

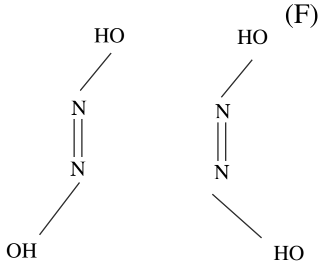
$NaNO_3 + H_2SO_4 \rightarrow NH_3\uparrow + NaHSO_4 + HNO_3$

$2HNO_3 \rightarrow H_2O + 3NO + 3O$

$[Fe(H_2O)_6]SO_4 + NO \rightarrow \underset{(C)}{[Fe(H_2O)_5NO]SO_4} + H_2O$

$\underset{(A)}{NH_4NO_3} \xrightarrow{\Delta} \underset{(D)}{N_2O} + \underset{(E)}{2H_2O}$

$N_2O + H_2O \longrightarrow \underset{(F)}{H_2N_2O_2}$



Trans cis

14. Identify (A) and (B) based on following reactions:

(i) $(A) \xrightarrow[\Delta]{NaOH} \underset{(gas)}{(B)} \xrightarrow{HCl}$ white fumes

(ii) After (B) is expelled completely, resultant alkaline solution again gives gas (B) on heating with zinc.

(iii) $(A) \xrightarrow{\Delta} N_2O + H_2O$

Sol. By (iii) (A) gives N_2O, H_2O on heating hence (A) is NH_4NO_3

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(i) $NH_4NO_3 + NaOH \xrightarrow{\Delta} NaNO_3 + \underset{(B)}{NH_3} + H_2O$

$\underset{(B)}{NH_3} + HCl \rightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$

(ii) $2NaOH + Zn \xrightarrow{\Delta} Na_2ZnO_2 + 2H$

$NaNO_3 + 8H \xrightarrow{\Delta} NaOH + \underset{(B)}{NH_3} + 2H_2O$

(NH_3 gas is obtained due to reduction of NO_3^- to NH_3)

15. A mineral popularly known as apatite is used to prepare a fertilizer, which provides phosphorus element to the soil.

(a) The fertilizer is obtained by treating apatite with H_2SO_4.

(b) When heated with silica and coke, it yields white phosphorus and calcium silicate.

Suggest formula for apatite and explain the chemical reactions (i) and (ii)

Sol. Chemically apatite is $Ca_3(PO_4)_2$

(a) When apatite is heated with H_2SO_4(s)

$\rightarrow Ca(H_2PO_4)_2$
(super phosphate of lime)

(b) When apatite mineral is heated with silica (SiO_2) and coke (C), white phosphorus is obtained as follows:

(i) $2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow \underset{\text{(calcium silicate)}}{6CaSiO_3} + 3P_2O_5$

(ii) $2P_2O_5 + 10C \rightarrow \underset{\text{(white phosphorus)}}{P_4} + 10CO$

16. (A)+tap water → white turbidity soluble in aq. NH_3

$(A) \xrightarrow{\Delta}$ residue (B) + (C) (oxides of N) + O_2

aq. (A) gives brown ring on adding $FeSO_4$ and conc. H_2SO_4. (C) is paramagnetic and forms dimer of vapour density 46. Identify (A), (B) and (C) and explain reactions.

Sol. (A)+tap water$\rightarrow$white turbidity soluble in a NH_3. Tap water has Cl^- and turbidity is soluble in a NH_3 hence, turbidity is of AgCl

(A) has Ag^+

(A) also gives ring test of NO_3^-

(A) is $AgNO_3$

$$2AgNO_3 \rightarrow 2Ag + \underset{(B)}{2NO_2} + \underset{(C)}{O_2}$$

NO_2 is paramagnetic due to one unpaired electron and thus forms dimer by using unpaired electron.

$$2NO_2 \rightleftarrows \underset{\text{dimer (V.D. = 46)}}{N_2O_4}$$

17. If Cu^{2+} and Cd^{2+} both are present, it is difficult to analyse. Outline a scheme to analyse in a mixture.

Sol. KCN forms complex with Cu^{2+} and Cd^{2+}

$$Cu^{2+} + KCN \rightarrow K_2[Cu(CN)_4] \rightarrow \underset{\text{Stable}}{K_3[Cu^{+1}(CN)_4]}$$

$$Cd^{2+} + KCN \rightarrow \underset{\text{Unstable}}{K_2[Cd(CN)_4]}$$

When H_2S gas is passed unstable complex of Cd^{2+} gives yellow ppt.

$$[Cd(CN)_4]^{2-} \rightarrow Cd^{2+} + 4CN^-, Cd^{2+} + S^{2-} \rightarrow \underset{\text{yellow}}{CdS\downarrow}$$

18. Identify (A), (B), (C) and (D) and explain reactions.

(A) (green coloured salt) + $K_2Cr_2O_7$ + conc. $H_2SO_4 \xrightarrow{\Delta}$ (B)

(B) (reddish brown gas) + NaOH $\rightarrow$ (C) (yellow coloured solution)

(C) + $(CH_3COO)_2Pb \rightarrow$ (D) (yellow ppt.)

(A) + NaOH + Br_2 water $\xrightarrow{\Delta}$ (C)

(C) + $(CH_3COO)_2Pb \xrightarrow{\Delta}$ (D)

Sol. (A): $CrCl_3$

(B): CrO_2Cl_2 [by chromyl-chloride test of Cl^-]

(C): Na_2CrO_4

(D): $PbCrO_4$

19. (A), an important laboratory reagent, turns red litmus blue, imparts golden yellow colour in flame and is a good precipitating agent. (A) reacts with Zn or Al forming H_2 gas. (A) gives white ppt. with $ZnCl_2$ or $AlCl_3$ but ppt. dissolves in excess of (A). What is (A) and explain reaction.

Sol. (A) turns red litmus blue $\Rightarrow$ (A) is basic in nature.

(A) imparts golden yellow colour in flame $\Rightarrow$ (A) has Na^+

(A) gives H_2 gas with Zn or Al $\rightarrow$ (A) is NaOH.

Explanation:

$$2NaOH + Zn \rightarrow Na_2Z_nO_2 + H_2\uparrow$$

$$2NaOH + 2H_2O + 2Al \rightarrow 2NaAlO_2 + 3H_2\uparrow$$

$$ZnCl_2 + 2NaOH \rightarrow \underset{\text{White ppt.}}{Zn(OH)_2\downarrow} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2[Zn(OH)_4] \text{ or } Na_2ZnO_2}$$

$$AlCl_3 + 3NaOH \rightarrow \underset{\text{White ppt.}}{Al(OH)_3\downarrow} + 3NaCl$$

$$Al(OH)_3 + NaOH \rightarrow \underset{\text{Sodium meta-aluminate}}{Na[Al(OH)_4] \text{ or } NaAlO_2}$$

20. What single reagent solution (including H_2O) could be used to effect the separation of the following of solids?

a. NaOH and $Fe(OH)_3$
b. $Ni(OH)_2$ and $Fe(OH)_3$
c. Cr_2O_3 and $Fe(OH)_3$
d. MnS and CoS
e. AgCl and AgI

Sol. (a) H_2O can dissolve NaOH, $Fe(OH)_3$ remains insoluble in water.

(b) NH_4OH dissolve $Ni(OH)_2$, $Fe(OH)_3$ is insoluble

$$Ni(OH)_4 + 4NH_4OH \rightarrow \underset{\text{Soluble}}{[Ni(NH_3)_4]^{2+}}$$

(c) Excess of NaOH can dissolve Cr_2O_3 but $Fe(OH)_3$ remains insoluble.

$$Cr_2O_3 + 3H_2O \rightarrow 2Cr(OH)_3$$

$$Cr(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{Na[Cr(OH)_4]}$$

(d) Dilute HCl dissolves MnS soluble while CoS remains insoluble.

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S\uparrow$$

(e) A NH_3 would dissolve AgCl while AgI remains insoluble

$$AgCl + 2NH_3(aq.) \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl}$$

Exercise

LEVEL 1

1. Which of the following salt on heating with conc. H_2SO_4 gives violet vapours?

(a) Iodide salt (b) Nitrate salt

(c) Sulphate salt (d) Bromide salt

2. Salts of which of the following metal are white?

(a) Zinc (b) Cobalt

(c) Chromium (d) Fe

3. A glassy bead formed by heating borax on a platinum wire loop is:

(a) Sodium tetraborate

(b) Sodium metaborate

(c) Sodium metaborate and boric anhydride

(d) Boric anhydride and sodium tetraborate

4. An oxalate salt gives which of the following gas in dry heating test:

(a) $CO + CO_2$ (b) Only CO_2

(c) Only CO (d) Oxalic acid vapours

5. The salts of which of the following elements are generally dark green coloured?

(a) Chromium (b) Copper(I)

(c) Barium (d) Cobalt

6. The chromyl chloride test is meant for which of the following ion?

(a) Cl^- ions (b) Both Cl^- and Br^- ions

(c) I^- ions (d) Cl^- and CrO_4^{2-} ions

7. Which of the following gases turn lime water milky?

(a) SO_2 (b) CO_2

(c) H_2S (d) Both (a) and (b)

8. Yellow ammonium sulphide solution can be used for the separation of which of the following pair of species?

(a) CuS and PbS (b) PbS and Bi_2S_3

(c) Bi_2S_3 and CuS (d) CdS and As_2S_3

9. Reddish-brown (chocolate) ppt. are formed by mixing solutions containing respectively:

(a) Cu^{2+} and $[Fe(CN)_6]^{4-}$ ions

(b) Ba^{2+} and SO_4^{2-} ions

(c) Pb^{2+} and I^- ions

(d) Pb^{2+} and SO_4^{2-} ions

10. Which of the following gives black precipitate on passing H_2S through it?

(a) Acidified zinc nitrate solution

(b) Ammonical barium chloride solution

(c) Magnesium nitrate solution

(d) Copper nitrate solution

11. All ammonium salts liberate ammonia gas when:

(a) Heated with water

(b) Heated with caustic soda

(c) Heated with H_2SO_4

(d) Heated with $NaNO_2$

12. Addition of solution containing $C_2O_4^{2-}$ ions to an aqueous solution containing Ba^{2+}, Sr^{2+} and Ca^{2+} will precipitate.

(a) Ca^{+2} (b) Ca^{+2} and Sr^{2+}

(c) Ba^{+2} and Sr^{2+} (d) All three

13. Sodium sulphide react with sodium nitroprusside to form a purple coloured Compound. During the reaction the oxidation state of iron:

(a) Changes from +2 to +3

(b) Changes from +3 to +2

(c) Changes from +2 to +4

(d) Remains unchaged

14. Which of the following sulphide is not soluble in dil HNO_3?

(a) PbS (b) HgS

(c) ZnS (d) Bi_2S_3

15. Cu^{2+} ions will be reduced to Cu^+ ion by addition of an aqueous solution of:

(a) KF (b) KCl

(c) KI (d) KOH

16. Precipitate of AgCl dissolves in liquid ammonia due to the formation of:

(a) $[Ag(NH_4)_2]OH$

(b) $[Ag(NH_4)_2]Cl$

(c) $[Ag(NH_3)_2]OH$

(d) $[Ag(NH_3)_2]Cl$

17. On adding a solution of CrO_4^{2-} ions to an aqueous solution containing Ba^{2+}, Sr^{2+} and Ca^{2+} ions. The precipitate obtained first of all will be:

(a) $CaCrO_4$ (b) $SrCrO_4$
(c) $BaCrO_4$ (d) A mixture of all the three

18. Brown ring test is used to detect:

(a) Iodide (b) Nitrate
(c) Iron (d) Bromide

19. When sodium thiosulphate solution is shaken with iodine, thiosulphate is changed to:

(a) Sulphite ion
(b) Sulphate ion
(c) Tetrathionate ion
(d) Sulphide ion

20. Reaction of $K_2Cr_2O_7$ with NaCl and conc. H_2SO_4 gives:

(a) $CrCl_3$ (b) $CrOCl_2$
(c) CrO_2Cl_2 (d) Cr_2O_3

21. Which of the following gives blood red colour with KCNS?

(a) Cu^{2+} (b) Fe^{3+}
(c) Al^{3+} (d) Zn^{2+}

22. Which of the following imparts green colour to the Bunsen's flame?

(a) $B(OMe)_3$ (b) Na(OMe)
(c) $Al(OPr)_3$ (d) $Sn(OH)_2$

23. The aqueous solutions of which of the following pairs of salts will give yellow precipitate separately with aqueous solutions of barium bromide?

(a) K_2CrO_4, $AgNO_3$ (b) $AgNO_3$, K_2SO_4
(c) K_2CrO_4, K_2SO_4 (d) $AgNO_3$, Na_2CO_3

24. An aqueous solution is prepared by dissolving a mixture containing $ZnCl_2$, $CdCl_2$ and $CuCl_2$. H_2S gas is now passed through the aqueous solution of salt to form black ppt. The ppt. contains:

(a) CdS, CuS (b) CdS, CuS, ZnS
(c) CuS, ZnS (d) Only CuS

25. Which of the following compound will turn black on adding NH_4OH to it?

(a) Lead chloride
(b) Silver chloride
(c) Mercurous chloride
(d) Barium chloride

26. Among the pair of species given below which react with each other on mixing their aqueous solutions to give yellow precipitate:

(I) KI and Silver nitrate
(II) KI and Lead (II) nitrate
(III) KI and KBr
(IV) KI and I_2

(a) I, II (b) II, III
(c) I, II, IV (d) Only I

27. Which salt would give a colourless gas having pungent smell with hot dil. H_2SO_4 and at the same time it will decolourise bromine water?

(a) Na_2SO_4 (b) $NaHSO_4$
(c) Na_2SO_3 (d) Na_2CO_3

28. Which of the following contains colourless gases which form white fumes on coming in contact with each other?

(a) SO_2, HCl (b) Cl_2, NH_3
(c) HCl, NH_3 (d) CO, Cl_2

29. Red vapour obtained by heating a mixture of KCl and potassium dichromate is passed through dil. Sodium hydroxide solution. The colour of the solution so obtained is:

(a) Bright red (b) Yellow
(c) green (d) Scarlet

30. Which of the following reagent can help in the separation of Cu^{2+} an Cd^{2+} ions in the solution?

(a) H_2S in acidic medium
(b) H_2S in alkaline medium
(c) KCN solution
(d) K_4 $[Fe(CN)_6]$ solution

LEVEL II

1. $Fe(OH)_3$ can be separated from $Al(OH)_3$ by addition of:

(a) $BaCl_2$ (b) Dil. HCl
(c) NaOH solution (d) NH_4Cl and NH_4OH

2. An aqueous solution of a substance, on treatment with dilute HCl, gives a white precipitate soluble in hot water. When H_2S is passed through the hot acidic solution, a black precipitate is formed. The substance is:

(a) Hg_2^{2+} salt (b) Cu^{2+} salt
(c) Ag^+ salt (d) Pb^{2+} salt

3. $CrCl_3 \xrightarrow[NH_4OH]{NH_4Cl} (A) \xrightarrow[H_2O]{Na_2O_2} (B) \xrightarrow[acetate]{Lead}$ (C) ; compound (C) is:

(a) Na_2CrO_4 (b) $Na_2Cr_2O_7$

(c) $Cr(OH)_3$ (d) $PbCrO_4$

4. $2Cu^{2+} + 5I^- \longrightarrow 2CuI\downarrow + [X]$

$[X] + 2S_2O_3^{2-} \longrightarrow 3[Y] + S_4O_6^{2-}$; X and Y are:

(a) I_3^- and I^- (b) I_2 and I_3^-

(c) I_2 and I^- (d) I_3^- and I_2

5. Which of the following reagents can separate a mixture of AgCl and AgI?

(a) KCN (b) $Na_2S_2O_3$

(c) HNO_3 (d) NH_3

6. $FeSO_4$ is used in the brown ring test for a nitrate. What is the oxidation state of Fe in the compound responsible for the brown colour of the ring?

(a) 0 (b) +1

(c) + 2 (d) + 3

7. In an alkaline solution, sodium nitroprusside gives a violet colour with:

(a) S^{2-} (b) SO_3^{2-}

(c) SO_4^{2-} (d) NO_2^-

8. Which of the following sulphides is white?

(a) CdS (b) PbS

(c) ZnS (d) SnS

9. A white sublimate substance, that turns black on treatment with an NH_3 solution can be:

(a) Hg_2Cl_2 (b) $HgCl_2$

(c) As_2O_3 (d) NH_4Cl

10. Which of the following pairs of cations can be separated by adding NH_4Cl and NH_4OH to the mixture and then passing H_2S through it?

(a) Fe^{3+}, Al^{3+} (b) Cr^{3+}, Ni^{2+}

(c) Al^{3+}, Cr^{3+} (d) Fe^{3+}, Cr^{3+}

11. Which of the following pairs of sulphides are insoluble in dilute HCl?

(a) CoS and NiS (b) CoS and MnS

(c) NiS and MnS (d) NiS and ZnS

12. On heating, a salt gives a gas which turns lime water milky and an acidified dichromate solution green. The salt may be:

(a) carbonate (b) sulphide

(c) sulphate (d) sulphite

13. Which of the following has the highest value of K_p?

(a) $BeCO_3$ (b) $MgCO_3$

(c) $CaCO_3$ (d) $BaCO_3$

14. $A + Na_2CO_3 \longrightarrow B + C,$

$A \xrightarrow{CO_2}$ (Milky) C

The chemical formula of A and B are respectively:

(a) NaOH and $Ca(OH)_2$

(b) $Ca(OH)_2$ and NaOH

(c) NaOH and CaO

(d) CaO and $Ca(OH)_2$

15. Which of the following salt on heating with concentrated H_2SO_4, coloured vapours do not evolve?

(a) NaBr (b) $NaNO_3$

(c) CaF_2 (d) KI

16. A salt made of bi-bivalent ions X and Y each of which is capable of decolourising acidified $KMnO_4$. The salt is likely to be:

(a) Ferric oxalate (b) Ferrous oxalate

(c) Ferrous sulphate (d) Stannic chloride

17. When concentrated H_2SO_4 is added to dry KNO_3, brown fumes are evolved. These fumes are due to:

(a) SO_2 (b) $SO_2 + SO_3$

(c) NO (d) NO_2

18. Freshly prepared chlorine water is added to the aqueous solution of some halide salt containing some CS_2. After shaking the contents, a violet colour appeared in CS_2 layer. The halide ion in solution is:

(a) Iodide (b) Bromide

(c) Chloride (d) Iodide as well as bromide.

19. For the confirmatory tests of acid radicals, sodium carbonate extract is prepared because:

(a) All anions react with Na

(b) Na is more reactive

(c) Na_2CO_3 is water soluble

(d) Sodium salts of almost all anions are water soluble.

20. In the precipitation of the radicals of iron group in qualitative analysis, NH_4Cl is added before adding NH_4OH. This causes:

(a) Decrease in the concentration of OH^- ions

(b) Removal of PO_4^{3-} ions

(c) Increase in the concentration of Cl^- ions

(d) Increase in the concentration of NH_4^+ ions

21. The aqueous solution of which of the following reagent will give Prussian blue coloured ppt. with an aqueous solution containing iron (III) ions?

(a) Potassium thiocyanate
(b) Potassium hexacyanoferrate (II)
(c) Potassium pyroantimonate
(d) All of these

22. Aqueous solution of salt A gives yellow precipitate with aqueous solution of K_2CrO_4. which of the following series of cation may be present in A?

(a) Pb^{2+}, Ag^{+} (b) Pb^{2+}, Ba^{2+}
(c) Ag^{+}, Cu^{2+} (d) Hg^{2+}, Ag^{+}

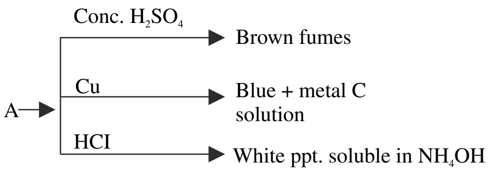
23. The reagent that can distinguish between silver and lead salt is:

(a) H_2S gas
(b) Hot dilute HCl solution
(c) NH_4Cl (solid) + NH_4OH (solution)
(d) NH_4Cl (solid) + $(NH_4)_2CO_3$ (solution)

24. A yellow turbidity, sometimes appears on passing H_2S gas even in the absence of the second group radicals. Explain why?

(a) Sulphur is present in the mixture as an impurity
(b) The fourth group radicals are precipitated as sulphides
(c) The H_2S is oxidized by some acidic radical present in solution
(d) The third group radicals are precipitated

25. Colourless salt (A)



The salt A can be:

(a) $Cu(NO_3)_2$ (b) AgBr
(c) $AgNO_3$ (d) $Pb(NO_3)_2$

26. Al^{3+}, Cr^{3+}, Fe^{3+} are grouped together for qualitative analysis because:

(a) Their carbonates are insoluble in ammonia
(b) Their hydroxides are insoluble in ammonia
(c) Their sulphides are insoluble in acid
(d) They belong to same group of periodic table

27. On addition of aqueous NaOH to a salt solution, a white gelatinous precipitate is formed, which dissolves in excess alkali. The salt solution contains:

(a) Chromous ions
(b) Aluminium ions
(c) Barium ions
(d) Iron ions

28. Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in:

(a) Red precipitate
(b) Blue precipitate
(c) Yellow precipitate
(d) No precipitate

29. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is:

(a) $Mg(NO_3)_2$ (b) Mg_3N_2
(c) NH_3 (d) MgO

30. A light green coloured salt (X) does not react with dilute and conc. H_2SO_4. Its aqueous solution becomes dark brown when sodium nitrite solution is added to it. X can be:

(a) Some salt of Ni (b) Some salt of copper
(c) $FeSO_4$ (d) Unpredictable

LEVEL III

ONE OR MORE THAN ONE CORRECT TYPE

1. Which of the following salts release reddish brown gas when heated in a dry test tube?

(a) $LiNO_3$ (b) KNO_3
(c) $Pb(NO_3)_2$ (d) $AgNO_3$

2. When Borax is heated it forms a colourless glassy bead because of formation of :

(a) B_2H_6 (b) $NaBO_2$
(c) B_2O_3 (d) $Na_2B_4O_7$

3. Which of the following metal chloride will give chromyl chloride test ?

(a) NaCl (b) KCl
(c) AgCl (d) $SbCl_3$

4. Which of the following statement(s) is/are correct with respect to bromide ions ?

(a) KBr on heating with MnO_2 and concentrated H_2SO_4 liberates Br_2 and SO_2 gases.

(b) KBr on heating with concentrated H_2SO_4 liberates Br_2 and SO_2 gases.

(c) KBr forms HBr with concentrated H_3PO_4.

(d) KBr(s) liberates Br_2 on gentile warming with concentrated H_2SO_4 and $K_2Cr_2O_7$(s).

5. KI solution is the reagent for :

(a) Hg^{2+} (b) Pb^{2+}

(c) Ag^+ (d) Cu^{2+}

6. Which of the following cations form(s) black precipitate(s) with H_2S(g)?

(a) Cu^{2+} (b) Sb^{3+}

(c) Pb^{2+} (d) Bi^{3+}

7. Which of the following is/are correct for potassium ferrocyanide?

(a) It gives a brown precipitate with Cu^{2+} ions.

(b) It gives a white preciptate of mixed salt with Ca^{2+} ions.

(c) It in excess gives a bluish white/white precipitate with Zn^{2+}

(d) It develops a deep red colouration with Fe^{3+}.

8. The following can be used to regulate the concentration of OH^- ions for the scheme of basic radical analysis (III group).

(a) NH_4NO_3 (b) NH_4Cl

(c) $(NH_4)_2SO_4$ (d) $(NH_4)_2CO_3$

9. Which of the following statement(s) is/are correct?

(a) Nickel salts give rosy red precipitate with dimethyl glyoxime in excess of NH_4OH.

(b) Fe(III) salts give red colour with potassium sulphocyanide

(c) In nitroprusside, the iron and NO exist as Fe(III) and NO.

(d) Mn(II) salts give white precipitate with NaOH which turns brown on adding Br_2 water.

10. Which statement(s) is/are correct with reference to the ferrous and ferric ions?

(a) Fe^{2+} gives brown colour with potassium ferricyanide

(b) Fe^{2+} gives blue colour with potassium ferricyanide

(c) Fe^{3+} gives red colour with potassium thiocyanate

(d) Fe^{2+} gives brown colour with potassium thiocyanate

11. Which of the following sulphates are soluble in water ?

(a) $CuSO_4$ (b) $PbSO_4$

(c) Ag_2SO_4 (d) $BaSO_4$

12. Which of the following substances on being heated will give a gas that turns lime water milky?

(a) Na_2CO_3 (b) $ZnCO_3$

(c) $ZnSO_3$ (d) $MgCO_3$

13. A yellow precipitate is obtained when :

(a) lead acetate solution is treated with K_2CrO_4

(b) $Pb(NO_3)_2$ solution is treated with K_2CrO_4

(c) $AgNO_3$ solution treated with KI

(d) H_2S is passed through a solution of $CdSO_4$

14. Which of the following species will be decomposed on acidification?

(a) $[Ag(NH_3)_2]^+$ (b) $[Cu(NH_3)_4]^{2+}$

(c) $[Zn(OH)_4]^{2-}$ (d) $[Pb(OH)_4]^{2-}$

PASSAGE BASED QUESTIONS

Passage # 1 (Q. 15 to 17)

A colourless inorganic compound (A) imparts a green colour to the flame. Its solution gives a white ppt. (B) with H_2SO_4. When heated with $K_2Cr_2O_7$ and conc. H_2SO_4, a brown red vapour/gas (C) is formed. The gas/vapour when passed through aqueous NaOH solution, it turns into a yellow solution (D) which forms yellow precipitate (E) with CH_3COOH and $(CH_2COO)_2Pb$

15. The colourless inorganic compound (A) is:

(a) $Ba(NO_3)_2$ (b) $BaCl_2$

(c) $CuCl_2$ (d) $CrBr_3$

16. The liberated gas vapour (C) is:

(a) Br_2 (b) NO_2

(c) CrO_2Cl_2 (d) Cl_2

17. The yellow ppt. formed when (D) reacts with CH_3COOH and $(CH_2COO)_2$ Pb is:

(a) PbI_2 (b) $PbCrO_4$

(c) $BaCrO_4$ (d) AgBr

Passage # 2 (Q. 18 to 20)

$$\text{Black solid} \xrightarrow[\Delta]{\text{KOH + Air}} \underset{\text{(green)}}{\text{(A)}} \xrightarrow{H_2SO_4} \underset{\text{(purple)}}{\text{(B)}} + \text{(C)}$$

(i) KI on reaction with alkaline solution of (B) changes into a compound (D).

(ii) The colour of the compound (B) disappears on treatment with the acidic solution of $FeSO_4$

(iii) With cold conc. H_2SO_4 compound (B) gives (E), which being explosive decomposes to yield (F) and oxygen.

18. Nature of compound (E) is:

(a) Acidic oxide

(b) Basic oxide

(c) Amphoteric oxide

(d) Neutral oxide

19. Colour of the solution obtained, when ferrous sulphate reacts with acidic solution of (B):

(a) Colourless (b) Pink

(c) Green (d) Yellow

20. Which of the following options is correct ?

(a) (C) and (F) are same compounds having same colour.

(b) (C) and (F) are different compounds having same colour.

(c) Compound (B) forms similar compound (E) with hot and conc. H_2SO_4.

(d) Compound (A) does not give same type of reaction in acidic and neutral medium.

Passage # 3 (Q. 21 to 23)

When a crystalline compound X is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas A is evolved. On passing A into caustic soda, a yellow solution of B is formed. A yellow precipitate of C is obtained when a solution of B is neutralised with acetic acid and then treated with a lead acetate solution. When X is heated with NaOH, a colourless gas is evolved which, when passed into a solution of $K_2[HgI_4]$, gives a reddish brown precipitate of D.

21. Compound (X) is:

(a) NH_4Br (b) NH_4Cl

(c) NH_4NO_2 (d) NH_4NO_3

22. If the solution B is colourless, which of the following ions would not be present in the solid X?

(a) Cl^- (b) Br^-

(c) NO_3^- (d) NO_2^-

23. Which of the following is the composition of the brown precipitate (D)?

(a) HgI_2 (b) $Hg(NH_2)I$

(c) HgO (d) $HgO.Hg(NH_2)I$

Passage # 4 (Q. 24 to 26)

(i) A white solid mixture of two salts containing a common cation is insoluble in water. It dissolved in dilute HCl producing some gases (with effervescence) that turns an acidified dichromate solution green. After the gases are passed through the acidified dichromate solution, the emerging gas turns baryta water milky.

(ii) On treatment with dilute HNO_3, the white solid gives a solution which does not directly give a precipitate with a $BaCl_2$ solution but gives a white precipitate when warmed with H_2O_2 and then treated with $BaCl_2$ solution.

(iii) The solution of the mixture in dilute HCl, when treated with NH_4Cl, NH_4OH and an Na_2HPO_4 solution, gives a white precipitate.

24. The gases evolved in (i) are:

(a) CO_2 and HCl (b) SO_2 and CO_2

(c) SO_2 and H_2S (d) NH_3 and CO_2

25. The white precipitate obtained in (ii) indicates the presence of a:

(a) carbonate (b) sulphide

(c) sulphite (d) chloride

26. The white precipitate obtained in (iii) consists of:

(a) $Ba_3(PO_4)_2$ (b) $Sr_3(PO_4)_2$

(c) $Ca_3(PO_4)_2$ (d) $MgNH_4PO_4.6H_2O$

INTEGER VALUE TYPE QUESTIONS

27. How many compounds liberate NH_3 on heating from the following?

(a) $(NH_4)_2\ SO_4$, (b) $(NH_4)_2\ CO_3$,

(c) NH_4Cl, (d) NH_4NO_3,

(e) $(NH_4)_2\ Cr_2O_7$

28. How many of the following reactions give yellow ppt.

(a) $NaBr + AgNO_3 \longrightarrow$

(b) $NaI + AgNO_3 \longrightarrow$

(c) $NaBr + Pb(NO_3)_2 \longrightarrow$

(d) $NaI + Pb(NO_3)_2 \longrightarrow$

(e) $Na_2S + Cd(CH_2COO)_2 \longrightarrow$

(f) $K_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow$

(g) $K_2CrO_4 + (CH_3COO)_2Ba \longrightarrow$

(h) $K_2CrO_4 + AgNO_3 \longrightarrow$

(i) NaBr + Cl_2 water (excess) $\longrightarrow$

29. An aqueous solution contains Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Bi^{3+} and Cd^{2+}. Out of these, how many ions will produce white precipitate with dilute HCl?

30. aq.$CuSO_4$ decolourizes on addition of KCN due to formation of complex (A). In complex "A".

(i) Number of d-orbital in hybridisation is/are "a"

(ii) Geometry of complex (b) :

(iii) Coordination number of Cu is "c". then find 8a + 7b + 5c.

(1) represents linear geometry

(2) represents tetrahedral geometry

(3) represents octahedral geometry

(4) represents square planer geometry

31. How many of the following pairs of ions can be separated by H_2S in dilute HCl?

(a) Bi^{3+} and Sn^{4+}, (b) Al^{3+} and Hg^{2+},

(c) Cd^{2+} and Zn^{2+}, (d) Fe^{3+} and Cu^{2+},

(e) As^{3+} and Sb^{3+}

Match the column type questions

32. Match the reagent which are used in qualitatiive analysis of gtiven anions :

	Column I	**Column II**
(A)	$AgNO_3$ solution	(a) CO_3^{2-}
(B)	$BaCl_2$ solution	(b) Cl^-
(C)	$PbNO_3$ solution	(c) S^{2-}
(D)	Acidified $KMnO_4$ solution	(d) NO_2^-

33.

	Column I	**Column II**
(A)	White turbidity	(a) $IO_3^- + SO_2$ + starch $\longrightarrow$
(B)	Rotten egg smell	(b) $SO_2 + MnO_4^- \longrightarrow$
(C)	Colourless solution	(c) Zn + NaOH + $SO_2 \longrightarrow$
(D)	Blue color	(d) $CO_2 + Ca(OH)_2 \longrightarrow$

34.

	Column I	**Column II**
(A)	Bi^{3+} give(s) black precipitate with	(a) H_2S (saturated solution in water)
(B)	Cu^{2+} give(s) black precipitate with	(b) Potassium thiocyanate solution
(C)	Zn^{2+} give(s) white precipitate with	(c) Potassium iodide solution
(D)	Ag^+ give(s) white precipitate with	(d) Potassium ferrocyanide solution

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. [X] + $H_2SO_4 \longrightarrow$ [Y] a colourless gas with irritating smell; [Y] + $K_2Cr_2O_7$ + $H_2SO_4 \longrightarrow$ green solution. [X] and [Y] is:

(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl

(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

[IIT-2003]

2. A dilute aqueous solution of a sodium salt froms white precipitate with $MgCl_2$, only after boiling. The anion of the sodium salt is:

(a) HCO_3^- (b) CO_3^{2-}

(c) NO_3^- (d) SO_4^{2-}

[IIT-2004]

3. The species present in solution when CO_2 is dissolved in water are:

(a) CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}

(b) HCO_3^-, CO_3^{2-}

(c) CO_3^{2-}, HCO_3^-

(d) CO_2, H_2CO_3

[IIT-2006]

4. A white precipitate is obtained when a solution is diluted with H_2O and boiled. On addition of excess NH_4Cl/ NH_4OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in ammonia solution or NH_4Cl.

(a) $Al(OH)_3$ (b) $Zn(OH)_2$

(c) $Mg(OH)_2$ (d) $Ca(OH)_2$

[IIT-2006]

5. In blue solution of copper sulphate excess of KCN is added then solution becomes colourless due to the formation of:

(a) $[Cu(CN)_4]^{2-}$

(b) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$

(c) $Cu(CN)_2$

(d) CuCN

[IIT-2006]

6. $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow$ white crystalline precipitate. The formula of crystalline precipitate is:

(a) $MgCl_2 . MgSO_4$ (b) $MgSO_4$

(c) $Mg(NH_4)PO_4$ (d) $Mg(PO_4)_2$

[IIT-2006]

7. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is:

(a) Pb^{2+} (b) Hg^{2+}

(c) Cu^{2+} (d) Co^{2+}

[IIT-2007]

8. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after some time. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salts(s) H is (are):

(a) NH_4NO_3 (b) NH_4NO_2

(c) NH_4Cl (d) $(NH_4)_2SO_4$

[IIT-2008]

Passage # 1 (Q. 9 to 11)

p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess additon of the reagent. Similarly, treatement of the solution of Y with the solution of potassium hexacyanoferrate(III) leads to a brown colouration due to the formation of Z.

[IIT-2009]

9. The compound X is:

(a) $NaNO_3$ (b) NaCl

(c) Na_2SO_4 (d) Na_2S

10. The compound Y is:

(a) $MgCl_2$ (b) $FeCl_2$

(c) $FeCl_3$ (d) $ZnCl_2$

11. The compound Z is:

(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$

(c) $Fe_4[Fe(CN_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

12. The equilibrium, $2Cu^I \rightleftarrows Cu^0 + C^{II}$ in aqueous medium at 25°C shifts towards the left in the presence of:

(a) NO_3^- (b) Cl^-

(c) SCN^- (d) CN^-

[IIT-2011]

Passage # 2 (Q. 13 to 15)

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH_3 dissolves O and give an intense blue solution.

[IIT-2011]

13. The metal rod M is:

(a) Fe (b) Cu

(c) Ni (d) Co

14. The compound N is:

(a) $AgNO_3$ (b) $Zn(NO_3)_2$

(c) $Al(NO_3)_3$ (d) $Pb(NO_3)_2$

15. The final solution contains:

(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$

(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$

(c) $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$

(d) $[Ag(NH_3)_2]^+$ and $[Ni(NH_3)_6]^{2+}$

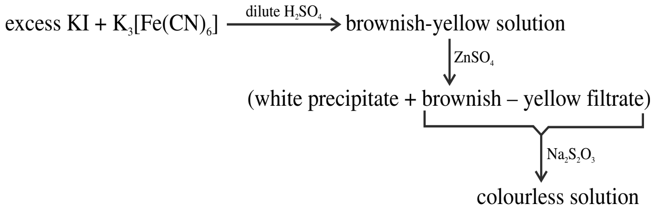
16. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates:

(a) CuS and HgS (b) MnS and CuS

(c) MnS and NiS (d) NiS and HgS

[IIT-2011]

17. For the given aqueous reaction which of the statement(s) is (are) true?



(a) The first reaction is a redox reaction

(b) White precipitate is $Zn_3[Fe(CN)_6]_2$

(c) Addition of filerate to starch solution gives blue colour

(d) White precipitates is soluble in NaOH solution

[IIT-2012]

18. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of:

(a) NO (b) NO_2

(c) N_2O (d) N_2O_4

[JEE Advanced - 2013]

19. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is:

(a) Fe(III) (b) Al(III)

(c) Mg(II) (d) Zn(II)

[JEE Advanced - 2013]

Passage # 3 (Q. 20 and 21)

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammonical medium. The precipitate (R) gave a coloured solution (s), when treated with H_2O_2 in an aqueous NaOH medium.

[JEE Advanced - 2013]

20. The precipitate P contains:

(a) Pb^{2+} (b) Hg_2^{2+}

(c) Ag^+ (d) Hg^{2+}

21. The coloured solution S contains:

(a) $Fe_2(SO_4)_3$ (b) $CuSO_4$

(c) $ZnSO_4$ (d) Na_2CrO_4

22. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of BLACK coloured sulphide is **[JEE Advanced - 2014]**

23. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are):

(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}

(c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

[JEE Advanced - 2015]

24. Which one of the following statement is correct?

(a) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl.

(b) Ferric ions gave a deep green precipitate on adding potassium ferrocyanide solution

(c) On boiling a solution having K^+, Ca^{2+} and HCO_3^- ions we get a precipitate of $K_2Ca(CO_3)_2$.

(d) Manganese salts give a violet borax bead test in the reducing flame

[AIEEE - 2013]

25. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is

(a) $(NH_4)_2Cr_2O_7$ (b) HgI_2

(c) HgO (d) Pb_3O_4

[AIEEE - 2003]

26. Which of the following compounds is not coloured yellow?

(a) $Zn_2[Fe(CN)_6]$ (b) $K_3[Co(NO_2)_6]$

(c) $(NH_4)_3[As(Mo_3O_{10})_4]$ (d) $BaCrO_4$

[JEE Main - 2015]

Answer Key

LEVEL I

1. (a) 2. (a) 3. (c) 4. (a) 5. (a) 6. (a) 7. (d) 8. (d) 9. (a) 10. (d)
11. (b) 12. (d) 13. (d) 14. (b) 15. (c) 16. (d) 17. (c) 18. (b) 19. (c) 20. (c)
21. (b) 22. (a) 23. (a) 24. (d) 25. (c) 26. (a) 27. (c) 28. (c) 29. (b) 30. (c)

LEVEL II

1. (c) 2. (d) 3. (d) 4. (a) 5. (d) 6. (b) 7. (a) 8. (c) 9. (a) 10. (b)
11. (a) 12. (d) 13. (a) 14. (b) 15. (c) 16. (b) 17. (d) 18. (a) 19. (d) 20. (a)
21. (b) 22. (b) 23. (b) 24. (c) 25. (c) 26. (b) 27. (b) 28. (d) 29. (b) 30. (c)

LEVEL III

1. (a, c, d) 2. (b, c) 3. (a,b) 4. (b,c,d) 5. (a, b, c, d) 6. (a, c, d) 7. (a, b, c) 8. (a, b)
9. (a, b, d) 10. (b,c) 11. (a, c) 12. (b, c, d) 13. (a,b, c, d) 14. (a, b, c, d) 15. (b) 16. (c)
17. (b) 18. (a) 19. (d) 20. (a) 21. (b) 22. (a) 23. (d) 24. (b)
25. (c) 26. (d) 27. (3) 28. (7) 29. (3) 30. (34) 31. (3)
32. A → a,b,c,d; B → a; C → a,b,c; D → b,c,d
33. A → d; B → c; C → b; D → a
34. A → a,c; B → a,b; C → a,d; D → b,d

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. (a) 2. (a) 3. (a) 4. (b) 5. (b) 6. (c) 7. (b) 8. (a, b) 9. (d) 10. (c)
11. (b) 12. (b, c, d) 13. (b) 14. (a) 15. (c) 16. (a) 17. (a, c, d) 18. (b) 19. (d) 20. (a)
21. (d) 22. (7) 23. (c, d) 24. (a) 25. (b) 26. (a)

Hints and Solutions

LEVEL I

1. **(a)** I^- ions are oxidized by H_2SO_4 to violet coloured I_2.

2. **(a)** Due to electronic configuration of Zn^{+2} is [Ar] $4s^0 3d^{10}$, salts of zinc are white (colourless).

3. **(c)** $Na_2B_4O_7 . 10H_2O \xrightarrow{\text{Strong heating}} \underbrace{2NaBO_2 + B_2O_3}_{\text{galssy bead}} + 10H_2O$

4. **(a)** Dry heating of oxalate slats give CO and CO_2.

5. **(a)** Chromium salts are in general green in colour.

6. **(a)** Chromyl chloride test is applied for the detection of Cl^- ion.

7. **(d)** Both CO_2 and SO_2 turn limewater ($Ca(OH)_2$) milky.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$

$Ca(OH)_2 + SO_2 \rightarrow \underset{\text{White}}{CaSO_3\downarrow} + H_2O$

8. **(d)** As_2S_3 is soluble in YAS (yellow ammonium sulphide) whereas CdS is not.

9. **(a)** $2Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow \underset{\text{Chocolate ppt.}}{Cu_2\,[Fe(CN)_6]}$

10. **(d)** $Cu(NO_3)_2 + H_2S \rightarrow \underset{\text{Black}}{CuS\downarrow} + 2HNO_3$

11. **(b)** $NH_4^+ + NaOH \rightarrow NH_3 + H_2O + Na^+$

12. **(d)** All the three ions will precipitate as their respective oxalates.

13. **(d)** $Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2\,[\overset{+2}{Fe}\,(CN)_5NO]} \rightarrow Na_4\,[\overset{+2}{Fe}\,(CN)_5(NOS)]$

There is no change in oxidation state of Fe.

14. **(b)** HgS is not soluble in dil. HNO_3. HgS is soluble in aqua regia.

15. **(c)** I^- ion acts as good reducing agent.

$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$

16. **(d)** $AgCl + NH_3 \rightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]Cl}$

17. **(c)** $BaCrO_4$ is precipitated first.

18. **(b)** Brown ring test is used to detect nitrate ion.

19. **(c)** $I_2 + S_2O_3^{-2} \rightarrow I^- + S_4O_6^{-2}$

20. **(c)** $NaCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow NaHSO_4 + KHSO_4 + H_2O + CrO_2Cl_2$

CrO_2Cl_2 is chromyl chloride.

21. **(b)** $FeCl_3 + KCNS \rightarrow \underset{\text{Blood red}}{Fe(SCN)Cl_2} + KCl$

22. **(a)** $H_3BO_3 + 3MeOH \rightarrow B(OMe)_3 + 3H_2O$

Methyl borate, $B(OMe)_3$ burns with green flame.

23. **(a)** $Ba^{+2} + K_2CrO_4 \rightarrow \underset{\text{Yellow}}{BaCrO_4\downarrow} + 2K^+$

$AgNO_3 + Br^- \rightarrow \underset{\text{yellow}}{AgBr\downarrow} + NO_3^-$

24. **(d)** All three Zn^{+2}, Cd^{+2} and Cu^{+2} form precipitate with H_2S but ZnS is white and

CdS is yellow in colour. The only black precipitate is CuS.

25. **(c)** $Hg_2Cl_2 + NH_4OH \rightarrow \underbrace{Hg + Hg(NH_2)}_{\text{black}} Cl + HCl + H_2O$

26. **(a)** $KI + AgNO_3 \rightarrow \underset{\text{yellow}}{AgI\downarrow} + KNO_3$

$2KI + Pb(NO_3)_2 \rightarrow \underset{\text{yellow}}{PbI_2\downarrow} + 2KNO_3$

27. **(c)** $Na_2SO_3 + H_2SO_4\ (dil) \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$

SO_2 is a colourless gas having pungent smell and it will decolourise bromine water.

28. **(c)** $NH_3 + HCl \rightarrow \underset{\text{(white fumes)}}{NH_4Cl\uparrow}$

29. **(b)** $K_2Cr_2O_7 + KCl + H_2SO_4 \rightarrow \underset{\text{(Red)}}{CrO_2Cl_2\uparrow}$

$CrO_2Cl_2 + NaOH \rightarrow \underset{\text{(Yellow)}}{Na_2CrO_4}$

30. **(c)** Both form colourless complex with KCN but complex of Cd^{+2} unstable. Complex of Cd^{+2} form yellow precipitate of CdS with H_2S.

LEVEL II

1. **(c)** $Al(OH)_3$ dissolves in excess NaOH while $Fe(OH)_3$ does not dissolves in NaOH.

2. **(d)** $Pb^{2+} + HCl(dil) \rightarrow \underset{\text{white}}{PbCl_2\downarrow}$ (soluble in hot water)

3. **(d)** $\underset{}{CrCl_3} \xrightarrow{NH_4Cl + NH_4OH} \underset{(A)}{Cr(OH)_3}$

$\underset{(A)}{Cr(OH)_3} \xrightarrow{Na_2O_2 + H_2O} \underset{(B)}{Na_2CrO_4}$

$\underset{(B)}{Na_2CrO_4} \xrightarrow{Pb(CH_3COO)_2} \underset{(C)}{PbCrO_4}$

4. **(a)** $2Cu^{2+} + 5I^- \rightarrow 2CuI + \underset{(X)}{I_3^-}$

$I_3^- + 2S_2O_3^{2-} \rightarrow \underset{(Y)}{3I^-} + S_4O_6^{2-}$

5. **(d)** AgCl forms soluble complex with NH_3 while AgI does not form soluble complex with NH_3.

6. **(b)** Brown ring complex is $[\overset{+1}{Fe}(H_2O)_5\overset{+1}{NO}]SO_4$

7. **(a)** $S^{2-} + Na_2[Fe(CN)_5 NO] \rightarrow \underset{\text{Violet}}{Na_4[Fe(CN)_5(NOS)]}$

8. **(c)** ZnS is white is colour.

9. **(a)** $\overset{+1}{Hg_2Cl_2} + NH_3 \rightarrow \underbrace{\overset{0}{Hg} + \overset{+2}{Hg(NH_2)}}_{\text{Black}} Cl + HCl$

10. **(b)** Fe^{+3}, Al^{+3} and Cr^{+3} are III group basic radicals while Ni^{+2} is IV group basic radical.

11. **(a)** CoS and NiS, both are insoluble in dilute HCl while ZnS and MnS are soluble in dilute HCl.

12. **(d)** $CaSO_3 \xrightarrow{\Delta} CaO + SO_2\uparrow$

SO_2 gas turns lime water milky and an acidified dichromate solution green.

13. **(a)** Order of thermal stability:

$BeCO_3 < MgCO_3 < CaCO_3 < BaCO_3$

$BeCO_3$ easily decomposes into $BeO + CO_2$

14. **(b)** $\underset{(A)}{Ca(OH)_2} + Na_2CO_3 \rightarrow \underset{(B)}{2NaOH} + \underset{(C)}{CaCO_3}$

$\underset{(A)}{Ca(OH)_2} \xrightarrow{CO_2} \underset{(C)}{CaCO_3}$

15. **(c)** $NaBr + H_2SO_4(conc.) \rightarrow Br_2\uparrow$ (reddish-brown)

$NaNO_3 + H_2SO_4(conc.) \rightarrow NO_2\uparrow$ (reddish-brown)

$CaF_2 + H_2SO_4(conc.) \rightarrow HF$ (colourless)

$KI + H_2SO_4(conc.) \rightarrow I_2\uparrow$ (violet)

16. **(b)** Ferrous oxalate consists of Fe^{2+} and $C_2O_4^{2-}$ each of which is capable of reducing MnO_4^- to Mn^{2+} ions.

17. **(d)** $KNO_3 + H_2SO_4(conc.) \rightarrow KHSO_4 + HNO_3$

$4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$

18. **(a)** Cl_2 oxidizes I^- ions to I_2 which dissolves in CS_2 to give violet colour.

19. **(d)** All sodium salts (except $NaHCO_3$) are soluble in water.

20. **(a)** $NH_4Cl \rightarrow NH_4^+ + Cl^-$
$NH_4OH \rightleftarrows NH_4^+ + OH^-$

NH_4Cl controls the concentration of OH^- ions by suppressing the ionization of NH_4OH due to common ion effect.

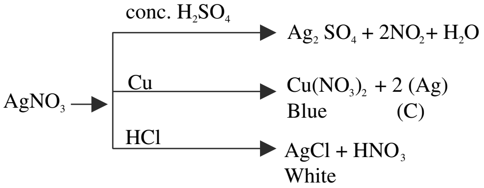
21. **(b)** $Fe^{+3} + K_4[Fe(CN)_6] \rightarrow \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + K^+$

22. **(b)** Both Pb^{2+} and Ba^{2+} gives yellow precipitate with aqueous solution of K_2CrO_4.

23 **(b)** Hot HCl will produce precipitate of AgCl with Ag^+ only. $PbCl_2$ will not precipitate because it is soluble in hot solution.

24. (c) Radicals such as NO_3^- oxidize H_2S to S which appears as turbidity.

25. (c) A is $AgNO_3$



26. (b) The hydroxides of these cations are insoluble in ammonical solution.

27. (b) $Al^{+3} + 3OH^- \rightarrow Al(OH)_3$ (white gelatinous precipitate)

$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + H_2O$

28. (d) DMG gives rose red precipitate with Ni^{+2} but not with Ni metal.

29. (b)
$$\begin{tikzcd} \underset{(X)}{3Mg} + N_2 \arrow[r] & \underset{(Y)}{Mg_3N_2} \arrow[r, "H_2O"] & Mg(OH)_2 + NH_3 \arrow[d, "CuSO_4"] \\ & & {[Cu(NH_3)_4]SO_4} \end{tikzcd}$$

30. (c) $FeSO_4$ solution gives black-brown colour with $NaNO_2$

LEVEL III

1. **(a, c, d)**

$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$

$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$

$2Pb(NO_3) \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$

$2AgNO_3 \xrightarrow{\Delta} Ag_2O + 2NO_2 + \frac{1}{2}O_2$

2. **(b, c)**

$Na_2B_4O_7.10H_2O\ \ddot{N}{\equiv}N\rightarrow\ \ddot{O}:\ \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy bead}} + 10H_2O$

3. **(a, b)**

NaCl and KCl give chromyl chloride test.

4. **(b, c, d)**

$MnO_2 + H_2SO_4(conc.) + KBr \xrightarrow{\Delta} KHSO_4 + MnSO_4 + H_2O + Br_2$

$KBr + H_2SO_4(conc.) \xrightarrow{\Delta} SO_2 + Br_2 + K_2SO_4 + H_2O$

$KBr + H_3PO_4(conc.) \xrightarrow{\Delta} KH_2PO_4 + HBr$

$K_2Cr_2O_7 + H_2SO_4(conc.) + KBr \rightarrow Cr_2(SO_4)_3 + Br_2 + H_2O + K_2SO_4$

5. **(a, b, c, d)**

$Hg^{2+} + 2I^- \longrightarrow \underset{\text{Red}}{HgI_2\downarrow}$

$Pb^{2+} + 2I^- \longrightarrow \underset{\text{Yellow}}{PbI_2\downarrow}$

$Ag^+ + I^- \longrightarrow \underset{\text{Yellow}}{AgI\downarrow}$

$2Cu^{2+} + 4I^- \longrightarrow \underset{\text{White}}{Cu_2I_2\downarrow} + I_2$

6. **(a, c, d)**

Cus, PbS, $Bi_2S_3 \longrightarrow$ black

$Sb_2S_3 \longrightarrow$ Orange

7. **(a, b, c)**

$Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3}$

8. **(a, b)**

$(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ can not be used to regulate the concentration of OH^- ions for III group basic radicals. Ba^{+2}(V group) can form precipitate $BaSO_4$ and $BaCO_3$.

9. **(a, b, d)**

In nitroprusside, the iron and NO exist as Fe(II) and NO^+.

10. **(b, c)**

$Fe^{+2} + K_3[Fe(CN)_6] \longrightarrow Fe_3\,[Fe(CN)_6]_2$ (which finally converts into $Fe_4[Fe(CN)_6]_3$)

$Fe^{+3} + KSCN \longrightarrow \underset{\text{blood red}}{Fe(SCN)_3}$

11. **(a, c)**

$CuSO_4$ and Ag_2SO_4 are water soluble.

12. **(b, c, d)**

CO_2 and SO_2 both gas can turn lime water milky.

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$

$ZnSO_3 \xrightarrow{\Delta} ZnO + SO_2\uparrow$

$MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$

13. **(a, b, c, d)**

$PbCrO_4$, AgI, CdS are yellow precipitate.

14. **(a, b, c, d)**

All complex will decompose on acidification.

15. **(b)** Compound (A) imparts a green colour to the flame. It implies that cation of compound is Ba^{+2}. This compound gives chromyl chloride test. It implies that anion of the compound is Cl^-.

16. **(c)** $\underset{(A)}{BaCl_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Ba(HSO_4)_2 + KHSO_4 + H_2O + \underset{(C)}{CrO_2Cl_2}\uparrow$

17. **(b)** Yellow precipitate (E) is $PbCrO_4$.

18. **(a)** $MnO_2 \xrightarrow[\Delta]{KOH + Air} \underset{(A)}{K_2MnO_4} \xrightarrow{H_2SO_4} \underset{(B)}{KMnO_4} + \underset{(C)}{MnO_2}$

$KMnO_4 + H_2SO_4$ (cold and conc.) $\longrightarrow Mn_2O_{7\,(E)}$

Mn_2O_7 is an acidic oxide

19. **(d)** $KMnO_4 + H_2SO_4 + FeSO_4 \longrightarrow$

$MnSO_4 + Fe_2(SO_4)_3 + H_2O + K_2SO_4$

Colourless Yellow

20. **(a)** (C) and (F) both are MnO_2

21. **(b)** Compound (X) gives chromyl chloride test and it also reacts with nesseler's reagent hence, (X) is NH_4Cl.

22. **(a)** If Br^- is present in (X) then Br_2 vapours are evolved which forms colourless $NaBr + NaOBr/NaBrO_3$ with NaOH.

If NO_3^- or NO_2^- is present in (X) then NO_2 gas is evolved which forms $NaNO_3$ and $NaNO_2$ with NaOH.

23. **(d)** $\underset{(X)}{NH_4Cl} + NaOH \rightarrow NH_3\uparrow$

$NH_3 + K_2HgI_4 + OH^- \rightarrow \underset{(D)}{HgO.Hg(NH_2)I\downarrow}$

24. **(b)** White solid consists of $MgCO_3$ and $MgSO_3$. With dilute HCl, this solid produces CO_2 and SO_2 gases.

25. **(c)** White precipitate in (ii) is $BaSO_4$.

It indicates presence of a sulphite.

26. **(d)** $MgCl_2 + NH_4OH + Na_2HPO_4 \rightarrow \underset{\text{(white)}}{Mg(NH_4)PO_4.6H_2O\downarrow}$

27. $(NH_4)_2SO_4 \xrightarrow{\Delta} NH_3 + H_2SO_4$

$(NH_4)_2CO_3 \xrightarrow{\Delta} NH_3 + CO_2 + H_2O$

$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

$(NH_4)_2Cr_2O7_4 \xrightarrow{\Delta} N_2 + Cr_2O_3 + H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

28. $NaBr + AgNO_3 \rightarrow AgBr$ (yellow)

$NaI + AgNO_3 \rightarrow AgI$ (yellow)

$NaI + Pb(NO_3)_2 \rightarrow PbI_2$ (yellow)

$Na_2S + Cd(CH_3COO)_2 \rightarrow CdS$ (yellow)

$K_2CrO_4 + Pb(CH_3COO)_2 \rightarrow PbCrO_4$ (yellow)

$K_2CrO_4 + (CH_3COO)_2Ba \rightarrow BaCrO_4$ (yellow)

$NaBr + Cl_2$ water (excess) $\rightarrow BrCl$ (yellow)

29. Hg_2Cl_2, $PbCl_2$, AgCl (all are white precipitate)

30. $CuSO_4(aq) + KCN_{(excess)} \rightarrow K_3[\overset{sp^3}{Cu}(CN)_4]$

(Tetrahedral)

a = 0 ; b = 2 ; c = 4

8a + 7b + 5c = 34

31. **(c)**

Al^{3+} (group III)	and	Hg^{2+} (group II)
Cd^{2+} (group II)	and	Zn^{2+} (group IV)
Fe^{3+} (group III)	and	Cu^{2+} (group II)
Bi^{3+} (group II)	and	Sn^{4+} (group II)
As^{3+} (group II)	and	Sb^{3+} (group II)

32. (A → a,b,c,d; B → a; C → a,b,c; D → b,c,d)

33. (A → d; B → c; C → b; D → a)

34. (A → a,c; B → a,b; C → a,d ; D → b,d)

PREVIOUS YEARS' QUESTIONS FOR JEE (MAIN AND ADVANCED)

1. **(a)** $\underset{[X]}{SO_3^{2-}} + H_2SO_4 \longrightarrow \underset{[Y]}{SO_2}$

$SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow \underset{\text{(green)}}{Cr_2(SO_4)_2} + K_2SO_4 + H_2O$

2. **(a)** $NaHCO_3 + MgCl_2 \xrightarrow{\Delta} \underset{\text{(white)}}{MgCO_3\downarrow}$

3. **(a)** $CO_2 + H_2O \longrightarrow \underset{(H^+,\ HCO_3^-,\ CO_3^{2-})}{H_2CO_3}$

4. **(b)** $Zn(OH)_2 + NH_3(\text{solution}) \longrightarrow [Zn(NH_3)_4]^{2+}$

Soluble complex

5. **(b)** $\overset{+2}{Cu}SO_4 + KCN(\text{excess}) \longrightarrow K_3[\overset{+1}{Cu}(CN)_4]$

6. **(c)** $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow \underset{\text{White}}{Mg(NH_4)PO_4}$

7. **(b)** $Hg^{2+} + KI \longrightarrow \underset{\text{red}}{HgI_2\downarrow}$

$HgI_2 + KI(\text{excess}) \longrightarrow \underset{\text{Soluble}}{K_2[HgI_4]}$

8. **(a,b)** $NH_4NO_3 + NaOH \longrightarrow NH_3 + NaNO_3$

$NaNO_3 + \text{Zn dust} \longrightarrow NH_3 + Na_2ZnO_2$

$NH_4NO_2 + NaOH \longrightarrow NH_3 + NaNO_2$

$NaNO_2 + \text{Zn dust} \longrightarrow NH_3 + Na_2ZnO_2$

9. **(d)** p-Amino-N, N-dimethylaniline + $\underset{(X)}{Na_2S}$ + $\underset{(Y)}{FeCl_3} \longrightarrow$ Methylene blue

$\underset{(Y)}{FeCl_3} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{blue}}{Fe_4[Fe(CN)_6]_3}$

$\underset{(Y)}{FeCl_3} + K_4[Fe(CN)_6] \longrightarrow \underset{(Z)}{Fe[Fe(CN)_6]}$

10. **(c)** $FeCl_3$

11. **(b)** $Fe[Fe(CN)_6$

12. **(b, c, d)**

With Cl^-, SCN^-, CN^- ions the more stable oxidation state of Cu is +1.

13. **(b)** $\underset{(M)}{Cu} + \underset{(N)}{AgNO_3} \rightarrow Ag + \underset{\text{light blue}}{Cu(NO_3)_2}$

$AgNO_3 + NaCl \rightarrow \underset{\substack{\text{White}\\(O)}}{AgCl\downarrow}$

$AgCl + NH_3 \rightarrow [Ag(NH_3)_2]^+$

$Cu(NO_3)_2 + NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

14 **(a)** $AgNO_3$

15. **(c)** $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$

16. **(a)** CuS and HgS

Cu^{2+} and Hg^{2+} are II group radicals.

17. **(a, c, d)**

$K_3[\overset{+3}{Fe}(CN)_6] + KI_{(excess)} \rightarrow K_4[\overset{+2}{Fe}(CN)_6] + \underset{\text{(Brownish yellow solution)}}{KI_3}$

$K_4[Fe(CN)_6] + ZnSO_4 \rightarrow K_2Zn_3[Fe(CN)_6]_2$ or $\underset{\text{white ppt.}}{K_2Zn[Fe(CN)_6]}$

$\underset{\text{(Brownish yellow filtrate)}}{I_3^-} + 2Na_2S_2O_3 \rightarrow \underset{\text{Clear solution}}{Na_2S_4O_6} + \underset{\text{(Turns starch solution blue)}}{2NaI + I_2}$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as,

$K_2Zn[Fe(CN)_6] + NaOH \longrightarrow \underset{\text{Soluble}}{[Zn(OH)_4]^{2-}} + [Fe(CN)_6]^{4-}$

18. **(b)** $4HNO_3 \xrightarrow{h\upsilon} 2H_2O + 4NO_2\uparrow + O_2\uparrow$

19. **(d)** Zn^{+2} is IV group radical.

20. **(a)** $PbCl_2$ is soluble in hot water.

21. **(d)** Q is group III radical

$\underset{(Q)}{Cr(OH)_3} + H_2O_2 + NaOH \longrightarrow \underset{\text{yellow solution}}{Na_2CrO_4\,(s)}$

22. PbS, CuS, HgS, Ag_2S, NiS, CoS (Black)

MnS (buff or pink)

SnS_2(yellow coloured)

Bi_2S_3(brown/black coloured)

23. **(c, d)**

Cu^{2+}, Pb^{2+}, Hg^{2+} and Bi^{3+}, all are group II radicals.

24 **(a)** AgI does not dissolve in NH_3.

25. **(b)** $HgI_2 + 2KI \rightarrow \underset{\text{Soluble}}{K_2[HgI_4]}$

26. **(a)** $Zn_2[Fe(CN)_6]$ is white in colour.