

**Editor-Babita Malik**

# **INORGANIC CHEMISTRY & SPECTROSCOPY**

(A SYSTEMATIC APPROACH)

**International E-Publication**

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**INORGANIC CHEMISTRY  
AND  
SPECTROSCOPY  
( A SYSTEMATIC APPROACH)**

*FOR CSIR/JRF/NET AND SET (CHEMICAL SCIENCES)  
(PROBLEMS WITH ITS SOLUTIONS)*

**Editor**

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## PREFACE

We are extremely beholden to my learned colleagues and inquisitive students for the tremendous support; they have accord to the previous book FUNDAMENTAL CONCEPT OF TRANSITION AND INNER TRANSITION ELEMENTS. This has prompted us to edit the next volume in accordance with the syllabi framed by UGC.

This book will be of interest to students and researchers involved in the study NET/JRF and GATE examinations. We are proud to say that this is one of the most in-depth, multi-dimensional review works of scientific researches. We have spent a lot of time reading firstly the introductory-cum-tutorial part and analyzing how the authors have approached the subject of Inorganic Chemistry and Spectroscopy.

Advanced undergraduate students enrolled in smart grid programs and students preparing for different competitive entrance examination will also find this book useful.

Several books are available which provide guidance to students appearing for NET/JRF and GATE examinations but there was a dearth of books which provide ample practice to the students by incorporating numerous exercises. The success of this e-book has been gratifying, it tells us that teachers have found it effective and that students have been found it useful and informative. Emphasis has been laid to incorporate a variety of practice problems for the benefit of the students. The unique feature of the book is the approach towards inorganic chemistry. It has been presented in the simplest manner covering all areas.

Our major objective is to develop confidence among the students who are appearing in NET/JRF and GATE examinations after post graduation by providing them solved objective type questions which covers the main aspect of the topic.

Keeping in view the need of the hour authors presented a unique book which aims at further enhancement of knowledge of the complex topics. The vast range of questions from a unique perspective gives a real comprehension of the various topics related to the concerned examinations.

We are confident that our presentation shall be well received by both the students as well as the worthy teachers throughout the country. We shall be eagerly awaiting their valuable suggestions and healthy criticism. Any suggestions for improvement of this book are welcome and will be gratefully acknowledged.

Authors

## ACKNOWLEDGMENT

Writing an acknowledgement becomes quite an uphill task, when so many persons contribute generously and whole heartedly for a project like this. One often finds it terrifically difficult to grip words to thank them, without whom this work would have been a non-entity. We are deeply indebted to a number of individuals who have made numerous contributions to the completion of this task. Some are identified below and others with apologies, perhaps, unwillingly overlooked.

We wish to express deep sense of gratitude to Dr. K K Sharma, Ex-Principal, Maharaj Singh College Saharanpur for his constant inspiration, intuitive guidance and timely help throughout the phase of my work.

We consider it most appropriate at this juncture to express our sincere thanks to Dr. Vijai Malik, Assistant Professor, Department of Botany, Maharaj Singh College Saharanpur for his kind advices, discussions and encouragement for writing this book.

The authors are also thankful to our students especially Mr. Navdeep Arora, Ms. Rakhi Verma, Ms. Gurmeet Kaur Bhatia and Mr. Arjun Tomar who provide all type of help for the completion of this book.

We shall ever remain grateful to all the staff members of Chemistry Department and all research scholars whose readily available help has been of immense value in completion of this work.

Last, but not the least, we bow our head to our parents for their affectionate love and blessings towards us throughout our education, which has placed us at present level of academics career.

### Authors

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## Chapter 1

### Chemistry of Transition Elements

(Contributed by: Dr. Dinkar Malik, Department of Chemistry, M. S. College, Saharanpur)

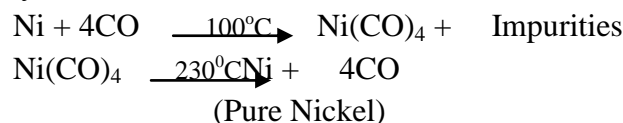
#### Critical Points:

- The first transition series is 3d-series having ten elements from  $_{21}\text{Sc}$  to  $_{30}\text{Zn}$ .
- The second transition series is 4d-series having ten elements from  $_{39}\text{Y}$  to  $_{48}\text{Cd}$ .
- The third transition series is 5d-series having ten elements from  $_{57}\text{La}$ ,  $_{72}\text{Hf}$  to  $_{80}\text{Hg}$ .
- $\text{Cu}^+$  is diamagnetic while  $\text{Co}^{+2}$  is paramagnetic.
- In the highest oxidation states, the transition metal show acidic character and form cationic complexes.
- Zn, Cd and Hg have relatively lower melting points than the other d-block element as they have completely filled (n-1) d-orbitals, their atoms are not expected to form covalent bonding among themselves.
- The existence of  $\text{Fe}^{+2}$  and  $\text{NO}^+$  in nitroprusside ion,  $[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$  can be established by measuring the magnetic moment of the solid compound which should correspond to  $\text{Fe}^{+2}$  ( $3d^6$ ) i.e. 4 unpaired electrons.
- 4d, 5d same group cations will have nearly same ionic size due to Lanthanide contraction.
- Misch metal is an alloy of rare earth metals with composition (Rare earth metals- 94.95%, Iron- 5% and trace amount of S, C, Ca, Al etc).
- Highest oxidation state (+8) is shown by Ru and Os in their oxides.
- Low oxidation state is generally shown by carbonyl compounds.
- First ionization energy of 5d elements is higher than those of 3d and 4d elements due to greater effective nuclear charge that is experienced over weak shielding of the nucleus by 4f electrons.
- Most of the transition metals alloys and compounds are used as catalysts in various processes.
- Catalytic property is due to the presence of vacant d-orbital, tendency to show variable oxidation states and their large surface area.
- Elements from Cr to Cu have almost same atomic radii because successive addition of d-electrons screened the outer electron (4s) from the inward pull of the nucleus.
- Transition metals can easily form alloys due to their almost equal atomic sizes, they can mutually substitute one another in the crystal lattice.
- Alloys having mercury one of the constituent elements are called amalgams.
- Transition metals show variable oxidation states due to participation of ns and (n-1) d electrons in bonding.



- Transition metals can trap some of the small size atoms such as C, H, B, N etc in the vacant spaces between the crystal lattice forming inter-orbital or interstitial compounds.

- Nickel is purified by Mond's Process.



- The values of  $E^\circ_{\text{R.P.}}$  of most of the transition elements except Cu and Hg is lower than that of hydrogen that is, a negative value, so they can easily displace hydrogen, from dilute acids.
- The values of  $E^\circ$  is mainly governed by these factors:
  - a) Heat of hydration
  - b) Heat of sublimation
  - c) Heat of ionization
- Acidic character of oxides increases with increase in oxidation number.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  is colored while  $[\text{Sc}(\text{H}_2\text{O})_6]^{+3}$  is colorless.
- 22 Carat Gold is an alloy of Cu and Au.
- Mercury is the only metal amongst transition elements which is liquid at  $0^\circ\text{C}$  due to weak metallic bond.

## Multiple Choice Questions

- Q.1. The \_\_\_\_\_ sphere is enclosed in brackets in formulas for complex species, and it includes the central metal ion plus the coordinated groups.
- (a) Ligand (b) Donor  
(c) Oxidation (d) Co-ordination
- Q.2. Which of following is least covalent or least acidic?
- (a)  $\text{VCl}_2$  (b)  $\text{VCl}_3$   
(c)  $\text{VCl}_4$  (d)  $\text{VOCl}_3$
- Q.3. There are 3 unpaired electrons in  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  and calculated value of magnetic moment is 3.87 B.M. which is quite different from the experimental value of 4.40 B.M. This is because of:
- (a) d-d\* transition  
(b) Change in orbital spin of the electron  
(c) Increase in no. of unpaired electrons.  
(d) Some contribution of the orbital motion of the electron to the magnetic moment.
- Q.4. In coordination chemistry, the donor atom of a ligand is:
- (a) A Lewis acid.  
(b) The counter ion  
(c) The central metal atom.  
(d) The atom in the ligand that shares an electron pair with the metal.
- Q.5. For  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  absorption maximum due to d-d transition is found at  $20000 \text{ cm}^{-1}$ . Therefore, the crystal field stabilization energy is:
- (a)  $-20000 \text{ cm}^{-1}$  (b)  $8000 \text{ cm}^{-1}$   
(c)  $4/9 \times 20000 \text{ cm}^{-1}$  (d)  $-8000 \text{ cm}^{-1}$
- Q.6. Amongst following the lowest degree of paramagnetism per mole of the compound at 298K will be shown by:
- (a)  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
(c)  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  (d)  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$
- Q.7. The oxidizing power of  $[\text{CrO}_4]^{2-}$ ,  $[\text{MnO}_4]^{2-}$  and  $[\text{FeO}_4]^{2-}$  follows the order:
- (a)  $[\text{CrO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-}$   
(b)  $[\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{CrO}_4]^{2-}$   
(c)  $[\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{CrO}_4]^{2-}$   
(d)  $[\text{CrO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-}$
- Q.8. Consider the coordination compound,  $\text{Na}_2[\text{Pt}(\text{CN})_4]$ . The Lewis acid is:
- (a)  $[\text{Pt}(\text{CN})_4]^{2-}$  (b)  $\text{Na}^+$   
(c)  $\text{CN}^-$  (d)  $\text{Pt}^{2+}$
- Q.9. In context with the transition elements which of the following statements is incorrect:
- (a) In addition to the normal oxidation state, the zero oxidation state is also shown by

these elements in complexes.

- (b) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
- (c) In the highest oxidation states, the first transition elements (Sc to Mn) all the 4s and 3d electrons are used for bonding.
- (d) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
- Q.10. Which of the following ions form most stable complex compound?
- (a)  $\text{Cu}^{+2}$  (b)  $\text{Ni}^{+2}$   
(c)  $\text{Fe}^{+}$  (d)  $\text{Mn}^{+2}$
- Q.11. The acidic, basic or amphoteric nature of  $\text{Mn}_2\text{O}_7$ ,  $\text{V}_2\text{O}_5$  and  $\text{CrO}$  are respectively
- (a) Acidic, acidic and basic (b) Basic, amphoteric and acidic  
(c) Acidic, amphoteric and basic (d) Acidic, basic and amphoteric
- Q.12. Using crystal field theory, identify from the following complex ions that shows same  $\mu_{\text{eff}}$  (spin only) values:
- (A)  $[\text{CoF}_6]^{3-}$ , (B)  $[\text{IrCl}_6]^{3-}$ , (C)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
(a) A and B (b) B and C  
(c) A and C (d) A, B and C
- Q.13. Consider the coordination compound,  $\text{K}_2[\text{Cu}(\text{CN})_4]$ . A coordinate covalent bond exists between:
- (a)  $\text{K}^{+}$  and  $\text{CN}^{-}$  (b)  $\text{Cu}^{2+}$  and  $\text{CN}^{-}$   
(c)  $\text{K}^{+}$  and  $[\text{Cu}(\text{CN})_4]^{2-}$  (d) C and N in  $\text{CN}^{-}$
- Q.14. The pair of compound having metals in their of highest oxidation is
- (a)  $\text{MnO}_2$ ,  $\text{FeCl}_3$  (b)  $[\text{NiCl}_4]^{-2}$ ,  $\text{CoCl}_4^{-}$   
(c)  $\text{MnO}_4^{-}$ ,  $\text{CrO}_2\text{Cl}_2$  (d)  $[\text{Fe}(\text{CN})_6]^{-3}$ ,  $\text{Co}(\text{CN})_3$
- Q.15. The radii of the elements from Cr to Cu are much closed to one another. This is due to:
- (a) Lanthanide contraction  
(b) Atomic radii do not remain constant but decrease in normal gradation  
(c) The fact that successive addition of d-electrons screened the outer electron (4s) from the inward pull of the nucleus.  
(d) Increase in radii due to increase in 'n' is compensated by decrease in radii due to increase in 'Z'.
- Q.16. Which of the following pairs of metals is purified by Van Arkel Method?
- (a) Ni and Fe (b) Ga and In  
(c) Zr and Ti (d) Ag and Au
- Q.17. The correct statement for Mn—O bond lengths in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is
- (a) All bonds are equal  
(b) Four bonds are longer than two bonds  
(c) Two bonds are longer than four bonds  
(d) They are shorter than the Mn—O bond in  $[\text{MnO}_4]^{2-}$

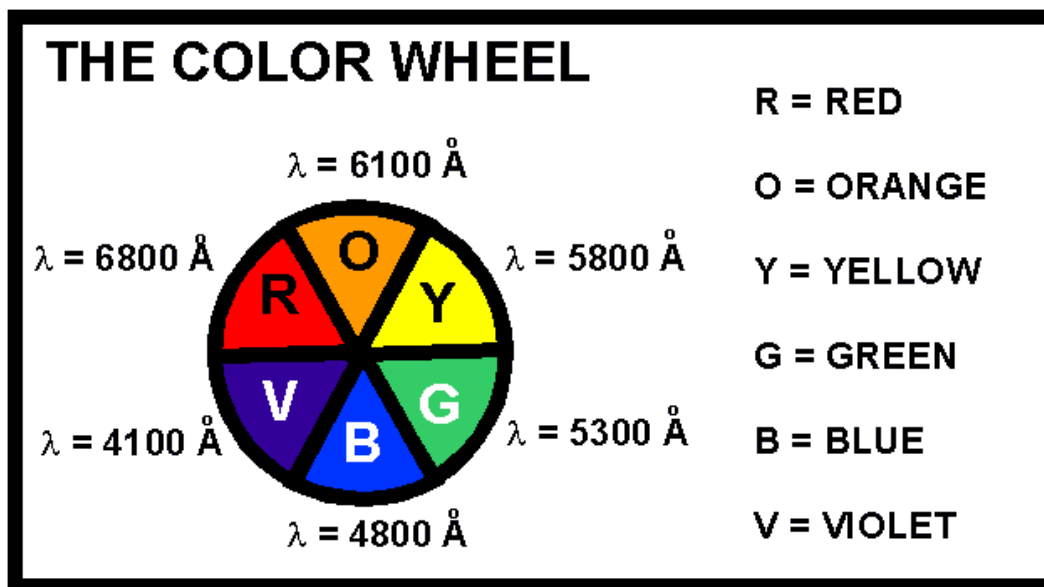
- Q.18. Select the **correct** IUPAC name for:  $[\text{FeF}_4(\text{H}_2\text{O})_2]^-$
- (a) diaquatetrafluoroiron(III) ion                      (b) diaquatetrafluoroferrate(III) ion  
(c) diaquatetrafluoroiron(I) ion                      (d) diaquatetrafluoroferrate(I) ion
- Q.19. Mercury is the only metal amongst transition elements which is liquid at  $0^\circ\text{C}$ . This is due to its:
- (a) Weak metallic bond.                      (b) High vapor pressure  
(c) High ionization energy.                      (d) Both (a) and (c).
- Q.20. In  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ , sodium nitroprusside:
- (a) Oxidation state of Fe is +2                      (b) This has  $\text{NO}^+$  as ligand  
(c) Both (a) and (b) are correct                      (d) None of the above is correct
- Q.21. A transition metal complex shows a magnetic moment of 5.20 BM at room temperature. The number of unpaired electron on the metal is:
- (a) 3                      (b) 4  
(c) 5                      (d) 2
- Q.22. Among the following, species expected to show fluxional behavior are:
- (A)  $[\text{NiCl}_4]^{2-}$  (tetrahedral)                      (B)  $\text{IF}_7$  (pentagonal bipyramidal)  
(C)  $[\text{CoF}_6]^{3-}$  (octahedral)                      (D)  $[\text{Fe}(\text{CO})_5]$  (trigonal bipyramidal)  
(a) B and C                      (b) B and D  
(c) C and D                      (d) A and D
- Q.23. (Valence Bond Theory) Magnetic measurements indicate that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  has 3 unpaired electrons. Therefore, the hybridization of the metal's orbital's in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is:
- (a)  $\text{sp}^3$                       (b)  $\text{sp}^2\text{d}$   
(c)  $\text{dsp}^2$                       (d)  $\text{sp}^3\text{d}^2$
- Q.24.  $\text{Ti}^{+2}$  is purple in color while  $\text{Ti}^{+4}$  is colorless because:
- (a)  $\text{Ti}^{+2}$  has  $3\text{d}^2$  configuration  
(b)  $\text{Ti}^{+4}$  has  $3\text{d}^2$  configuration  
(c)  $\text{Ti}^{+4}$  is a very small cation when compared to  $\text{Ti}^{+2}$  hence, does not absorb any radiation.  
(d)  $\text{Ti}^{+2}$  has one unpaired electron.
- Q.25. Select the incorrect statement(s):
- (a)  $\text{Cu}^+$  is diamagnetic while  $\text{Co}^{+2}$  is paramagnetic.  
(b)  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  is colored while  $[\text{Sc}(\text{H}_2\text{O})_6]^{+3}$  is colorless.  
(c) Ionization energy of 5d elements are greater than those of 3d and 4d elements.  
(d) Transition elements cannot form complexes.
- Q.26. The number of moles of  $\text{KMnO}_4$  that will be needed to react completely with one mole of ferrous oxalate  $\text{Fe}(\text{C}_2\text{O}_4)$  in acidic solution is
- (a)  $3/5$                       (b)  $2/5$   
(c)  $4/5$                       (d) 1

- Q.27.  $[\text{MnO}_4]^-$  is deep purple in color whereas  $[\text{ReO}_4]^-$  is colorless. This is due to greater energy required for
- d-d transition in the Re compound compared to the Mn compound.
  - d-d transition in the Mn compound compared to the Re compound.
  - Charge transfer from O to Re compared to O to Mn.
  - Charge transfer from O to Mn compared to O to Re.
- Q.28. Which one of the following complexes can exhibit geometrical isomerism?
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (square planer)
  - $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$  (tetrahedral)
  - $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (square planer)
  - $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  (octahedral)
- Q.29. The atomic number of potassium is 19 and that of manganese is 25. Although  $[\text{MnO}_4]^-$  has a dark violet color, that  $\text{K}^+$  is colorless. This is due to the fact that
- Mn is a transition element, while K is not.
  - In Mn high positive oxidation state allows charge transfer transition.
  - The effective atomic no. of Mn in  $[\text{MnO}_4]^-$  is 24 while for  $\text{K}^+$ , the effective atomic no. is 18.
  - $[\text{MnO}_4]^-$  is negatively charged species while  $\text{K}^+$  has a positive charge.
- Q.30. When  $\text{Na}_2\text{CO}_3$  is added to an aqueous solution of  $\text{CuSO}_4$ , which of the following is precipitated?
- $\text{Cu}(\text{CO}_3)_2$
  - $\text{Cu}(\text{OH})(\text{CO}_3)$
  - $\text{Cu}(\text{HCO}_3)_2$
  - $\text{Cu}(\text{OH})_2$
- Q.31. Sulphur trioxide can be obtained by which of the following reaction: \
- $\text{CaSO}_4 + \text{C} \xrightarrow{\Delta}$
  - $\text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\Delta}$
  - $\text{S} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta}$
  - $\text{H}_2\text{SO}_4 + \text{PCl}_5 \xrightarrow{\Delta}$
- Q.32. Among the following complexes:  
 (A)  $[\text{Co}(\text{ox})_3]^{3-}$ , (B)  $\text{trans-}[\text{CoCl}_2(\text{en})_2]^+$ , (C)  $[\text{Cr}(\text{EDTA})]^-$   
 the chiral one(s) is/are:
- A and B
  - B and C
  - C only
  - A and C
- Q.33. (Valence Bond Theory) The coordination complex,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  has one unpaired electron. Which of the following statements are **true**?
- The complex is octahedral.
  - The complex is an outer orbital complex.
  - The complex is  $d^2sp^3$  hybridized.
  - The complex is diamagnetic.
  - The coordination number is 6.
- 1, 4
  - 1, 2, 5
  - 2, 3, 5
  - 2, 3
- Q.34. Which of following complex is most easily reduced?
- $\text{V}(\text{CO})_6$
  - $\text{Cr}(\text{CO})_6$
  - $\text{Fe}(\text{CO})_5$
  - $\text{Ni}(\text{CO})_4$

- Q.35. The number of unpaired electrons present in  $\text{Cr}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  are respectively:
- (a) 2, 3, 4 and 4 (b) 4, 4, 3 and 2  
(c) 4, 4, 2 and 3 (d) 1, 4, 2 and 3
- Q.36. In Nitroprusside ion, the iron and NO exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and NO. These forms can be differentiated by:
- (a) Estimating the concentration of iron.  
(b) Measuring the concentration of  $\text{CN}^-$ .  
(c) Measuring the solid state magnetic moment.  
(d) Thermally decomposing the compound.
- Q.37. Which statement most correctly describes crystal field theory for a d block complex of unspecified geometry?
- (a) The theory considers covalent interactions between a metal centre and the surrounding ligands.  
(b) The theory considers electrostatic interactions between a metal centre and the surrounding ligands which are taken to be point charges.  
(c) The theory rationalizes the non-degeneracy of the metal d orbitals for considering the electrostatic repulsions between point charge ligands and electrons in the metal d orbitals.  
(d) The theory rationalizes why the metal d orbitals are split into two levels.
- Q.38. (Crystal Field Theory) Which one of the following statements is **FALSE**?
- (a) In an octahedral crystal field, the d electrons on a metal ion occupy the  $e_g$  set of orbitals before they occupy the  $t_{2g}$  set of orbitals.  
(b) Diamagnetic metal ions cannot have an odd number of electrons.  
(c) Low spin complexes can be paramagnetic.  
(d) In high spin octahedral complexes,  $\Delta_{\text{oct}}$  is less than the electron pairing energy, and is relatively very small.
- Q.39. The number of manganese in tetrahedral and octahedral sites, respectively in  $\text{Mn}_3\text{O}_4$  is :
- (a) One  $\text{Mn}^{+2}$  and two  $\text{Mn}^{+3}$  (b) One  $\text{Mn}^{+3}$  and two  $\text{Mn}^{+2}$   
(c) Two  $\text{Mn}^{+3}$  and one  $\text{Mn}^{+2}$  (d) Two  $\text{Mn}^{+2}$  and one  $\text{Mn}^{+3}$
- Q.40. Which of the following transition metal is present in misch metal?
- (a) La (b) Sc  
(c) Ni (d) Cr
- Q.41. Formula of thiosulphate, manganate and arsenate respectively are:
- (a)  $\text{S}_4\text{O}_6^{-2}$ ,  $\text{MnO}_4^{-2}$ ,  $\text{AsO}_3^{-3}$  (b)  $\text{S}_2\text{O}_3^{-2}$ ,  $\text{MnO}_4^{-2}$ ,  $\text{AsO}_4^{-3}$   
(c)  $\text{S}_2\text{O}_3^{-2}$ ,  $\text{MnO}_4^{-2}$ ,  $\text{AsO}_3^{-3}$  (d)  $\text{S}_4\text{O}_6^{-2}$ ,  $\text{MnO}_4^{-2}$ ,  $\text{AsO}_4^{-3}$
- Q.42. Which of the following correctly places the ligands in their order in the spectrochemical series ?
- (a)  $\text{Br}^- < \text{Cl}^- < \text{NH}_3 < \text{H}_2\text{O}$  (b)  $\text{I}^- < \text{Br}^- < \text{H}_2\text{O} < \text{OH}^-$   
(c)  $\text{F}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$  (d)  $\text{I}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{en}$

- Q.43. (Crystal Field Theory) When the valence d orbitals of the central metal ion are split in energy in an octahedral ligand field, which orbitals are raised **least** in energy?
- (a)  $d_{xy}$  and  $d_{x^2-y^2}$  (b)  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$   
 (c)  $d_{xz}$  and  $d_{yz}$  (d)  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$
- Q.44. Which Oxides will not give metal on heating?
- (a) ZnO (b)  $\text{Ag}_2\text{O}$   
 (c) HgO (d) All of these
- Q.45. In a reaction the Ferrous ( $\text{Fe}^{+2}$ ) ion is oxidized to Ferric ( $\text{Fe}^{+3}$ ) ion. The equivalent weight of the ion in the above reaction is equal to
- (a) Half of the atomic weight (b) 1/5 of the atomic weight  
 (c) The atomic weight (d) Twice the atomic weight
- Q.46. Which of the following is not an element?
- (a) Graphite (b) Diamond  
 (c) 22-Carat Gold (d) Rhombic sulphur
- Q.47. (Crystal Field Theory) Consider the complex ion  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  with 5 unpaired electrons. Which response includes all the following statements that are **true**, and no false statements?
- I. It is diamagnetic.  
 II. It is a low spin complex.  
 III. The metal ion is a  $d^5$  ion.  
 IV. The ligands are weak field ligands.  
 V. It is octahedral.
- (a) I, II (b) III, IV, V  
 (c) I, IV (d) II, V
- Q.48. Which of the following correctly places the metal centers in their order in the spectrochemical series?
- (a)  $\text{Mn(II)} < \text{Fe(III)} < \text{Rh(III)}$  (b)  $\text{Co(III)} < \text{Co(II)} < \text{Rh(III)}$   
 (c)  $\text{Pt(IV)} < \text{Pd(II)} < \text{Ni(II)}$  (d)  $\text{Pd(II)} < \text{Ni(II)} < \text{Pt(IV)}$
- Q.49. Interstitial compounds are formed by
- (a) Fe, Ni (b) Fe, Co  
 (c) Co, Ni (d) All of these
- Q.50. One of the following metal forms a volatile carbonyl compound and this property is taken advantage for its extraction. The metal is
- (a) Fe (b) Ni  
 (c) Co (d) W
- Q.51. In following reaction
- $$y\text{MnO}_4^- + x\text{H}^+ + \text{C}_2\text{O}_4^{2-} \longrightarrow y\text{Mn}^{++} + 2\text{CO}_2 + x/2 \text{H}_2\text{O}$$
- x and y are :
- (a) 2 and 16 (b) 16 and 2  
 (c) 8 and 16 (d) 5 and 2

- Q.52. (Crystal Field Theory) Consider the violet-colored compound,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  and the yellow compound,  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ . Which of the following statements is false?



- (a) Both chromium metal ions are paramagnetic with 3 unpaired electrons.  
 (b)  $\Delta_{\text{oct}}$  for  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is calculated directly from the energy of yellow light.  
 (c)  $\Delta_{\text{oct}}$  for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is less than  $\Delta_{\text{oct}}$  for  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .  
 (d) A solution of  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  transmits light with an approximate wavelength range of 4000 - 4200 angstroms.
- Q.53. AgCl and NaCl are colorless. NaBr and NaI are also colorless but AgBr and AgI are colored. This is due to:  
 (a)  $\text{Ag}^+$  polarizes  $\text{Br}^-$  and  $\text{I}^-$   
 (b)  $\text{Ag}^+$  has unpaired d- orbital.  
 (c)  $\text{Ag}^+$  depolarizes  $\text{Br}^-$  and  $\text{I}^-$   
 (d) None of the above.
- Q.54. (Crystal Field Theory) Strong field ligands such as  $\text{CN}^-$ :  
 (a) Usually produce high spin complexes and small crystal field splittings.  
 (b) Usually produce low spin complexes and small crystal field splittings.  
 (c) Usually produce low spin complexes and high crystal field splittings.  
 (d) Usually produce high spin complexes and high crystal field splittings.
- Q.55. The atomic number of Vanadium (V), Chromium (Cr), Manganese (Mn) and Iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation energy?  
 (a) V (b) Cr  
 (c) Mn (d) Fe
- Q.56. Which metal complex ion is expected to have a Jahn- Teller distortion?  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Cr}(\text{NH}_3)_6]^{2+}$



- (c)  $[\text{Cr}(\text{CN})_6]^{3-}$  (d)  $[\text{Cr}(\text{bpy})_3]^{3+}$
- Q.57. Different (variable) oxidation state is shown by transition element. It is due to the fact:
- (a) ns electrons may be excited to (n-1) d orbitals.  
 (b) (n-1) d electrons may be excited to ns orbitals.  
 (c) (n-1) d electron may get involved along with ns electron in bonding.  
 (d) None of the above fact is correct.
- Q.58. Which of the following complex ion is tetrahedral?
- (a)  $[\text{PdCl}_4]^{2-}$  (b)  $[\text{PtCl}_4]^{2-}$   
 (c)  $[\text{NiCl}_4]^{2-}$  (d)  $[\text{AuCl}_4]^-$
- Q.59. Which of the following weighs less when weighed in magnetic field:
- (a)  $\text{VCl}_3$  (b)  $\text{ScCl}_3$   
 (c)  $\text{TiCl}_3$  (d)  $\text{FeCl}_3$
- Q.60. Match up the correct formula and magnetic property. Which pair is correct?
- (a)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  (paramagnetic) (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (diamagnetic)  
 (c)  $[\text{CoF}_6]^{3-}$  (diamagnetic) (d)  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  (diamagnetic)
- Q.61. Arrange  $\text{Ce}^{+3}$ ,  $\text{La}^{+3}$ ,  $\text{Pm}^{+3}$  and  $\text{Yb}^{+3}$  in increasing order of their ionic radii:
- (a)  $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$   
 (b)  $\text{Ce}^{+3} < \text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3}$   
 (c)  $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3}$   
 (d)  $\text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3} < \text{Yb}^{+3}$
- Q.62. Which statement is incorrect about typical metal carbonyl complexes  $\text{M}(\text{CO})_n$ ?
- (a) They are likely to obey 18 electron rule  
 (b) They contain  $\pi$ -acceptor ligands  
 (c) M is in zero oxidation state  
 (d) They are likely to be paramagnetic
- Q.63. Which transition metal reduces steam to evolve hydrogen?
- (a) Mn (b) Fe  
 (c) Cu (d) Pt
- Q.64. Which of the following is a  $\pi$ -donor ligand?
- (a)  $\text{Cl}^-$  (b)  $\text{NH}_3$   
 (c) CO (d)  $\text{PF}_3$
- Q.65. Highest (+7) oxidation is shown by:
- (a) Co (b) Cr  
 (c) V (d) Mn
- Q.66. Which of the following complexes does not obey the 18-electron rule?
- (a)  $[\text{Fe}(\text{CO})_4]^{2-}$  (b)  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$   
 (c)  $[\text{Mn}(\text{CO})_5]^-$  (d)  $[\text{Co}(\text{CO})_4]^-$
- Q.67. Select the correct statement(s).
- (a)  $\text{Fe}^{+2}$  is stable and  $\text{Fe}^{+3}$  is unstable in aerated water.  
 (b) Stabilities of variable oxidation state can be explained by standard electrode

potential.

- (c)  $\text{Cr}^{+2}$  is stable and  $\text{Cr}^{+3}$  is unstable in aqueous solution.
- (d) All of the above are correct statements.
- Q.68. Which of the following statements is incorrect?
- (a) The electronic spectrum of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  contains three absorptions.
- (b) Absorptions in the electronic spectrum of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  are extremely weak.
- (c) For a tetrahedral  $d^4$  complex, three absorptions are expected in its electronic spectrum.
- (d) The absorption in the electronic spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is assigned to the  $T_{2g} \rightarrow E_g$  transition.
- Q.69. Select the correct statement(s).
- (a) When  $\text{FeCl}_3$  solution is added to  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution, in addition to  $\text{Fe}^{\text{III}}[\text{Fe}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is also formed due to side redox reaction.
- (b) When  $\text{FeCl}_2$  solution is added to  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution, in addition to  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is also formed due to side redox reaction.
- (c)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is diamagnetic, while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is paramagnetic.
- (d)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is paramagnetic, while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is diamagnetic.
- Q.70.  $[\text{Cr}(\text{CN})_6]^{3-}$  is expected to be:
- (a) Paramagnetic with  $\mu_{\text{eff}} = 3.87$  B.M. (b) Diamagnetic
- (c) Paramagnetic with  $\mu_{\text{eff}} < 3.87$  B.M. (d) Paramagnetic with  $\mu_{\text{eff}} > 3.87$  B.M.
- Q.71. For which pair of complexes is the order of values of  $\Delta_{\text{oct}}$  correct?
- (a)  $[\text{Rh}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+}$  (b)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{Fe}(\text{CN})_6]^{3-}$
- (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{CrF}_6]^{3-} > [\text{Cr}(\text{CN})_6]^{3-}$
- Q.72. Which of the following statement is true?
- (a)  $\text{Cu}^{+2}$  is colourless ion.
- (b) Ions of d-block element are coloured due to d-d transition.
- (c) Ions of f-block elements are colourless due to f-f transition.
- (d)  $[\text{Sc}(\text{H}_2\text{O})_6]^{+3}$ ,  $[\text{Ti}(\text{H}_2\text{O})_6]^{+4}$  are coloured complexes
- Q.73. The visible spectra of salts of following complexes are measured in aqueous solutions. For which complex would the spectrum contain absorptions with the highest  $\epsilon_{\text{max}}$  values?
- (a)  $[\text{MnO}_4]^-$  (b)  $[\text{CoCl}_4]^{2-}$
- (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- Q.74. How many microstates are possible for a  $d^2$  configuration, including both weak and strong field limits?
- (a) 15 (b) 45
- (c) 10 (d) 90
- Q.75. Maximum oxidation of Os is:
- (a) +5 (b) +6
- (c) +7 (d) +8
- Q.76. The d-d transition in an octahedral  $[\text{NiX}_6]^{2+}$  complexes are;

- (a) Laporte forbidden but spin allowed.
  - (b) Laporte forbidden and spin forbidden.
  - (c) Laporte allowed and spin allowed.
  - (d) Laporte allowed but spin forbidden.
- Q.77. For which of the following configurations for an octahedral, first row d- block metal ion do you expect there to be an orbital contribution to the magnetic moment?
- (a)  $t_{2g}^2$
  - (b)  $t_{2g}^3$
  - (c)  $t_{2g}^6 e_g^1$
  - (d)  $t_{2g}^6 e_g^2$
- Q.78. First ionization energy of 5d elements is higher than those of 3d and 4d elements. This is due to:
- (a) Greater effective nuclear charge acting on outer valence electrons.
  - (b) Greater effective nuclear charge is experienced because of weak shielding of the nucleus by 4f electrons.
  - (c) Both (a) and (b)
  - (d) None of the above.
- Q.79. Why does the absorption spectrum of aqueous  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  exhibit a broad band with a shoulder?
- (a) The ground state of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is Jahn-Teller distorted
  - (b) The excited state of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  undergoes Jahn-Teller distortion
  - (c)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is a  $d^2$  ion and therefore there are two absorptions
  - (d)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is partly reduced to  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$  in aqueous solution and two absorptions which are close in energy are observed, one for each species
- Q.80. Color in transition metal compounds is attributed to:
- (a) Small size of metal ions
  - (b) Absorption of light UV region
  - (c) Complete (ns) sub shell
  - (d) Incomplete (n-1) d sub shell
- Q.81. Which of the following ion does not form colored complex?
- (a) Ni (II)
  - (b) Sc (II)
  - (c) Fe (II)
  - (d) Cr (VI)

## Answers

1- (d)	2- (a)	3- (d)	4- (d)	5- (d)	6- (b)
7- (a)	8- (d)	9- (b)	10- (a)	11- (c)	12- (c)
13- (b)	14- (c)	15- (c)	16- (c)	17- (a)	18- (b)
19- (a)	20- (c)	21- (b)	22- (b)	23- (d)	24- (a)
25- (d)	26- (a)	27- (c)	28- (a)	29- (b)	30- (c)
31- (b)	32- (d)	33- (b)	34- (a)	35- (b)	36- (c)
37- (c)	38- (a)	39- (a)	40- (a)	41- (b)	42- (d)
43- (b)	44- (a)	45- (c)	46- (c)	47- (b)	48- (a)
49- (d)	50- (b)	51- (b)	52- (b)	53- (a)	54- (c)
55- (b)	56- (b)	57- (c)	58- (c)	59- (b)	60- (b)
61- (a)	62- (d)	63- (b)	64- (a)	65- (d)	66- (b)
67- (b)	68- (c)	69- (a,b,c)	70- (a)	71- (a)	72- (b)
73- (a)	74- (b)	75- (d)	76- (a)	77- (a)	78- (b)
79- (b)	80- (d)	81- (d)			

## Chapter 2

### Chemistry of f-Block Elements

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#### Critical Points:

- Lanthanides and Actinides are collectively known as f block elements because last electron enters into f orbital of the antepenultimate shell.
- General electronic configuration –  $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$
- The least basic hydroxide among Lanthanides is  $\text{Lu}(\text{OH})_3$ .
- Uranium fluoride co-precipitate with  $\text{CaF}_2$ .
- The regular decrease in the size of lanthanide ions from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$  due to increase in effective nuclear charge is known as Lanthanide Contraction.
- The magnetic moment of  $\text{Eu}^{+3}$  and  $\text{Sm}^{+3}$  complexes are higher than those of calculated by spin only values.
- Consequences of Lanthanide Contraction :
  - (a) Similarity in size of some elements of II<sup>nd</sup> and III<sup>rd</sup> transition series e.g. Zr-Hf, Nb-Ta and Mo-W are known as twins.
  - (b) Difficulty in separation of Lanthanides due to their similar chemical properties and similar size.
  - (c) The covalent character of hydroxides of lanthanides increases as the size decreases from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$ .
  - (d) The basic strength of hydroxides of lanthanides decreases with decreases in size from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$ .
  - (e) Tendency to form stable complexes from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$  increases as the size decreases in that order.
- $\text{M}^{+2}$  ions of lanthanide can be easily converted into  $\text{M}^{+3}$  ions by gain of electrons through reduction.
- The total magnetic moment of lanthanides with a Landé's splitting factor follows the relation:
 
$$\mu = g \sqrt{J(J+1)}$$
- $\beta$ -diketone complexes of  $\text{Eu}^{+3}$  and  $\text{Pr}^{+3}$  are known as shift reagents e.g.  $\text{Eu}(\text{dpm})_2$  and  $\text{Eu}(\text{fod})_3$ .
- The elements with atomic number 58 to 71 are called Lanthanides (Ce to Lu).
- The elements with atomic number 90 to 103 are called Actinides (Th to Lr).
- $\text{Ce}^{+4}$  behave as a very good oxidizing agent.
- $\text{La}^{+3}$  ions behave as hard Lewis acids.
- Cerium ammonium nitrate has coordination number 12 because  $\text{NO}_3$  behaves as bidentate ligand.
- Lanthanides have lesser tendency to form complexes than transition metals.

- Shift reagents provide a method for spreading out NMR absorption patterns without increasing the strength of the applied magnetic field.
- According to VSEPR theory, Cerium ammonium Nitrate has Distorted Icosahedral structure.
- The absorption bands of f-block elements are sharp line like peak due to weak metal-ligand interaction.
- Ion exchange method is the most effective and rapid method for the separation and purification of lanthanides.
- The term lanthanide was introduced by Victor Goldschmidt.
- Oxocations of actinides are stable in aqueous solution due to their high charge density e.g.  $\text{UO}_2^{+2}$  however oxocations of lanthanides are unstable in aqueous solution.
- Gel permeation chromatography can be used to separate Fatty acid and Low molecular weight peptides.
- Actinides have greater tendency to form complexes because of higher nuclear charge and greater multiplicity of oxidation states as compared to lanthanides.
- The ground state forms of  $\text{Sm}^{+3}$  and  $\text{Eu}^{+3}$  are  $^6\text{H}_{5/2}$  and  $^7\text{F}_0$  respectively.
- $\text{Sm}^{+2}$ ,  $\text{Eu}^{+2}$  and  $\text{Yb}^{+2}$  are good reducing agent.
- The absorption bands in Lanthanides are sharp line like peak.
- There is a slight increase in electro negativity of the trivalent ions from La to Lu.

## Multiple Choice Questions

- Q.1. Which one of the following pairs consists of a good oxidizing and a good reducing agent respectively?
- (a) Ce(IV), Ln(III) (b) Ln(III), Eu(II)  
(c) Ce(IV), Eu(II) (d) Ln(III), Ce(III)
- Q.2. Unlike d-d transitions, the f-f transitions
- (a) Do not change much with change in ligand.  
(b) Change significantly with change in ligand.  
(c) Appear at low energies i.e., at the near-IR region.  
(d) Appear as broad bands.
- Q.3. The distortion in the structure of Ceric Ammonium Nitrate is due to:
- (a) Bi dentate nitrate ligand (b) Mono dentate nitrate ligand  
(c) Bi dentate nitrite ligand (d) Mono dentate nitrite ligand
- Q.4. Which reaction is likely to result in the successful conversion of  $\text{La}_2\text{O}_3 (s)$  to  $\text{LaCl}_3 (s)$ ?
- (a)  $\text{La}_2\text{O}_3 (s) + 6 \text{Cl}_2(g) \rightarrow 2 \text{LaCl}_3 (s) + 3 \text{Cl}_2\text{O}(g)$   
(b)  $\text{La}_2\text{O}_3 (s) + 3 \text{COCl}_2(g) \rightarrow 2 \text{LaCl}_3 (s) + 3 \text{CO}_2 (g)$   
(c)  $\text{La}_2\text{O}_3 (s) + 6 \text{NaCl}(s) \rightarrow 2 \text{LaCl}_3 (s) + 6 \text{Na}_2\text{O}$   
(d)  $\text{La}_2\text{O}_3 (s) + 6 \text{HCl}(aq) \rightarrow 2 \text{LaCl}_3 (s) + 3 \text{H}_2\text{O}(l)$
- Q.5. The correct sequence of ionic radii in increasing order of the given lanthanide cations is:
- (a)  $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$  (b)  $\text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3} < \text{Yb}^{+3}$   
(c)  $\text{Ce}^{+3} < \text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3}$  (d)  $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3}$
- Q.6. Uranium fluoride co-precipitate with:
- (a)  $\text{CaF}_2$  (b)  $\text{AgF}$   
(c)  $\text{MgF}_2$  (d)  $\text{LiF}$
- Q.7. Statement I: U (VI) is more stable than Nd(VI).  
Statement II: The valence electron in U are in 5f, 6d and 7s orbital's.
- (a) Statement I and II are correct and II is correct explanation of I.  
(b) Statement I and II are correct but II is not correct explanation of I.  
(c) Statement I is correct and II is incorrect.  
(d) Statement I and II both are incorrect.
- Q.8. The metallic radii are abnormally high for which of the following pairs?
- (a) Eu, Yb (b) Sm, Tm  
(c) Gd, Lu (d) Nd, Ho
- Q.9. Consider the following statement for  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] (Z)$
- A. Coordination number of Ce is 12  
B. Z is paramagnetic in nature  
C. Z is an oxidizing agent
- The correct statements are:
- (a) B and C (b) A, B and C  
(c) A and B (d) A and C

- Q.10. In which of the following compound stoichiometry is not followed:
- (a)  $\text{UO}_2$  (b)  $\text{U}_3\text{O}_8$   
 (c)  $\text{UO}_4$  (d)  $\text{UO}_3$
- Q.11. Uranium exhibits several oxidation states because:
- (a) It is an inner transition element  
 (b) 5f orbital participate in bonding  
 (c) Its atomic weight is high  
 (d) It forms strong bond with oxygen
- Q.12. For uranocene, the correct statement(s) is/are
- I- oxidation state of uranium is +4.  
 II- It has cyclo-octatetraenide ligand.  
 III- It is a bent sandwich compound.  
 IV- It has -2 charge
- (a) I and II (b) II and III  
 (c) I and IV (d) II only
- Q.13. The least basic among the following is:
- (a)  $\text{Al}(\text{OH})_3$  (b)  $\text{La}(\text{OH})_3$   
 (c)  $\text{Lu}(\text{OH})_3$  (d)  $\text{Ce}(\text{OH})_3$
- Q.14. The nuclides among the following capable of undergoing fission by thermal neutrons are:
1.  $^{233}\text{U}$  2.  $^{235}\text{U}$  3.  $^{239}\text{Pu}$  4.  $^{232}\text{Th}$
- (a) 1,2 and 4 (b) 1,3 and 4  
 (c) 2,3 and 4 (d) 1,2 and 3
- Q.15. Which one among the following lanthanides exhibits radioactive nature?
- (a) Sm (b) Eu  
 (c) Gd (d) Pm
- Q.16. Which of the following statements are TRUE for the lanthanides?
- I- The observed magnetic moment of  $\text{Eu}^{+3}$  at room temperature is higher than that calculated from spin-orbit coupling.  
 II- Lanthanide oxides are predominantly acidic in nature.  
 III- The stability of  $\text{Sm}(\text{II})$  is due to its half-filled subshell.  
 IV- Lanthanide (III) ions can be separated by ion exchange chromatography.
- Correct answer is
- (a) I and IV (b) I and II  
 (c) I and III (d) II and III
- Q.17. The pair of lanthanides with the highest third ionization energy is:
- (a) Eu, Gd (b) Eu, Yb  
 (c) Dy, Yb (d) Lu, Yb
- Q.18. In nature Thorium exists as:
- (a)  $^{231}\text{Th}$  (b)  $^{233}\text{Th}$   
 (c)  $^{232}\text{Th}$  (d)  $^{234}\text{Th}$



- Q.19. Statement I: The sizes of Zr and Hf are similar.  
Statement II: Size of Hf is affected by lanthanide contraction.
- Statement I and II are correct and II is correct explanation of I.
  - Statement I and II are correct but II is not correct explanation of I.
  - Statement I is correct and II is incorrect.
  - Statement I and II both are incorrect.
- Q.20.  $M^{+2}$  ions of lanthanide can be easily converted into  $M^{+3}$  ions by
- Loss of electrons through oxidation.
  - Gain of electrons through reduction.
  - By oxidation and reduction both.
  - None of them.
- Q.21. The total magnetic moment of lanthanides with a Landé's splitting factor follows the relation:
- $\mu = g \sqrt{J(J+1)}$
  - $\mu = \sqrt{n(n+2)}$
  - $\mu = \sqrt{4S(S+1) + L(L+1)}$
  - None
- Q.22. Among the following compounds, the powerful fluorinating agent is:
- $UF_3$
  - $UF_4$
  - $UF_6$
  - $UF_5$
- Q.23. The lanthanide  $+3$  ion having highest partition co-efficient between tri-n-butyl phosphate and concentrated  $HNO_3$  is:
- $La^{+3}$
  - $Eu^{+3}$
  - $Na^{+3}$
  - $Lu^{+3}$
- Q.24. Hindered  $\beta$ -diketones like dpmH (dpmH = dipivaloylmethane) are used for the separation of Lanthanides because complexes formed with dpmH can be separated by:
- Gel permeation chromatography
  - Gas chromatography
  - Gel filtration chromatography
  - Ion exchange chromatography
- Q.25. Which of the following ligand forms a stable complex with  $Ln^{+3}$  ion?
- $C_2H_4$
  - $H_2O$
  - $PPh_3$
  - $CO$
- Q.26. The electronic configuration of Gadolinium is  $[Xe] 4f^7 5d^1 6s^2$ , whereas that of  $Gd^{+2}$  is:
- $[Xe] 4f^5 5d^0 6s^2$
  - $[Xe] 4f^6 5d^0 6s^2$
  - $[Xe] 4f^6 5d^1 6s^1$
  - $[Xe] 4f^7 5d^1 6s^0$
- Q.27. Actinides have a greater tendency to form complexes as compared to lanthanides because actinides have:
- Large size of ions
  - Low multiplicity of atoms

- (c) High nuclear charge (d) Low nuclear charge
- Q.28.  $\text{La}^{+3}$  ions are:  
 (a) Hard lewis acids (b) Hard lewis bases  
 (c) Soft lewis acids (d) Soft lewis bases
- Q.29. Which of the following configuration is not possible for lanthanides?  
 (a)  $4f^1 5d^1 6s^2$  (b)  $4f^4 5d^0 6s^2$   
 (c)  $4f^2 5d^0 6s^2$  (d)  $4f^7 5d^0 6s^2$
- Q.30. Which one among the following element belongs to actinides series?  
 (a) Sm (b) Eu  
 (c) Cm (d) Pm
- Q.31. A comparison of the valence electron configuration of the elements, Sm and Eu suggests that:  
 (a) Sm is a better one electron reductant than Eu  
 (b) Sm is a better one electron oxidant than Eu  
 (c) Facile oxidation state is +2 for both the elements  
 (d) Both of these display similar redox behavior
- Q.32. Which one of the following pairs absorbs radiations in UV and IR region respectively:  
 1. Sm, Yb                      2. Ce, Yb                      3. La, Lu                      4. Gd, Lu  
 (a) 1 and 2 only (b) 1 and 3 only  
 (c) 2 and 3 only (d) 2 only
- Q.33. Which one of the following shows the highest solubility in hot concentrated NaOH?  
 (a)  $\text{Nd}(\text{OH})_3$  (b)  $\text{La}(\text{OH})_3$   
 (c)  $\text{Lu}(\text{OH})_3$  (d)  $\text{Sm}(\text{OH})_3$
- Q.34. Ceric ammonium nitrate has coordination number 12 because  
 (a)  $\text{NO}_3$  behaves as mono dentate ligand  
 (b)  $\text{NO}_3$  behaves as bi dentate ligand  
 (c)  $\text{NO}_3$  behaves as mono dentate as well as bi dentate ligand  
 (d)  $\text{NO}_3$  is neither mono dentate nor bi dentate ligand
- Q.35. Which of the following elements are soluble in liquid ammonia?  
 (a) Pm and Sm (b) Ce and Ho  
 (c) Tm and Lu (d) Eu and Yb
- Q.36. One of the consequences of lanthanide contraction is:  
 (a) Zr & Zn have the same oxidation state  
 (b) Zr & Hf have almost same atomic radius  
 (c) Zr & Nb have smaller oxidation state  
 (d) Zn & Dy have almost same atomic radius
- Q.37. The most common oxidation state of lanthanides is:  
 (a) +4 (b) +3 (c) +6 (d) +2
- Q.38. Which of the following pair of lanthanides can act as oxidizing and reducing agents?  
 (a) Sm, Dy (b) Nd, Gd

- (c) Dy,Er (d) Ho,Er
- Q.39. Ceric ammonium nitrate has distorted structure due to:
- (a) Highest oxidation state of Ce  
(b) 20 faces of the structure  
(c) bidentate ligand  $\text{NO}_3$   
(d) highest coordinated structure
- Q.40. According to VSEPR theory the structure of Ceric ammonium Nitrate is:
- (a) Distorted Icosahedral  
(b) Symmetrical Octahedral  
(c) Symmetrical Icosahedral  
(d) Distorted Octahedral
- Q.41. The lanthanide (III) ion having the highest partition coefficient between tri-n-butyl Phosphate and concentrated  $\text{HNO}_3$  is:
- (a)  $\text{Eu}^{+3}$  (b)  $\text{Nd}^{+3}$   
(c)  $\text{Lu}^{+3}$  (d)  $\text{La}^{+3}$
- Q.42. The colour of Ceric Ammonium Nitrate is due to:
- (a) d-d transition  
(b) Metal to Ligand charge transfer transition  
(c) Crystal field transition  
(d) Ligand to Metal charge transfer transition
- Q.43. Which element among lanthanides has smallest atomic radius?
- (a) Cerium (b) Holmium  
(c) Europium (d) Gadolinium
- Q.44. Which of the following is true for lanthanides?
- (a)  $\text{H.E}_3 < \text{I.E}_3$  (b)  $\text{H.E}_4 > \text{I.E}_4$   
(c)  $\text{L.E}_3 < \text{I.E}_3$  (d)  $\text{L.E}_3 > \text{I.E}_3$
- Q.45. The term lanthanide was introduced by:
- (a) Grignberg (b) Sir Thomas  
(c) Victor Goldschmidt (d) Albert Wright
- Q.46. The separation of Lanthanides is possible by:
- (a) Normal method (b) Ion - exchange method  
(c) Permutit method (d) Chromatographic method
- Q.47. Consider the following lanthanide(III) ions:  
1. Nd(III) 2. Dy(III) 3. Gd(III)  
The magnetic moment close to spin only value is (are) for:
- (a) 1 and 3 only (b) 1 and 3 only  
(c) 3 only (d) 2 and 3 only
- Q.48. The ground state term symbol for Nb (atomic number 41) is  ${}^6\text{D}$ . The electronic configuration corresponding to this term symbol is:
- (a)  $[\text{Kr}] 4\text{d}^3 5\text{s}^2$  (b)  $[\text{Kr}] 4\text{d}^4 5\text{s}^1$

- (c)  $[\text{Kr}] 4d^5 5s^0$  (d)  $[\text{Kr}] 4d^3 5s^1 5p^1$
- Q.49. Which of the following lanthanides has largest metallic radius?  
 (a) Eu (b) Sm  
 (c) Lu (d) Pr
- Q.50. Which of the following lanthanide is a man made element.  
 (a) Sm (b) Pm  
 (c) Dy (d) Tm
- Q.51. Gel permeation chromatography can be used to separate which of the following:  
 A. Lanthanides B. Alkaline earths  
 C. Fatty acids D. Low molecular weight peptides
- The correct answer is:  
 (a) A and B (b) B and C  
 (c) C and D (d) A and D
- Q.52.  $M^{+4}$  ions of Lanthanides can be converted into  $M^{+3}$  ions by  
 (a) Gain of electron through Oxidation.  
 (b) Loss of electron through Reduction.  
 (c) Loss of electron through Oxidation.  
 (d) Gain of electron through Reduction.
- Q.53. The coordination number of Ce in Ceric ammonium nitrate is:  
 (a) 10 (b) 11  
 (c) 12 (d) 14
- Q.54. Elements from atomic no 58 (Ce) to 71 (Lu) are:  
 (a) Actinides (b) Lanthanides  
 (c) Transition Metals (d) Alkali Metals
- Q.55. The ground state forms of  $\text{Sm}^{+3}$  and  $\text{Eu}^{+3}$  respectively are:  
 (a)  $^7F_0$  and  $^6H_{5/2}$  (b)  $^6H_{5/2}$  and  $^7F_0$   
 (c)  $^2F_{5/2}$  and  $^5I_4$  (d)  $^7F_6$  and  $^2F_{7/2}$
- Q.56. Which of the following lanthanides are anti cancer agents?  
 (a) Ce, Ln (b) Gd, Dy  
 (c) Eu, Ce (d) Yr, Ho
- Q.57. The mineral from first ever lanthanide was extracted  
 (a) Monazite (b) Gadolinite  
 (c) Yttria (d) Feldspar
- Q.58. The absorption bands in Lanthanides are:  
 (a) Broad peak (b) Sharp line like peak  
 (c) Diffused peak (d) Broad and sharp peak
- Q.59. Eu and Yb elements show similar reactivity as that of:  
 (a) Li (b) Na  
 (c) Tl (d) Ba
- Q.60. Which of the following ion is colorless?

- (a)  $\text{Pm}^{+3}$  (b)  $\text{Ce}^{+3}$   
 (c)  $\text{Sm}^{+3}$  (d)  $\text{Eu}^{+3}$
- Q. 61. Which of the following lanthanide ion has highest magnetic moment?  
 (a)  $\text{Dy}^{+3}$  (b)  $\text{Gd}^{+3}$   
 (c)  $\text{Sm}^{+3}$  (d)  $\text{Tb}^{+3}$
- Q.62. The general electronic configuration of inner transition metals is:  
 (a)  $(n-2)f^{1-14}$  (b)  $(n-2)f^{1-14}(n-1)d^0ns^2$   
 (c)  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$  (d)  $(n-2)f^{1-14}ns^2$
- Q.63. The electronic configuration of Gadolinium is:  
 (a)  $4f^6 5d^0 6s^2$  (b)  $4f^7 6d^0 6s^2$   
 (c)  $4f^7 5d^1 6s^2$  (d)  $4f^8 5d^1 6s^2$
- Q.64. Identify the pairs in which the covalent radii of elements are almost similar:  
 1. Nb, Ta      2. Mo, W      3. La, Lu      4. Sc, Y  
 (a) 1 and 2 only (b) 1 and 3 only  
 (c) 2 and 3 only (d) 3 and 4 only
- Q.65. Which among the following will be the most stable compound of Tb?  
 (a)  $\text{Tb}(\text{OH})_2$  (b)  $\text{Tb}(\text{OH})_3$   
 (c)  $\text{Tb}(\text{OH})_4$  (d)  $\text{Tb}_2\text{O}_3$
- Q.66. Which among the following groups of lanthanides is used to make an alloy for flint of cigarette lighter?  
 (a) Ce, La, Pr, No (b) Ce, Pr, No, Lu  
 (c) La, Pm, Sm, Pr (d) Pr, La, Lu, Ce
- Q.67. In a nuclear reactor oxides of which of the following metals are used as a fuel material?  
 (a) Uranium    2- Thorium    3- Actinium    4- Plutonium  
 Select the correct answer using the codes given below:  
 (a) 1 and 3 (b) 2 and 3  
 (c) 1, 2 and 4 (d) 2, 3 and 4
- Q.68. The basic character of Lanthanides decreases from  
 (a)  $\text{Lu}(\text{OH})_3$  to  $\text{La}(\text{OH})_3$   
 (b)  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$   
 (c) Increases from  $\text{La}(\text{OH})_3$  to  $\text{Gd}(\text{OH})_3$  and then decreases up to  $\text{Lu}(\text{OH})_3$   
 (d) Decreases from  $\text{La}(\text{OH})_3$  to  $\text{Gd}(\text{OH})_3$  and then Increases up to  $\text{Lu}(\text{OH})_3$
- Q.69. Which lanthanide is used as a knocking agent in gasoline?  
 (a) Ce (b) Er  
 (c) Lu (d) Yb
- Q.70. Which lanthanide has the highest tendency to get oxidized in air?  
 (a) Lu (b) Eu  
 (c) Tm (d) Gd
- Q.71. Consider the following statements:

1. The size of the lanthanides  $M^{+3}$  ions decreases as the atomic number of M increases.
2. Electronic spectra of lanthanides show very broad bands.
3. Co-ordination number six is very common among lanthanide complexes.

Which of the following statements given above is/are correct?

- |               |             |
|---------------|-------------|
| (a) 1 and 2   | (b) 1 and 3 |
| (c) 1,2 and 3 | (d) 1 only  |

Q.72. In a nuclear reactor, oxides of which of the following metals are used as a fuel material?

- |       |       |       |       |
|-------|-------|-------|-------|
| (a) U | 2. Th | 3. Ac | 4. Pu |
|-------|-------|-------|-------|

Select the correct answer using the codes given below:

- |               |               |
|---------------|---------------|
| (a) 1 and 3   | (b) 2 and 3   |
| (c) 1,2 and 4 | (d) 2,3 and 4 |

Q. 73. Fast breeder reactors are based on which one of the following?

- Conversion of  $U^{238}$  to  $Pu^{239}$  and removing the moderator.
- Conversion of  $Th^{232}$  to  $Pu^{239}$  and using the moderator.
- Conversion of  $Th^{232}$  to  $U^{235}$  and removing the coolant.
- Conversion of  $U^{238}$  to  $U^{233}$  and removing the coolant.

Q.74. The lanthanide that is used in controlling rods of nuclear power plant and carbon arc lamps is:

- |        |        |
|--------|--------|
| (a) Er | (b) Sm |
| (c) Ce | (d) Nd |

Q.75. The lanthanides which are stable in oxidation states other than +3 are:

- |           |           |
|-----------|-----------|
| (a) Ce,Sm | (b) Ce,Er |
| (c) Ce,Lu | (d) Ce,Eu |

Q.76. The ligand field bands of lanthanide complexes are generally sharp line like peak than those of transition metal complexes because:

- Transitions are allowed for lanthanide complexes.
- f orbital's have higher energy than d orbital's.
- f orbital's compared to d orbital's interact less effectively with ligands.
- Intensity of the bands is higher for lanthanides complexes.

Q.77. Consider the ions Eu (III), Gd(III), Sm(III) and Lu(III). The observed and calculated Magnetic Moment is closest for the pair:

- |                     |                     |
|---------------------|---------------------|
| (a) Lu(III),Gd(III) | (b) Eu(III),Lu(III) |
| (c) Sm(III),Gd(III) | (d) Eu(III),Sm(III) |

Q.78. Which of the following compound shows a charge transfer band?

- |                            |                            |
|----------------------------|----------------------------|
| (a) Lanthanum nitrate      | (b) Ceric ammonium nitrate |
| (c) Manganese (II) acetate | (d) Copper (II) sulphate   |

Q. 79. Among the following statements, identify the correct ones for the complexes of lanthanide (III) ions:

- Metal-ligand bond is significantly ionic.

- (b) Complexes rarely show isomerism.  
 (c) The co-ordination number is not more than 8.  
 (d) The magnetic moment are not accounted even approximately by spin only value for majority of lanthanides.
- (a) 1,2 and 3 (b) 1 and 4  
 (c) 1,2 and 4 (d) 2 and 3
- Q.80. The electrostatic forces of the lanthanide complexes are:  
 (a) Bidirectional (b) Unidirectional  
 (c) Omni directional (d) Tri directional
- Q.81. The trivalent ions of lanthanides form more stable complexes with:  
 (a) O donor ligand (b) S donor ligand  
 (c) N donor ligand (d) P donor ligand
- Q.82. The actual magnetic moment shows a large deviation from the spin only formula in case of:  
 (a)  $Ti^{+3}$  (b)  $V^{+3}$   
 (c)  $Gd^{+3}$  (d)  $Sm^{+3}$
- Q.83. The coordination number and geometry of Ce in  $[Ce(NO_3)_6]^{2-}$  are respectively:  
 (a) 6 and octahedron (b) 6 and trigonal prism  
 (c) 8 and cubic (d) 12 and icosahedrons
- Q.84. The most stable oxidation state for U is:  
 (a) +3 (b) +4  
 (c) +5 (d) +6
- Q.85. In neutron capture nuclear reactions, the lanthanide which capture neutron the fastest is:  
 (a) Pm (b) Nd  
 (c) Eu (d) Sm
- Q.86. Which of the following names for lanthanides was later on rejected by the Scientists?  
 (a) Inner transition elements (b) Rare earth metals  
 (c) Inner core metals (d) f- block elements
- Q.87. Which one of the following is a valuable laboratory source of  $\alpha$ - particle?  
 (a) Np (b) Pu  
 (c) U (d) Am
- Q.88. The structure of Ceric ammonium nitrate has:  
 (a) 12 faces and 20 vertices (b) 12 faces and 12 vertices  
 (c) 20 faces and 20 vertices (d) 20 faces and 12 vertices
- Q.89. Metal electrides of Lanthanum and Cerium have:  
 (a)  $M^{+3}$  and  $(I_2)^{e-}$  ions (b)  $M^{+3}$  and  $I_2^-$  ions  
 (c)  $M^{+3}$  and  $I^-$  ions (d)  $M^{+3}$  and  $I_2$  ions
- Q.90. Most reactive lanthanides get tarnished in the presence of air due to the formation of:  
 (a)  $Ln_2S_{3.x}H_{2O}$  (b)  $LnN.2H_2O$   
 (c)  $Ln_2O_3$  (d)  $Ln(OH)_3$

Q.91. Direct excitation of lanthanides is difficult due to:

- (a) High extinction coefficient
- (b) High energy required for f-f transition
- (c) Low excitation coefficient
- (d) Low ionization energy



**Answers**

1- (c)	2- (a)	3- (a)	4- (b)	5- (a)	6- (a)
7- (b)	8- (a)	9- (d)	10- (c)	11- (b)	12- (a)
13- (a)	14- (d)	15- (d)	16- (a)	17- (b)	18- (c)
19- (a)	20 - (a)	21 - (a)	22- (c)	23- (d)	24- (b)
25- (d)	26 - (d)	27- (c)	28- (a)	29- (c)	30- (c)
31- (b)	32 -(d)	33 - (c)	34- (b)	35- (d)	36- (b)
37- (b)	38- (a)	39- (c)	40- (a)	41- (c)	42 - (d)
43- (b)	44- (d)	45- (c)	46 – (b)	47 - (c)	48- (b)
49- (d)	50 - (b)	51 – (c)	52- (d)	53- (c)	54- (b)
55 - (b)	56- (a)	57- (b)	58 - (b)	59 - (d)	60 - (b)
61 - (b)	62 - (c)	63 - (c)	64- (a)	65- (b)	66- (a)
67- (c)	68- (b)	69- (a)	70- (d)	71- (d)	72- (c)
73- (a)	74- (b)	75- (d)	76- (c)	77- (a)	78- (b)
79- (c)	80- (c)	81- (a)	82- (d)	83- (d)	84- (d)
85- (c)	86- (b)	87- (d)	88- (a)	89- (a)	90- (c)
91- (c)					

## Chapter 3

### Spectroscopy

(Contributed by: Dr. Punam Yadav, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- Conjugation decreases the frequency at which absorption occurs in IR spectroscopy.
- IR spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes.
- X-rays absorption of electromagnetic radiation results in ionization of molecules.
- The carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride follows the order Anhydride > ketone > amide.
- In IR spectroscopy, the C-O bond has a lower frequency than the C-N bond because O atom has more mass than an N atom.
- Only one EPR signal is observed for octahedral Ni(II) complex.
- In the atomic adsorption spectroscopic estimation of Fe(III) using  $O_2/H_2$  flame, the absorbance decreases with the addition of  $SO_4^{2-}$  ions.
- Argon gas is commonly used in generating plasma in Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES).
- The frequency of the stretching vibration of a bond in IR spectroscopy depends on the masses of the atoms and the stiffness of the bond.
- In atomic adsorption spectroscopy, the atomization process utilizes flame for its activation.
- The oxidation state of metal ion in the catalyst can be deduced by HPLC.
- The polar molecules like HCl, HBr etc are active in rotational microwave, infrared absorption as well as rotational Raman spectra.
- The absorption at  $\lambda_{max}$  279 nm ( $\epsilon = 15$ ) in the UV spectrum of acetone is due to  $\sigma \rightarrow \sigma^*$  transition.
- Hydrogen bonding broadens the absorption of oxygen-hydrogen band of  $CH_3OH$  in infrared spectroscopy.
- The total number of fine and hyperfine EPR lines expected for octahedral high spin Mn(II) complex are 5 and 30.
- HPLC techniques would be most useful to identify and quantify the presence of a known impurity in a drug substance.
- In mass spectrometry the analyzed substance is ionized.
- The two characteristic stretching frequencies ( $cm^{-1}$ ) observed in the IR spectrum of compounds containing  $NO_2$  group are 1550 and 1350.
- For  $CO_2$  molecule all the vibrational modes are either IR or Raman active.
- A mass spectrometry delivers the evidence about the molecular mass of a substance.

- The anti Stokes lines are generally weaker in intensity because the atoms are generally in the ground state.
- The source of ultra violet radiation used in UV-visible spectrophotometer is mercury vapour lamp.
- The infra red and Raman spectrum of  $\text{BF}_3$  are expected to show more absorption peaks in Raman in comparison to IR.
- The rotational constant of non polar molecules such as  $\text{H}_2$ ,  $\text{N}_2$  etc. cannot be determined by spectroscopic methods.
- The H-H bond distance in  $\text{H}_2$  molecule can be determined by Rotational Raman Spectroscopy.
- Raman frequencies for ESR and NMR are found in the Microwave and Radiofrequency spectral region respectively.
- Cis and trans cinnamic acids can be most readily distinguished and identified by UV spectral studies.
- The vibrational stretching frequency of  $\text{N}_2$  can be determined by using Raman Spectroscopy.
- The UV light source used in UV-visible spectrophotometer is Deuterium Lamp.
- The number of IR active vibrational modes in ammonia is six.
- Naphthalene and acetophenone compounds can be readily separated by TLC method.

## Multiple Choice Questions

- Q.1. Which compound would be expected to show intense IR absorption at 2820, 2710 and 1705  $\text{cm}^{-1}$ ?
- (a)  $\text{CH}_3\text{COCH}_2\text{CH}_3$  (b) But 1-yne  
(c)  $\text{PhCOCH}_3$  (d)  $\text{PhCHO}$
- Q.2. The number of lines that appear in the EPR spectra of  $[\text{C}_6\text{H}_6]^-$  is:
- (a) 5 (b) 11  
(c) 7 (d) 13
- Q.3. The presence of hydrogen bonding in an organic compound can easily be established utilizing the following technique:
- (a) Mass Spectra (b) CD-ORD  
(c) IR Spectra (d) NMR Spectra
- Q.4. Which compound would be expected to show intense IR absorption at 2250  $\text{cm}^{-1}$ ?
- (a)  $(\text{CH}_3)_2\text{CHCN}$  (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
(c)  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$
- Q.5. Ethyne ( $\text{HC}\equiv\text{CH}$ ) does not show IR absorption in the region 2000-2500  $\text{cm}^{-1}$  because:
- (a)  $\text{C}\equiv\text{C}$  stretches occur at about 1640  $\text{cm}^{-1}$ .  
(b) There is a change in the dipole moment when the  $\text{C}\equiv\text{C}$  bond in ethyne stretches.  
(c) There is no change in the dipole moment when the  $\text{C}\equiv\text{C}$  bond in ethyne stretches.  
(d)  $\text{C}\equiv\text{H}$  stretches occur at lower energies.
- Q.6. Which of the following will most conveniently confirm if a non solid sample is impure?
- (a) Mass Spectra (b) Melting Point  
(c) IR Spectra (d) NMR Spectra
- Q.7. Which of the following molecules will not absorb infrared radiations?
- (a)  $\text{COCl}_2$  (b)  $\text{Cl}_2$   
(c)  $\text{CO}_2$  (d)  $\text{CO}$
- Q.8. Which compound would be expected to show intense IR absorption at 3363, 3185, 1660  $\text{cm}^{-1}$ ?
- (a)  $(\text{CH}_3)_2\text{CHNH}_2$  (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   
(c)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$  (d)  $\text{CH}_3\text{CH}_2\text{CONH}_2$
- Q.9. Which compound would show a larger than usual M+2 peak in the mass spectrum?
- (a)  $(\text{CH}_3)_2\text{CHNH}_2$  (b)  $\text{CH}_3\text{CH}_2\text{SCH}_3$   
(c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (d)  $\text{CH}_3\text{CH}_2\text{COOH}$
- Q.10. The stark splitting for a given field is larger for a molecule AX as compared to BX. Which of the following is true? ( $\mu$  is the dipole moment)
- (a)  $\mu_{\text{AX}} = \mu_{\text{BX}}$  (b)  $\mu_{\text{AX}} > \mu_{\text{BX}}$   
(c)  $\mu_{\text{AX}} < \mu_{\text{BX}}$  (d)  $\mu_{\text{AX}} = 2\mu_{\text{BX}}$
- Q.11. Consider the compounds,  
(I)  $\text{SnF}_4$  (II)  $\text{SnCl}_2$  (III)  $\text{R}_2\text{SnCl}$   
The nuclear quadrupole splitting are observed in

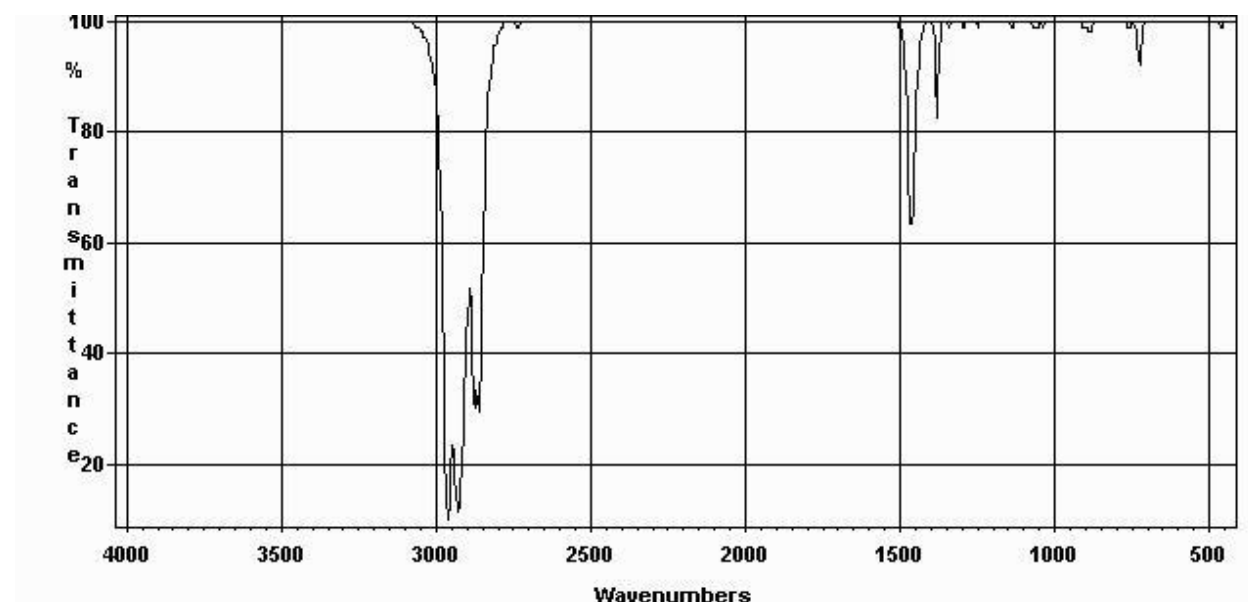
- (a) I, II and III (b) I and II  
(c) II and III (d) I and III
- Q.12. Which compound would be expected to show intense IR absorption at  $1715\text{ cm}^{-1}$ ?  
(a)  $(\text{CH}_3)_2\text{CHNH}_2$  (b)  $(\text{CH}_3)_2\text{CHCOOH}$   
(c) Hex-1-yne (d) 2-Methyl Hexane
- Q.13. When a high energy electron impacts molecule M in the ionization chamber, what type of species is initially produced?  
(a) Cation (b) Radical Cation  
(c) Radical Anion (d) Anion
- Q.14. The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is:  
(a) Anhydride > amide > ketone (b) Ketone > amide > anhydride  
(c) Amide > anhydride > ketone (d) Anhydride > ketone > amide
- Q.15. Which of the following spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes?  
(a) EPR (b) Mass  
(c) IR (d) NMR
- Q.16. Which compound would be expected to show intense IR absorption at  $1640\text{ cm}^{-1}$ ?  
(a) Hex-1-ene (b) 2-Methyl Heptane  
(c)  $\text{CH}_3\text{CH}_2\text{COCH}_3$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- Q.17. Which compound would be expected to show intense IR absorption at  $3367, 3282\text{ cm}^{-1}$ ?  
(a) But-1-ene (b)  $\text{Ph CH}_2\text{NH}_2$   
(c)  $\text{CH}_3\text{CH}_2\text{OCH}_3$  (d)  $\text{PhCOOH}$
- Q.18. If Mossbauer spectrum of  $\text{Fe}(\text{CO})_5$  is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with:  
(a) Three Lines (b) Four Lines  
(c) Five Lines (d) Six Lines
- Q.19. In IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at:  
(a)  $1670\text{ cm}^{-1}$  (b)  $1700\text{ cm}^{-1}$   
(c)  $1730\text{ cm}^{-1}$  (d)  $1760\text{ cm}^{-1}$
- Q.20. Absorption of what type of electromagnetic radiation results in ionization?  
(a) Microwaves (b) X-rays  
(c) Infrared light (d) Radio waves
- Q.21. In IR spectroscopy, the C-O bond has a \_\_\_\_\_ frequency than the C-N bond because \_\_\_\_\_.  
(a) lower, an O atom has more mass than an N atom  
(b) higher, an O atom has an even number of neutrons  
(c) higher, an O atom has more electronegativity than an N atom  
(d) higher, an O atom has more mass than an N atom
- Q.22. The number of EPR signals observed for octahedral Ni(II) complex is:  
(a) One (b) Two  
(c) Three (d) Zero

- Q.23. Among the following, those can act as Mossbauer nuclei are:  
(I)  $^{129}\text{I}$  (II)  $^{57}\text{CO}$  (III)  $^{57}\text{Fe}$  (IV)  $^{121}\text{Sb}$   
(a) I, II, III and IV (b) II, III and IV  
(c) I, II and IV (d) I, III and IV
- Q.24. The IR spectrum of a sample contains absorptions at 3050, 2950, and 1620  $\text{cm}^{-1}$ . To what class of organic compound does this sample most likely belong?  
(a) Alkyne (b) Alkene  
(c) Ester (d) Alcohol
- Q.25. When a compound contains a sulfur atom, its mass spectrum contains a larger than usual \_\_\_\_\_ peak.  
(a) M+2 (b) M-2  
(c) M-1 (d) M+1
- Q.26. In the atomic absorption spectroscopic estimation of Fe(III) using  $\text{O}_2/\text{H}_2$  flame, the absorbance decreases with the addition of:  
(a) EDTA (b)  $\text{CO}_3^{-2}$   
(c)  $\text{Cl}^-$  (d)  $\text{SO}_4^{-2}$
- Q.27. The correct order of the isomeric shift in Mossbauer spectra ( $^{57}\text{Fe}$  source) of iron compounds is:  
(a)  $\text{Fe(II)} > \text{Fe(III)} > \text{Fe(IV)}$  (b)  $\text{Fe(III)} > \text{Fe(II)} > \text{Fe(IV)}$   
(c)  $\text{Fe(IV)} > \text{Fe(III)} > \text{Fe(II)}$  (d)  $\text{Fe(IV)} > \text{Fe(II)} > \text{Fe(III)}$
- Q.28. Which of the following has a C-H stretch that occurs at the highest stretching frequency?  
(a) Hexane (b) Hex-1-ene  
(c) Hex-1-yne (d) Hex-2-yne
- Q.29. The gas commonly used in generating plasma in Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) is:  
(a)  $\text{CO}_2$  (b)  $\text{N}_2\text{O}$   
(c)  $\text{H}_2$  (d) Ar
- Q.30. Among the isomers of  $\text{C}_4\text{H}_6$  given below, the compound which exhibits an absorption band at 3300  $\text{cm}^{-1}$  in the IR spectrum, is:  
(a) 1,3-butadiene (b) 1-butyne  
(c) 2-butyne (d) cyclobutene
- Q.31. The frequency of the stretching vibration of a bond in IR spectroscopy depends on what two quantities?  
(a) The electronegativity of the atoms and the nuclear charges of the atoms  
(b) The masses of the atoms and the stiffness of the bond  
(c) The stiffness of the bond and the electronegativity of the atoms  
(d) the electronegativity of the atoms and the masses of the atoms
- Q.32. Which of the following stretches tends to be the least intense?  
(a)  $\text{C}=\text{O}$  (b)  $\text{C}=\text{C}$   
(c)  $\text{C}-\text{H}$  (d)  $\text{O}-\text{H}$  (Carboxylic acid)
- Q.33. Out of the following, the one which is not an excitation source for IR spectrometer is

- (a) Deuterium Lamp (b) Mercury Arc  
(c) Nernst Glower (d) Tungsten Filament Lamp
- Q.34. The total number of ways in which two non identical spin  $-1/2$  particles can be oriented relative to a constant magnetic field is:  
(a) 1 (b) 2  
(c) 3 (d) 4
- Q.35. In atomic adsorption spectroscopy, the atomization process utilizes:  
(a) Electric Field (b) Magnetic Field  
(c) Flame (d) Electron Beam
- Q.36. Which of the following compounds would contain characteristic IR stretches at  $3300$  and  $2200\text{cm}^{-1}$ ?  
(a)  $(\text{CH}_3)_2\text{CHCN}$  (b)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$   
(c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$  (d)  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$
- Q.37. In addition to a carbonyl stretch, which of the following molecules exhibits two characteristic stretches at  $2700$  and  $2800\text{ cm}^{-1}$ ?  
(a)  $\text{CH}_3\text{CH}_2\text{CHO}$  (b)  $\text{CH}_3\text{CH}_2\text{COOH}$   
(c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$  (d)  $\text{CH}_3\text{CH}_2\text{COOCH}_3$
- Q.38. The oxidation state of metal ion in the catalyst can be deduced by:  
(a) Atomic Adsorption Spectroscopy (b) HPLC  
(c) Gas Chromatography (d) Mossbauer Spectroscopy
- Q.39. The molecule active in rotational microwave, infrared absorption as well as rotational Raman spectra is:  
(a)  $\text{CO}_2$  (b)  $\text{H}_2$   
(c)  $\text{SF}_6$  (d)  $\text{HCl}$
- Q.40. The number of hyperfine split lines observed in ESR spectrum of methyl radical is:  
(a) 1 (b) 6  
(c) 8 (d) 4
- Q.41. Which of the following molecules would have the highest frequency carbonyl stretch?  
(a)  $(\text{CH}_3\text{CH}_2)_2\text{CO}$  (b)  $\text{CH}_3\text{CH}_2\text{COOCH}_3$   
(c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$
- Q.42. One of the following functional groups, sometimes shows a single weak to medium IR adsorption peak in the  $2100$  to  $2250\text{ cm}^{-1}$  range. Depending on the structure of the compound this peak is sometimes not present, making it easy to misinterpret the spectrum. Which functional group is it?  
(a) Alkene (b) Alcohol  
(c) Alkyne (d) Carboxylic Acid
- Q.43. The absorption at  $\lambda_{\text{max}} 279\text{ nm}$  ( $\epsilon = 15$ ) in the UV spectrum of acetone is due to  
(a)  $\pi \rightarrow \pi^*$  transition (b)  $n \rightarrow \pi^*$  transition  
(c)  $\sigma \rightarrow \sigma^*$  transition (d)  $\pi \rightarrow \sigma^*$  transition
- Q.44. The correct value of isomer shift ( in Mossbauer spectra) and its explanation for  $\text{Fe(II)} - \text{TPP}$  and  $\text{Fe(III)} - \text{TPP}$  respectively from the following are: (TPP = Tetraphenylporphyrinate)

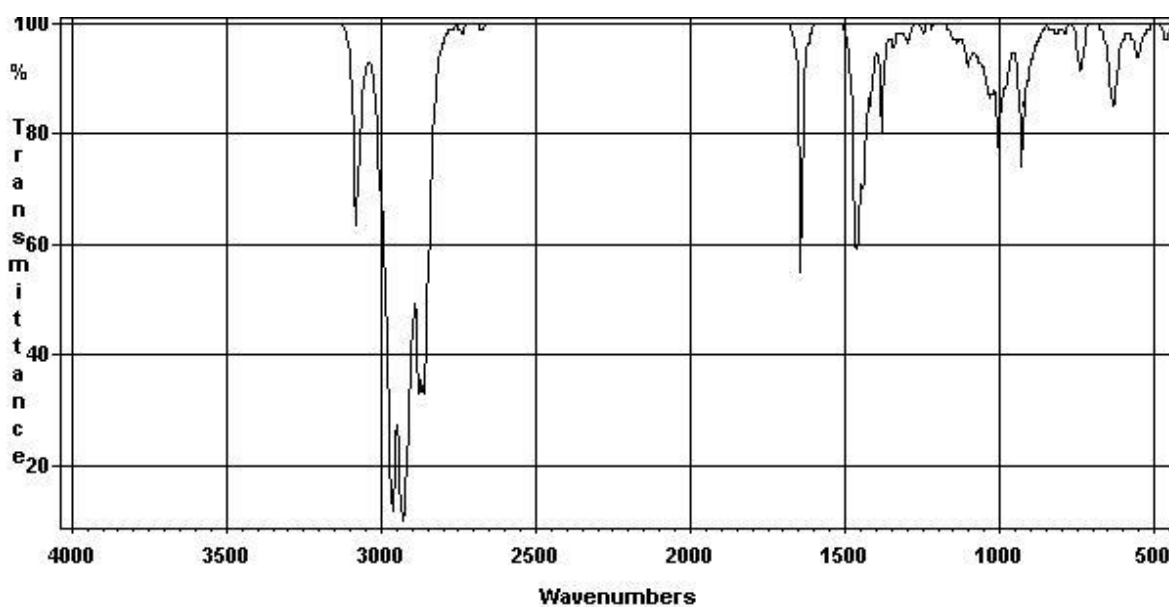
- (A)  $0.52 \text{ mms}^{-1}$  (B)  $0.45 \text{ mms}^{-1}$  (C) Increase in s electron density  
 (D) Decrease in s electron density  
 (a) A and D, B and C (b) A and C, B and C  
 (c) B and D, A and D (d) B and D, A and C

Q.45. What is the structure of the compound that gives the following infrared spectrum?



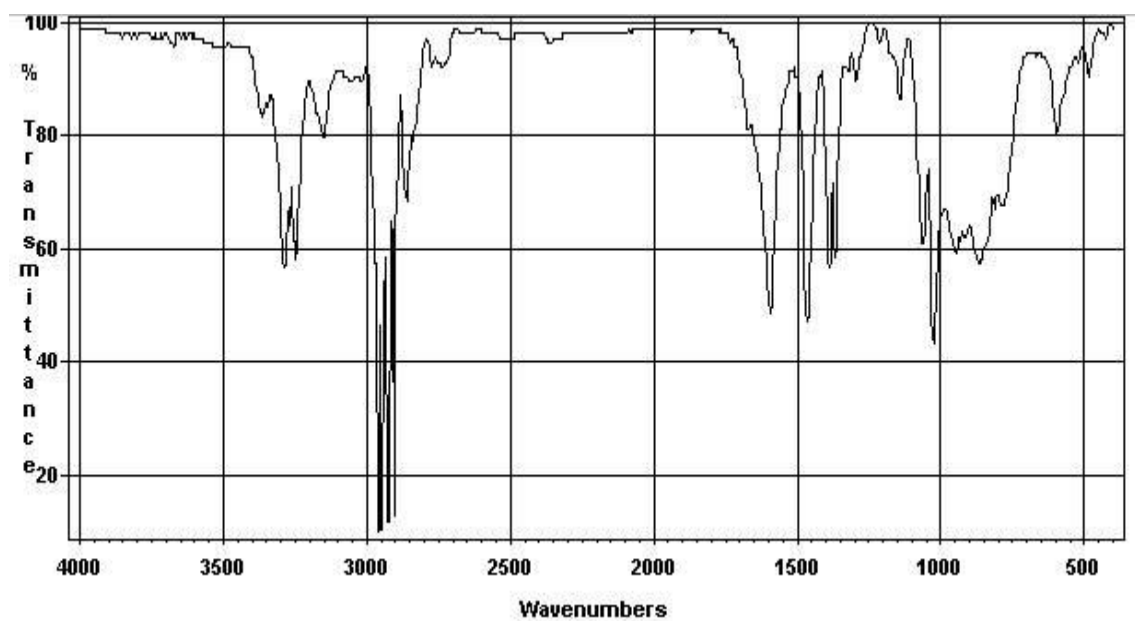
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  (b)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- Q.46. Why is the oxygen-hydrogen absorption of  $\text{CH}_3\text{OH}$  such a broad band in the infrared?  
 (a) Rotational energy levels broaden the absorption.  
 (b) Hyperconjugation resonance broadens the absorption.  
 (c) Resonance broadens the absorption.  
 (d) Hydrogen bonding broadens the absorption.
- Q.47. The total number of fine and hyperfine EPR lines expected for octahedral high spin  $\text{Mn(II)}$  complex are :  
 (a) 3 and 30 (b) 5 and 33  
 (c) 4 and 24 (d) 5 and 30
- Q.48. Which of the following bonds would show the strongest absorption in the IR?  
 (a) carbon-hydrogen (b) sulfur-hydrogen  
 (c) oxygen-hydrogen (d) nitrogen-hydrogen
- Q.49. The number of lines in the ESR spectrum of  $\text{CD}_3$  is (the spin of D is 1)  
 (a) 4 (b) 1  
 (c) 7 (d) 3
- Q.50. What is the structure of the compound that gives the following infrared spectrum?





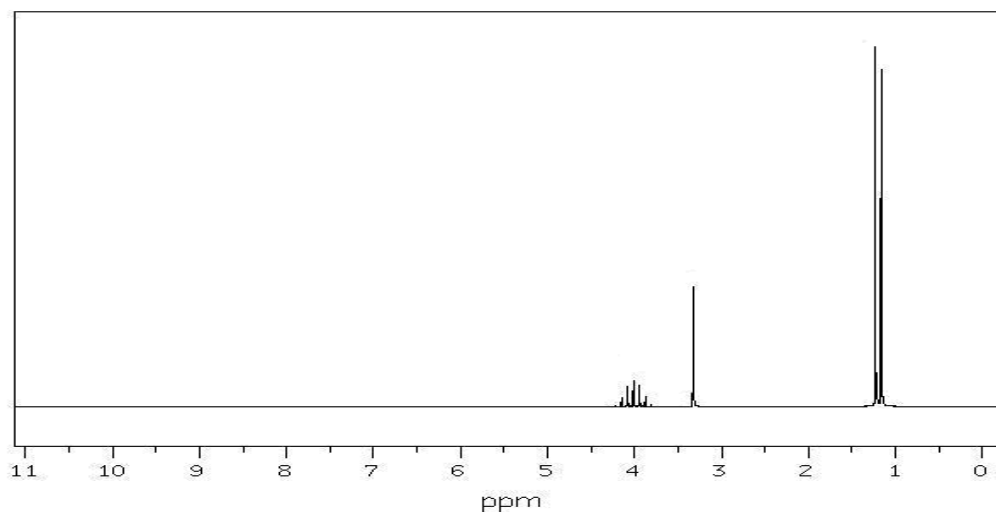
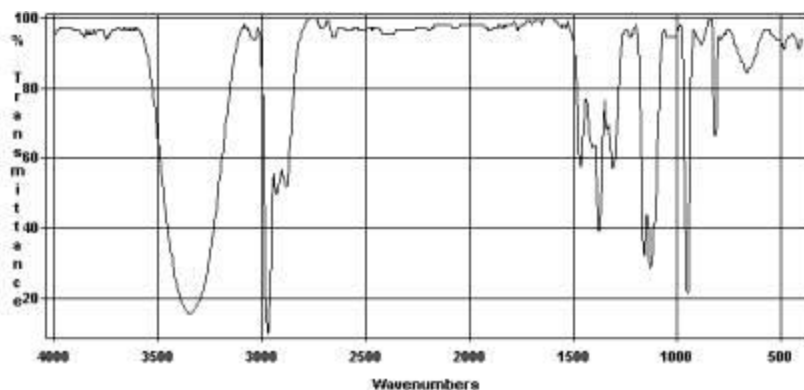
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$                       (b)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$                       (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

Q.51. What is the structure of the compound that gives the following infrared spectrum?



- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$                       (b)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$                       (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

Q.52. What is the structure of the compound that gives the following infrared and PMR spectra?



- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (b)  $(\text{CH}_3)_2\text{CHOH}$   
 (c)  $(\text{CH}_3)_2\text{CHNH}_2$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- Q.53. Which of the following techniques would be most useful to identify and quantify the presence of a known impurity in a drug substance?
- (a) NMR (b) MS  
 (c) HPLC (d) IR
- Q.54. In a mass spectrometry,
- (a) The analyzed substance remains intact.  
 (b) Large quantities of the substance is required.  
 (c) The analyzed substance is ionized.  
 (d) The analyzed substance is unionized.
- Q.55. The two characteristic stretching frequencies ( $\text{cm}^{-1}$ ) observed in the IR spectrum of compounds containing  $\text{NO}_2$  group are:
- (a) 3400 and 3300 (b) 1550 and 1350  
 (c) 2250 and 1760 (d) 1860 and 1760
- Q.56. For  $\text{CO}_2$  molecule:
- (a) All the vibrational modes are either IR or Raman active.  
 (b) The number of IR and Raman active vibrations will be same.

- (c) All vibrations are IR active.  
(d) All vibrations are Raman active.
- Q.57. A mass spectrometry delivers the evidence about:  
(a) The color of a substance.  
(b) The molecular mass of a substance.  
(c) The reactivity of a substance.  
(d) The polarity of a substance.
- Q.58. The anti Stokes lines are generally weaker in intensity because:  
(a) The molecules absorb the radiation completely.  
(b) The incident radiation is un-polarized.  
(c) The atoms are generally in the ground state.  
(d) The vibrational energies are small.
- Q.59. Of the molecules  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{H}_2$  the ones that will absorb infra red radiations are:  
(a)  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{C}_6\text{H}_6$   
(b)  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{C}_6\text{H}_6$   
(c)  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{C}_6\text{H}_6$   
(d)  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2$
- Q.60. The infra red spectrum of  $\text{CO}_2$  exhibits the following number of absorptions:  
(a) 1  
(b) 2  
(c) 3  
(d) 4
- Q.61. Which of the following electronic transition is disallowed?  
(a)  $\pi \rightarrow \pi^*$  transition  
(b)  $n \rightarrow \pi^*$  transition  
(c)  $\sigma \rightarrow \sigma^*$  transition  
(d)  $\delta \rightarrow \delta^*$  transition
- Q.62. IR stretching frequencies of carbonyl groups in aldehydes and acid chlorides in  $\text{cm}^{-1}$  are:  
(a) 1730-1700 and 1650-1580  
(b) 1680-1660 and 1730-1700  
(c) 1730-1700 and 1820-1770  
(d) 1680-1660 and 1820-1770
- Q.63. The source of ultra violet radiation used in UV-visible spectrophotometer is:  
(a) Mercury Vapour Lamp  
(b) Hydrogen Vapour Lamp  
(c) Sodium Vapour Lamp  
(d) Halogen Vapour Lamp
- Q.64. You are trying to find out if a thiocyanate ligand is bonded to a metal ion through the N or S atom. Which technique would be MOST useful to you?  
(a) EPR  
(b) Mass  
(c) IR  
(d) NMR
- Q.65. The infra red and Raman spectrum of  $\text{BF}_3$  are expected to show:  
(a) The same number of peaks.  
(b) More absorption peaks in IR in comparison to Raman.  
(c) More absorption peaks in Raman in comparison to IR.  
(d) Absorption peaks present in Raman and absent in IR.
- Q.66. Which of the following species is ESR active?  
(a)  $\text{KMnO}_4$   
(b)  $\text{K}_2\text{Cr}_2\text{O}_7$   
(c)  $\text{VO}_2^+$   
(d)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$

- Q.67. Among the following molecules, one having the highest zero point vibrational energy is  
(a)  $\text{CH}_4$  (b)  $\text{H}_2\text{O}$   
(c)  $\text{HF}$  (d)  $\text{NH}_3$
- Q.68. Identify the molecule whose rotational constant cannot be determined by spectroscopic methods:  
(a)  $\text{CH}_4$  (b)  $\text{H}_2$   
(c)  $\text{CO}_2$  (d)  $\text{HCl}$
- Q.69. The H-H distance in  $\text{H}_2$  molecule can be determined by:  
(a) Microwave rotational spectroscopy (b) NMR spectroscopy  
(c) IR spectroscopy (d) Rotational Raman spectroscopy
- Q.70. Raman frequencies for ESR and NMR are respectively in the spectral region:  
(a) Microwave and far-IR. (b) Far IR and microwave.  
(c) Radiofrequency and microwave. (d) Microwave and radiofrequency.
- Q.71. Which of the following molecules will have  $n \rightarrow \pi^*$  transition at the longest wavelength?  
(a)  $\text{CH}_3\text{COC}_2\text{H}_5$  (b)  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$   
(c)  $\text{CH}_3\text{COC}_6\text{H}_5$  (d)  $\text{HCHO}$
- Q.72. In the UV spectrum of cyclohexanone, the absorption at  $\lambda_{\text{max}} \sim 215 \text{ nm}$  is due to the transition:  
(a)  $\sigma \rightarrow \pi$  transition (b)  $\pi \rightarrow \pi^*$  transition  
(c)  $\sigma \rightarrow \sigma^*$  transition (d)  $\pi \rightarrow n$  transition
- Q.73. The band that gives the most intense band in the infrared spectrum for its stretching vibration is:  
(a) C-H (b) S-H  
(c) O-H (d) N-H
- Q.74. Cis and trans cinnamic acids can be most readily distinguished and identified by:  
(a) Chemical shift of the olefinic hydrogen's  
(b) Coupling constant of the olefinic hydrogen's  
(c) IR spectra  
(d) UV spectra
- Q.75. The most convenient spectroscopic technique to establish the presence of inter molecular hydrogen bonding in hydroxyl compounds is:  
(a) UV (b) Mass  
(c) IR (d) EPR
- Q.76. The vibrational stretching frequency of  $\text{N}_2$  can be determined by using:  
(a) Raman Spectroscopy (b) NMR Spectroscopy  
(c) IR Spectroscopy (d) Microwave Spectroscopy
- Q.77. The UV light source used in UV-visible spectrophotometer is:  
(a) Deuterium Lamp (b) Mercury Lamp  
(c) Sodium Lamp (d) Tungsten Lamp

- Q.78. The number of hyper lines in the EPR spectrum of a one electron reduced product of  $[\text{Co}_3(\text{CO})_6\text{Se}]$  ( $I = 7/2$  for Co nucleus) is:
- (a) 22 (b) 19  
(c) 15 (d) 18
- Q.79. Which among the following electronic transitions will have the lowest energy?
- (a)  $n \rightarrow \pi^*$  transition (b)  $\pi \rightarrow \pi^*$  transition  
(c)  $\sigma \rightarrow \sigma^*$  transition (d)  $n \rightarrow \sigma^*$  transition
- Q.80. Among the following diatomic molecules, the one that shows EPR signals is:
- (a)  $\text{B}_2$  (b)  $\text{N}_2$   
(c)  $\text{C}_2$  (d)  $\text{Li}_2$
- Q.81. The number of IR active vibrational modes in ammonia is:
- (a) 2 (b) 4  
(c) 6 (d) 3
- Q.82. Which of the two compounds will be most readily separated by TLC?
- (a) Acetophenone and 4-methyl acetophenone  
(b) Benzoin acid and 3-toluic acid  
(c) Naphthalene and anthracene  
(d) Naphthalene and acetophenone
- Q.83. Hydrogen absorbency index and nitrogen rules are related to:
- (a) UV Spectroscopy (b) IR Spectroscopy  
(c) NMR Spectroscopy (d) Mass Spectroscopy

**Answers**

1- (d)	2- (c)	3- (c)	4- (a)	5- (c)	6- (b)
7- (b)	8- (d)	9- (b)	10- (b)	11- (c)	12- (b)
13- (b)	14- (d)	15- (c)	16- (a)	17- (b)	18- (d)
19- (d)	20 - (b)	21 - (a)	22- (a)	23- (d)	24- (b)
25- (a)	26 - (d)	27- (a)	28- (c)	29- (d)	30- (b)
31- (b)	32 - (b)	33 - (b)	34- (c)	35- (c)	36- (c)
37- (a)	38- (b)	39- (d)	40- (d)	41- (b)	42 - (c)
43- (c)	44- (b)	45- (d)	46 - (d)	47 - (d)	48- (c)
49- (c)	50 - (b)	51 - (d)	52- (b)	53- (c)	54- (c)
55 - (b)	56- (a)	57- (b)	58 - (c)	59 - (a)	60 - (c)
61 - (b)	62 - (c)	63 - (a)	64- (c)	65- (c)	66- (d)
67- (a)	68- (b)	69- (d)	70- (d)	71- (b)	72- (b)
73- (c)	74- (d)	75- (c)	76- (a)	77- (a)	78- (a)
79- (a)	80- (a)	81- (c)	82- (d)	83- (d)	

## Chapter 4

### NMR Spectroscopy

(Contributed by: Dr. Punam Yadav, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- Electromagnetic radiation in the radio wave region is used in  $^1\text{H}$  NMR spectroscopy.
- $^{13}\text{C}$  NMR spectroscopy can be used to distinguish between isophthalic and terephthalic acids.
- Two signals will be observed in the proton decoupled  $^{13}\text{C}$  NMR for hexamethylbenzene.
- A singlet, a triplet, and a quartet are observed for the signals in the off-resonance decoupled  $^{13}\text{C}$  spectrum of 2-chloropropene.
- The approximate chemical shift of an alkynyl carbon in  $^{13}\text{C}$  NMR spectroscopy is 70 ppm.
- 2,2-dichloropropane exhibits only one signal in the  $^1\text{H}$  NMR spectra.
- The order of chemical shift ( $\delta$  value) in the  $^1\text{H}$  NMR spectrum of crotonaldehyde is  $\text{CHO} > \text{olefinic} > \text{Me}$ .
- The  $^1\text{H}$  NMR spectrum of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$  recorded at room temperature has one singlet.
- The pattern of  $^{14}\text{N}$  NMR spectrum of 1,4-dichlorobenzene is  $A_4$ .
- The relative area of each peak in a quartet spin-spin splitting pattern 1:3:3:1.
- The low temperature  $^{19}\text{F}$  NMR spectrum of  $\text{IF}_5$  molecule in solution exhibits one doublet and one quintet.
- Any process faster than 0.01 sec will be recorded as an average by NMR spectroscopy.
- In the broad band decoupled  $^{13}\text{C}$  NMR spectrum the number of signals expected for bicyclo [2.2.1] heptane are three.
- The  $^{31}\text{P}$  NMR spectrum of  $\text{PF}_4\text{N}(\text{CH}_3)_2$  at room temperature and low temperature (173K) shows quintet and triplet of triplets respectively.
- In the  $^1\text{H}$  NMR spectrum of toluene, the resonance due to  $\text{CH}_3$  group is expected at 1.25 ppm.
- In a  $^1\text{H}$  NMR spectrum,  $^1\text{H}$  nuclei that are located near to electronegative atoms tend to be deshielded relative to  $^1\text{H}$  nuclei that are not near to electronegative atoms.
- The signal for the hydrogen bonded to oxygen in ethanol appears as a triplet in pure ethanol and as a singlet in ethanol that contains a trace amount of acid because proton exchange causes spin decoupling.
- In the broad band decoupled  $^{13}\text{C}$  NMR spectrum, the number of signals for Catechol, Resorcinol and Hydroquinone are three, four and two respectively.
- Bathochromic shift is also known as red shift.

- Water is not used as solvent in NMR Spectroscopy.
- The  $^{19}\text{F}$  NMR spectrum of  $\text{ClF}_3$  shows doublet and triplet for a T-shaped structure.
- Felix Bloch and Edward M. Purcell were awarded Noble Prize in Physics for Phenomenon of NMR.
- In NMR if the atom contains three nearby protons then these will produce quartet.
- The reference material used in NMR Spectroscopy is Tetramethyl Silane.
- If a proton is coupled with N other equivalent protons the number of peaks in multiplet is N+1 and the relative intensities of these multiplets are determined by Pascal's triangle.
- In comparison to the frequency of the EPR transition, the NMR transition frequency is almost same.
- $^{19}\text{F}$  NMR spectrum of meridional isomer of octahedral  $\text{RhCl}_3\text{F}_3$  complex, [ $^{103}\text{Rh}$  ( $I=1/2$ );  $^{19}\text{F}$  ( $I=1/2$ ) assuming  $J_{\text{Rh-F}} > J_{\text{F-F}}$ ] will show two doublets and two triplets.
- The  $^{31}\text{P}$  NMR spectrum of  $\text{P}_4\text{S}_3$  consists of a doublet and a quartet.
- The fine structure and intensity ratios expected in the proton NMR spectrum of  $^{14}\text{NH}_4^+$  ion (for  $^{14}\text{N}$   $I=1$ ) are triplet 1:1:1
- For any NMR active nucleus, the magnitude of radiofrequency required for observing NMR phenomenon depends on: both magnetic field and choice of the nucleus.
- The  $^1\text{H}$  NMR chemical shift of  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  are 4.26, 3.05, 2.68 and 2.16 respectively.
- The sensitivity of a 600 MHz spectrometer is more than that of a 60 MHz spectrometer because according to the Boltzmann distribution law, the excess population in the lower spins state increases with increasing applied magnetic field.



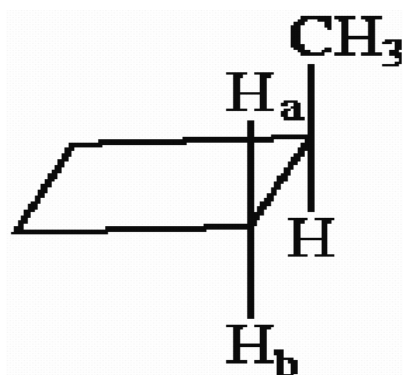
## Multiple Choice Questions

- Q.1. The energy difference between the allowed spin states for a  $^1\text{H}$  nucleus is \_\_\_\_\_ the strength of the external magnetic field in which it is placed.
- (a) exponentially related to (b) inversely proportional to  
(c) logarithmically related to (d) directly proportional to
- Q.2.  $^1\text{H}$  nuclei located near electronegative atoms tend to be \_\_\_\_\_ relative to  $^1\text{H}$  nuclei which are not.
- (a) resonanced (b) shielded  
(c) deshielded (d) split
- Q.3. The  $^1\text{H}$  NMR spectrum of 1,4-dimethoxybenzene will have
- (a) two singlets (b) two doublets and one singlet  
(c) ten singlets (d) two doublets and two singlet
- Q.4. The number of signals expected for the compounds m- and p- dichlorobenzenes in the broad band decoupled  $^{13}\text{C}$  NMR spectra, respectively,
- (a) 6 and 4 (b) 4 and 4  
(c) 4 and 2 (d) 3 and 2
- Q.5. Electromagnetic radiation in the \_\_\_\_\_ region is used in  $^1\text{H}$  NMR spectroscopy.
- (a) X-ray (b) Radio wave  
(c) Infrared (d) Microwave
- Q.6. The protons marked  $\text{H}_a$  and  $\text{H}_b$  in the molecule below are:

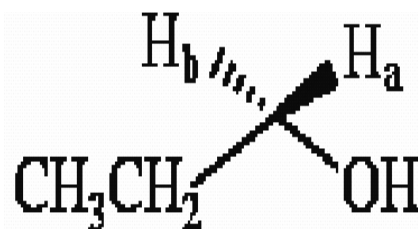


- (a) Chemically equivalent (b) Enantiotopic  
(c) Diastereotopic (d) Endotopic
- Q.7. Which technique can be used to distinguish between isophthalic and terephthalic acids?
- (a)  $^{13}\text{C}$  NMR spectroscopy (b) IR spectroscopy  
(c) UV-Vis spectroscopy (d) Mass spectrometry
- Q.8. How many signals will be observed in the proton decoupled  $^{13}\text{C}$  NMR for hexamethylbenzene?
- (a) 4 (b) 1  
(c) 2 (d) 3
- Q.9. What multiplicities are observed for the signals in the off-resonance decoupled  $^{13}\text{C}$  spectrum of 2-chloropropene?
- (a) A singlet, a doublet and a triplet (b) 3 singlets  
(c) A singlet, a triplet, and a quartet (d) 2 singlets and a doublet
- Q.10. What is the approximate chemical shift of an alkynyl carbon in  $^{13}\text{C}$  NMR spectroscopy?
- (a) 10 ppm (b) 200 ppm

- (c) 70 ppm (d) 30 ppm
- Q.11. An organic compound with molecular formula  $C_3H_6Cl_2$  exhibit only one signal in the  $^1H$  NMR spectra. The compound is:
- (a) 2,2-dichloropropane (b) 1,2-dichloropropane  
(c) 1,3-dichloropropane (d) 1,1-dichloropropane
- Q.12. The order of chemical shift ( $\delta$  value) in the  $^1H$  NMR spectrum of crotonaldehyde is:
- (a) Olefinic > CHO > Me (b) CHO > Me > olefinic  
(c) CHO > olefinic > Me (d) Olefinic > Me > CHO
- Q.13. The protons marked  $H_a$  and  $H_b$  in the molecule below are:



- (a) Chemically equivalent (b) Enantiotopic  
(c) Diastereotopic (d) Endotopic
- Q.14. The protons marked  $H_a$  and  $H_b$  in the molecule below are



- (a) Chemically equivalent (b) Enantiotopic  
(c) Diastereotopic (d) Endotopic
- Q.15. The multiplicity of the signal in  $^{31}P$  NMR spectrum of  $PD_3$  is:
- (a) Singlet (b) Septet with unequal intensities  
(c) Quartet with equal intensities (d) Septet with equal intensities
- Q.16. The  $^1H$  NMR spectrum of  $(\eta^5-C_5H_5)_2 Fe$  recorded at room temperature is:
- (a) One singlet (b) Two singlets  
(c) One multiplet (d) Two multiplets
- Q.17. The pattern of  $^{14}N$  NMR spectrum of 1,4-dichlorobenzene is:
- (a) AX (b) AM  
(c) AB (d)  $A_4$

- Q.18. If a molecule contains 4 elements of unsaturation and signals in the  $^1\text{H}$  NMR spectrum between  $\delta 7.0$  and  $8.0$  ppm, what structural group is likely to be present?
- (a) A carbon-carbon triple bond (b) A carbonyl group  
(c) An aromatic ring (d) A hydroxyl group
- Q.19. In the  $^1\text{H}$  NMR spectrum of bromoethane the methylene group is split into a quartet by the  $\alpha$  and  $\beta$  nuclear spins of the protons on the neighboring methyl group. If the external magnetic field,  $B_0$ , directs upward, which sequence of nuclear spins contributes to the second farthest peak down field within the spin-spin splitting pattern?
- (a)  $\downarrow\downarrow\downarrow$  (b)  $\uparrow\downarrow\uparrow$   
(c)  $\uparrow\downarrow\downarrow$  (d)  $\uparrow\uparrow\uparrow$
- Q.20. What is the relative area of each peak in a quartet spin-spin splitting pattern?
- (a) 1:2:2:1 (b) 1:2:1  
(c) 1:4:4:1 (d) 1:3:3:1
- Q.21. The low temperature  $^{19}\text{F}$  NMR spectrum of  $\text{IF}_5$  molecule in solution should exhibit which of the following patterns? (Ignore any magnetic coupling effects to the iodine nucleus)
- (a) One singlet (b) One singlet and one quintet  
(c) One doublet and one quintet (d) One quartet and one triplet
- Q.22. How many signals will vinyl chloride have in its  $^1\text{H}$  NMR spectrum?
- (a) 3 (b) 2  
(c) 4 (d) 1
- Q.23. Which of the following will occur farthest downfield?
- (a) The hydrogen of benzene (b) The hydrogen of ethene  
(c) The hydrogen of ethyne (d) The hydrogen of dimethyl ether
- Q.24. The  $^1\text{H}$  NMR spectrum of an organic compound molecular formula  $\text{C}_4\text{H}_8$  exhibited only a singlet at  $\delta = 1.9$  ppm. The compound is:
- (a) 1-butene (b) trans-2-butene  
(c) cis-2-butene (d) cyclobutane
- Q.25. Any process faster than \_\_\_\_\_ will be recorded as an average by NMR spectroscopy.
- (a) 0.0005 sec (b) 0.1 sec  
(c) 0.001 sec (d) 0.01 sec
- Q.26. An NMR spectrometer that operates at a frequency of 60 MHz for  $^{13}\text{C}$  NMR spectra, operates at what frequency for  $^1\text{H}$  NMR spectra?
- (a) 60 MHz (b) 240 MHz  
(c) 30 MHz (d) 120 MHz
- Q.27. The chemical shifts of a doublet signal for a proton in a spectrum are 4.08 and 4.06 using a 400 MHz NMR spectrometer. The coupling constant in (Hz) is:
- (a) 8 (b) 0.02  
(c) 8.14 (d) 10
- Q.28. In the broad band decoupled  $^{13}\text{C}$  NMR spectrum the number of signals expected for bicyclo [2.2.1] heptane are:
- (a) 3 (b) 2

- (c) 5 (d) 7
- Q.29. The  $^{31}\text{P}$  NMR spectrum of  $\text{PF}_4\text{N}(\text{CH}_3)_2$  at room temperature and low temperature (173K) respectively shows (assume that N and H do not couple):  
 (a) Triplet and quintet (b) Quintet and triplet of triplets  
 (c) Quintet and triplet (d) Triplet and triplet of triplets
- Q.30. How many different types of protons (given unique chemical shifts in  $^1\text{H}$  NMR) are present in styrene:  
 (a) 3 (b) 4  
 (c) 6 (d) 5
- Q.31. In the  $^1\text{H}$  NMR spectrum of toluene, the resonance due to  $\text{CH}_3$  group is expected at:  
 (a)  $\delta$  0.5 (b)  $\delta$  3.5  
 (c)  $\delta$  1.25 (d)  $\delta$  2.5
- Q.32. The IR spectrum of a compound with the formula  $\text{C}_6\text{H}_{14}\text{O}$  does not have an absorption band in the region from  $3100\text{--}3600\text{ cm}^{-1}$  and also does not have an absorption band in the region from  $1650\text{--}1800\text{ cm}^{-1}$ . To what functional class must this compound belong?  
 (a) Alcohol - would have O-H stretch in  $3100\text{--}3600$  region  
 (b) Ketone - would have C=O stretch in  $1650\text{--}1800$  region  
 (c) Ether  
 (d) Ester - would have C=O stretch in  $1650\text{--}1800$  region, also needs two 'O's for ester
- Q.33. In a  $^1\text{H}$  NMR spectrum,  $^1\text{H}$  nuclei that are located near to electronegative atoms tend to be \_\_\_\_\_ relative to  $^1\text{H}$  nuclei that are not near to electronegative atoms.  
 (a) split (b) have a more intense signal  
 (c) shielded (d) deshielded
- Q.34. The compound whose  $^1\text{H}$  NMR spectrum is shown below has the molecular formula  $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$  and has an infrared absorption peak at  $1740\text{ cm}^{-1}$ . What is its structure?  
 (a)  $\text{ClCH}_2\text{COCH}_2\text{OCH}_3$  (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCOCl}$   
 (c)  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{Cl}$  (d)  $\text{ClCH}_2\text{COOCH}_2\text{CH}_3$
- Q.35. A compound has a molecular ion peak in its mass spectrum at  $m/z$  58, and a strong absorption band in its IR spectrum at  $1720\text{ cm}^{-1}$ . What is the structure of the compound?  
 (a)  $\text{CH}_2=\text{CHCH}_2\text{OH}$  (b)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$   
 (c)  $\text{HCOOCH}_2\text{CH}_3$  (d)  $\text{CH}_3\text{COCH}_3$
- Q.36. Why does the signal for the hydrogen bonded to oxygen in ethanol appear as a triplet in pure ethanol and as a singlet in ethanol that contain a trace amount of acid?  
 (a) Spin exchange causes spin decoupling.  
 (b) Electron exchange causes spin decoupling.  
 (c) Proton exchange causes spin decoupling.  
 (d) Chemical exchange causes spin decoupling.
- Q.37. In the broad band decoupled  $^{13}\text{C}$  NMR spectrum, the number of signals for:  
 (A) Catechol (B) Resorcinol (C) Hydroquinol  
 respectively are:  
 (a) Six, four and two (b) Three, four and two  
 (c) Six, six and four (d) Three, four and four
- Q.38.  $^1\text{H}$  NMR spectrum of HD would show:  
 (a) A singlet (b) A doublet

- (c) A triplet with intensity ratio 1:2:1      (d) A triplet with intensity ratio 1:1:1
- Q.39. The NMR experiment consists of measuring the energy associated with what physical phenomenon?
- (a) Excitation of a core electron from an atom.  
(b) Flipping the magnetic spin vector of a nucleus (having a non-zero magnetic moment) in a strong magnetic field.  
(c) Activating a molecular vibration.  
(d) Promoting an electron from the HOMO to the LUMO.
- Q.40. A compound has the molecular formula  $C_5H_{10}$  and shows a single line in the  $^1H$  NMR spectrum, at 1.50 ppm. Select the structure most consistent with this data.
- (a) Pentane      (b) Cyclopentane  
(c) Pentene      (d) Cyclopentene
- Q.41. Which one of the following factors does not affect the chemical shift?
- (a) Inductive effect      (b) Anisotropic effect  
(c) Concentration      (d) Hydrogen bonding
- Q.42. Bathochromic shift is also known as
- (a) Hypochromic shift      (b) Hyperchromic shift  
(c) Red shift      (d) Hypsochromic shift
- Q.43. Which one of the following solvent is not used in NMR Spectroscopy?
- (a) Carbon disulfide      (b) Deuterated chloroform  
(c) Carbon tetrachloride      (d) Water
- Q.44. 4-Hydroxybenzoic acid exhibited signals at  $\delta$  171, 162, 133, 122 and 116 ppm in its broad band decoupled  $^{13}C$  NMR spectrum. The correct assignment of the signals is:
- (a)  $\delta$  171 (C-4), 162 (COOH), 133 (C-3&5) 122 (C-1) and 116 (C-2&6)  
(b)  $\delta$  171 (COOH), 162 (C-4), 133 (C-2&6) 122 (C-1) and 116 (C-3&5)  
(c)  $\delta$  171 (C-4), 162 (COOH), 133 (C-2&6) 122 (C-1) and 116 (C-3&5)  
(d)  $\delta$  171 (COOH), 162 (C-4), 133 (C-3&5) 122 (C-1) and 116 (C-2&6)
- Q.45. The  $^{19}F$  NMR spectrum of  $ClF_3$  shows:
- (a) Doublet and triplet for a T-shaped structure  
(b) Singlet for a trigonal planar structure  
(c) Singlet for a trigonal pyramidal structure  
(d) Doublet and singlet for a T-shaped structure
- Q.46. Free radical substances showing paramagnetism due to the magnetic movement of unpaired electron, which spectroscopy is applied for its determination?
- (a) NMR      (b) ESR  
(c) IR      (d) PMR
- Q.47. The scientists' \_\_\_\_\_ were awarded Noble Prize in Physics for Phenomenon of NMR:
- (a) Hery and Moseley      (b) Felix Bloch and Edward M. Purcell  
(c) Beer and Lambert      (d) Frederic William Herschel
- Q.48. The transition between a triplet excited state and singlet excited state is known as:
- (a) Allowed      (b) Forbidden  
(c) Both      (d) None of these
- Q.49. The number of peaks shown by Iso propyl alcohol in an  $^1H$  NMR spectrum is:
- (a) Four      (b) Two

- (c) Three (d) Five
- Q.50. The ratio of relative intensities of carbon signals in the first order  $^{13}\text{C}$  NMR spectrum of  $\text{CD}_3\text{Cl}$  is:
- (a) 1:4:6:4:1 (b) 1:3:3:1  
(c) 1:6:15:20:15:6:1 (d) 1:3:6:7:6:3:1
- Q.51. In NMR spectroscopy, the product of the nuclear 'g' factor ( $g_n$ ), the nuclear magneton ( $\beta_n$ ) and the magnetic field strength ( $B_n$ ) gives that
- (a) Energy of transition from  $\alpha$  to  $\beta$  state (b) Chemical shift  
(c) Spin-spin coupling constant (d) Magnetogyric ratio
- Q.52. Consider the following statements for [18] annulene
- [A] It is aromatic  
[B] The inner portion resonate at  $\delta$  9.28 in its  $^1\text{H}$  NMR spectrum  
[C] There are six protons in the shielded zone
- (a) A, B and C (b) A and B only  
(c) B and C only (d) A and C only
- Q.53. In NMR if the atom contains three nearby protons then these will produce:
- (a) Doublet (b) Triplet  
(c) Quartet (d) Sestet
- Q.54. The reference material used in NMR Spectroscopy is
- (a) Trimethyl silane (b) Tetramethyl silane  
(c) Both of these (d) None of these
- Q.55. If a proton is coupled with N other equivalent protons the number of peaks in multiplet is N+1 and the relative intensities of these multiplets are determined by
- (a) Cram's rule (b) Pascal's triangle  
(c) Chemical shift (d) Bedth's rule
- Q.56. The number of signals that appear in the broad band decoupled  $^{13}\text{C}$  NMR spectrum of phenanthrene and anthracene, respectively are:
- (a) Ten and four (b) Ten and ten  
(c) Seven and four (d) Seven and seven
- Q.57. In comparison to the frequency of the EPR transition, the NMR transition frequency is
- (a) Much lighter (b) Much lower  
(c) Almost same (d) None of these
- Q.58.  $^{19}\text{F}$  NMR spectrum of meridional isomer of octahedral  $\text{RhCl}_3\text{F}_3$  complex, [ $^{103}\text{Rh}$  ( $I=1/2$ );  $^{19}\text{F}$  ( $I=1/2$ ) assuming  $J_{\text{Rh-F}} > J_{\text{F-F}}$ ] will show
- (a) One doublet (b) Two doublets and one triplet  
(c) Two doublets and two triplets (d) One singlet and two triplets
- Q.59. A borane (X) is reacted with ammonia to give a salt of borohydride (Y). The  $^{11}\text{B}$  NMR spectrum of Y consists of a triplet and a quintet. The borane X is:
- (a)  $\text{B}_2\text{H}_6$  (b)  $\text{B}_3\text{H}_9$   
(c)  $\text{B}_4\text{H}_8$  (d)  $\text{B}_5\text{H}_9$

- Q.60. In the proton decoupled  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectrum of  $(\text{CH}_3)_3\text{P}=\text{O}$ , the number of lines observed respectively are:
- (a) Two and one (b) One and two  
(c) Three and One (d) Two and two
- Q.61. In  $\text{ClF}_3$  were to be stereochemically rigid, its  $^{19}\text{F}$  NMR spectrum (I for  $^{19}\text{F}=1/2$ ) would be (assume that Cl is not NMR active):
- (a) A doublet and a triplet (b) Two singlet  
(c) A doublet and a singlet (d) A singlet
- Q.62. The  $^{31}\text{P}$  NMR spectrum of  $\text{P}_4\text{S}_3$  consists of:
- (a) A doublet and a quartet (b) Two doublets  
(c) A doublet and a triplet (d) A singlet
- Q.63. The  $^1\text{H}$  NMR spectrum of a compound with molecular formula  $\text{C}_3\text{H}_7\text{NO}$  shows the following features:
- |                       |               |         |         |
|-----------------------|---------------|---------|---------|
| Chemical Shift (ppm): | 6.50          | 2.25    | 1.10    |
| Shape:                | Broad singlet | quartet | triplet |
- Which of the following is in agreement with the information?
- (a)  $(\text{CH}_3)_2\text{C}=\text{NOH}$  (b)  $\text{CH}_3\text{COCH}_2\text{NH}_2$   
(c)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  (d)  $\text{HCON}(\text{CH}_3)_2$
- Q.64. The fine structure and intensity ratios expected in the proton NMR spectrum of  $^{14}\text{NH}_4^+$  ion (for  $^{14}\text{N} I=1$ ) are:
- (a) Doublet 1:1 (b) Triplet 1:1:1  
(c) Triplet 1:2:1 (d) Singlet
- Q.65. For any NMR active nucleus, the magnitude of radiofrequency required for observing NMR phenomenon depends on:
- (a) Strength of magnetic field (b) Choice of the nucleus  
(c) Both onmagnetic field and choice of the nucleus  
(d) The nuclear energy levels
- Q.66. How many signals would you expect to see for 1,4-dinitro benzene in its  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra?
- (a) One of its  $^1\text{H}$  NMR and two of its  $^{13}\text{C}$  NMR spectra  
(b) Two of its  $^1\text{H}$  NMR and three of its  $^{13}\text{C}$  NMR spectra  
(c) Two of its  $^1\text{H}$  NMR and one of its  $^{13}\text{C}$  NMR spectra  
(d) One of its  $^1\text{H}$  NMR and one of its  $^{13}\text{C}$  NMR spectra
- Q.67. Which of the following compounds show(s) three signals in its  $^1\text{H}$  NMR spectrum?
- (a) 2-chloro-2-methylbutane (b) 3-chloropentane  
(c) 2-chloropentane (d) Both a and b
- Q.68. In the  $^{19}\text{F}$  NMR spectrum of  $\text{PF}_5$ , the number of signals and multiplicity at room temperature are:
- (a) One, doublet (b) One, singlet  
(c) Two, singlet (d) Two, doublet

- Q.69. The  $^1\text{H}$  NMR chemical shift of  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  are:  
(a) 2.16, 2.68, 3.05, 4.26 (b) 4.26, 3.05, 2.68, 2.16  
(c) 4.26, 3.05, 2.16, 2.68 (d) 2.16, 3.05, 2.68, 4.26
- Q.70. An organic compound ( $\text{MF} \cdot \text{C}_8\text{H}_{10}\text{O}$ ) exhibited the following  $^1\text{H}$  NMR spectral data  $\delta$  2.5 (3 H,s), 3.8 (3H,s), 6.8 (2H,d,J 8Hz), 7.2 (2H, d, J 8Hz) ppm. The compound among the choices is:  
(a) 4-ethylphenol (b) 2-ethylphenol  
(c) 4-methylanisol (d) 4-methylbenzylalcohol
- Q.71. In the  $^1\text{H}$  NMR spectrum of  $\text{CH}_3\text{CH}_2\text{Cl}$ , the quartet for the  $\text{CH}_2$  group has a coupling constant of 7 Hz. What is the coupling constant for the  $\text{CH}_3$  triplet?  
(a) 0 (b) 3.5  
(c) 7 (d) 10.5
- Q.72. The NMR spectrum of  $\text{AX}_3$  exhibits lines at  $\delta=2.1$  and 2.3 ppm (for X type proton) and  $\delta=4.1, 4.3, 4.5$  and 4.7 ppm (for A type proton), measured from TMS with an instrument operating at 100 MHz. The chemical shift (in ppm) of A and X protons and coupling constant (in Hz) are respectively.  
(a) 4.4, 2.2 and 20 (b) 2.2, 4.4 and 10  
(c) 2.2, 4.4 and 5 (d) 4.3, 2.1 and 20
- Q.73. The uncertainty in the NMR frequency of a compound in liquid state (relaxation time=1s) is 0.1 Hz. The uncertainty in the frequency (in Hz) of same compound in solid state (relaxation time= $10^{-4}$ s) is:  
(a)  $10^{-4}$  (b)  $10^{-3}$   
(c) 100 (d) 1000
- Q.74. An AX system gave 4 times at 4.72, 4.6, 1.12 and 1.0 ppm away from the TMS using an NMR spectrometer operating at 100 MHz. What are the values of  $J_{\text{AX}}$  (in Hz) and  $\delta_{\text{AX}}$  (in ppm), respectively:  
(a) 12 and 3.6 (b) 6 and 3.6  
(c) 12 and 2.86 (d) 6 and 2.86
- Q.75. The sensitivity of a 600 MHz spectrometer is more than that of a 60 MHz spectrometer because:  
(a) Population of spin states is inversely proportional to the applied magnetic field.  
(b) Population of spin states is directly proportional to the applied magnetic field.  
(c) According to the Boltzmann distribution law, the excess population in the lower spins state increases with increasing applied magnetic field.  
(d) The spectral scan width is more for a 600 MHz spectrum as compared to a 60 MHz spectrum.
- Q.76.  $^1\text{H}$  NMR spectrum of [18] annulene shows:  
(a) Only one peak at  $\delta$  7.2 (18 H). (b) Only one peak at  $\delta$  5.0 (18 H).  
(c) Two peaks at  $\delta$  9.0 (12 H) and  $\delta$  3.0 (6 H).  
(d) Two peaks at  $\delta$  9.0 (6 H) and  $\delta$  3.0 (12 H).



- Q.77. How many absorption lines will 2-methylpent-2-ene have in its proton decoupled  $^{13}\text{C}$  NMR spectrum?
- (a) 4 (b) 3  
(c) 6 (d) 5
- Q.78. How many signals does 2,2,4-trimethylpentane have in its  $^1\text{H}$  NMR spectrum?
- (a) 4 (b) 3  
(c) 2 (d) 5
- Q.79. The low temperature  $^1\text{H}$  NMR spectrum of the Fischer carbene complex  $[(\text{CO})_5\text{Cr}(\text{C}(\text{OCH}_3)\text{Me})]$  shows for the methoxy group:
- (a) Two singlets of unequal intensity.  
(b) Four resonances in the ratio 1:3:3:1 due to coupling with methyl group.  
(c) One single resonance for the methyl group.  
(d) Three peaks due to different environments for each hydrogen on the methyl group.
- Q.80. In the 400 MHz  $^1\text{H}$  NMR spectrum, of organic compound exhibited a doublet. The two lines of the doublets are  $\delta$  2.35 and 2.38 ppm. The coupling constant value is:
- (a) 6 Hz (b) 3 Hz  
(c) 12 Hz (d) 9 Hz
- Q.81. Given  $\gamma (^1\text{H}) = 2.7 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$ . The resonance frequency of a proton in magnetic field of 12.6 T is close to:
- (a) 60 Hz (b) 540 Hz  
(c) 110 Hz (d) 780 Hz
- Q.82. The number of signals observed in  $^1\text{H}$  NMR spectrum of 3,5-dibromotoluene is:
- (a) 4 (b) 3  
(c) 2 (d) 6

**Answers**

1- (d)	2- (c)	3- (a)	4- (c)	5- (b)	6- (a)
7- (a)	8- (c)	9- (c)	10- (c)	11- (a)	12- (c)
13- (c)	14- (b)	15- (b)	16- (a)	17- (d)	18- (c)
19- (b)	20 - (d)	21 - (c)	22- (a)	23- (a)	24- (d)
25- (d)	26 - (b)	27- (a)	28- (a)	29- (b)	30- (c)
31- (c)	32 - (c)	33 - (d)	34- (d)	35- (d)	36- (c)
37- (b)	38- (d)	39- (b)	40- (b)	41- (c)	42 - (c)
43- (d)	44- (b)	45- (a)	46 - (b)	47 - (b)	48- (b)
49- (c)	50 - (d)	51 - (a)	52- (d)	53- (c)	54- (b)
55 - (b)	56- (c)	57- (c)	58 - (c)	59 - (a)	60 - (a)
61 - (a)	62 - (a)	63 - (c)	64- (b)	65- (c)	66- (a)
67- (d)	68- (a)	69- (b)	70- (c)	71- (c)	72- (a)
73- (d)	74- (a)	75- (c)	76- (c)	77- (d)	78- (a)
79- (b)	80- (c)	81- (b)	82- (b)		

## Chapter 5

### Co-ordination Chemistry and Distortion in Complex Compounds

(Contributed by: Dr. Dinkar Malik, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- Zieses salt has square planar geometry.
- In trisilyl amine three  $sp^2$  orbital's are involved in  $\sigma$  bonding giving a plane trigonal structure.
- The no. metal-metal bonds in  $[W_2(OPh)_6]$  is three.
- The ground state term of  $V^{+3}$  ion is  $^3F_2$ .
- trans- $[Pt(NH_3)_2Cl_2]$  does not show optical isomerism because it is super- imposable on its mirror image.
- The dark purple colour of  $KMnO_4$  is due to ligand to metal charge transfer spectra.
- If  $t_{2g}$  orbital is unsymmetrically filled than there is less Jahn-Teller distortion and If  $e_g$  orbital is unsymmetrically filled then Jahn-Teller distortion will be large. However in case of symmetrically filled orbitals there is no Jahn-Teller distortion.e.g. in  $Cu^{+2}$  ( $d^9$  configuration)  $e_g$  will be unsymmetrically filled. Hence large distortion occurs in this complex.
- Tropylium exists in +1 oxidation state.
- Jahn-Teller effect is not observed in high spin  $d^3$ ,  $d^8$  and  $d^{10}$  complexes.
- The complex ion  $[Cu(NH_3)_6]^{+2}$ , the number of possible d-d transitions will be: one.
- Jahn Teller effect is the separation of the degenerate electronic states in a given symmetry so as to remove degeneracy.
- The complexes  $[Co(NH_3)_3NO_2]Cl_2$  and  $[Co (NH_3)_5(ONO)]Cl_2$  are example of Linkage isomers.
- The pale colour of  $[Mn(H_2O)_6]^{+2}$  is due to Spin forbidden d-d transition.
- CO, NO,  $PPh_3$  are well known as  $\pi$ - acid ligands.
- Fe - Oxygen transport (Haemoglobin, haemocyanin) oxygen storage (myoglobin)
- Mn- Oxidation of  $H_2O_2$  to  $O_2$  (Photosynthesis II)
- Mo- Nitrogen fixation (Nitrogenase)
- Zn- Hydrolysis of peptide linkage (carboxy peptidase),  
Decarboxylation of oxalo acetic acid (oxaloacetate carboxylase)
- Cu- Oxidation of alcohol (alcohol dehydrogenase)
- Electron transfer (Blue copper protein)
- Dismutation of superoxide (Superoxide dismutase)
- Jahn-Teller effect is in the field of Vibronic interactions.
- EDTA is an hexadentate ligand.
- The number of microstates in term  $^1G$  is nine.
- In general the  $\pi$ - accepting ability of phosphine increases as the electro-negativity of the substituent increases.

- In haemoglobin iron is present in +2 oxidation state.
- Unlike d-d transition, f-f transitions do not change much with the change in ligand.
- *cis* -  $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$  is used in chemotherapy in cancer.
- The oxidation state of Iron in the complex hemoglobin is +2.
- Spin-orbit coupling of d-electron takes place when  $t_{2g}$  orbital's are asymmetrically filled.
- The self-indicating silica gel (impregnated with cobalt chloride) turns pink on absorbing moisture and becomes blue on heating. The pink and blue color is respectively due to  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  and  $[\text{CoCl}_4]^{-2}$  respectively.
- $\text{MnO}_4^-$  involves ligand to metal charge transfer (LMCT).
- The metal fragments  $d^n$ -  $\text{ML}_m$  is isolobal with CH is  $d^9$ -  $\text{ML}_3$ .
- $\text{V}(\text{CO})_6$  does not obey EAN and 18-electron rule.
- The oxidation state of iron in met-haemoglobin is +3.
- In trigonal bipyramidal complexes the two ligands lie on z-axes and three in xy-plane, somewhere in between the axes. In xy plane there are 4 electrons and on z-axes there is only one electron in  $d_{z^2}$  orbital.  

$$d_{xz} = d_{yz} < d_{xy} = d_{x^2-y^2} < d_{z^2}$$
- The total no. of Cu-O bonds present in the crystalline copper(II) acetate monohydrate are ten.
- $\text{V}(\text{CO})_6$  does not obey EAN rule.

## Multiple Choice Questions

- Q.1. The no. of absorption band observed in  $[\text{FeF}_6]^{-3}$  and  $[\text{CoF}_6]^{-3}$  respectively are,  
 (a) 1 and 3 (b) 0 and 1  
 (c) 0 and 3 (d) 3 and 1
- Q.2. The no. metal-metal bonds in  $[\text{W}_2(\text{OPh})_6]$  is:  
 (a) 1 (b) 2  
 (c) 3 (d) 4
- Q.3. The Optical isomerism is not shown by the complexes:  
 (a)  $[\text{Cr}(\text{ox})_3]^{-3}$  (b)  $[\text{Co}(\text{EDTA})]^{-}$   
 (c)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]$  (d)  $\text{trans-}[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$
- Q.4. The ground state term of  $\text{V}^{+3}$  ion is:  
 (a)  $^3\text{F}_2$  (b)  $^5\text{D}_0$   
 (c)  $^3\text{F}_4$  (d)  $^3\text{D}_{5/2}$
- Q.5. Amongst the following the strongest oxidizing anion is:  
 (a)  $\text{CrO}_4^{-2}$  (b)  $\text{VO}_4^{-3}$   
 (c)  $\text{FeO}_4^{-2}$  (d)  $\text{MnO}_4^{-2}$
- Q.6. Which of the following acts as a  $\pi$ -acid ligand?  
 (a)  $\text{F}^-$  (b)  $\text{O}^{-2}$   
 (c)  $\text{CO}$  (d)  $\text{NH}_3$
- Q.7. The oxidation state of molybdenum in  $[(\eta^7\text{-tropylium})\text{Mo}(\text{CO})_3]^+$  is :  
 (a) +2 (b) +1  
 (c) 0 (d) -1
- Q.8. Which of the following is a hexadentate ligand?  
 (a) Acetyl Acetonato (b) 1,10 phenanthroline  
 (c) Ethylene Diamine (d) Ethylene diamine tetraacetic acid
- Q.9. The dark purple colour of  $\text{KMnO}_4$  is due to:  
 (a) d-d transition (b) Ligand field transition  
 (c) Charge transfer transition (d)  $\sigma - \pi^*$  transition
- Q.10. The complex which exhibit lowest energy electronic absorption band is:  
 (a)  $[\text{NiCl}_4]^{-2}$  (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$   
 (c)  $[\text{Ni}(\text{CN})_4]^{-2}$  (d)  $\text{Ni}(\text{CO})_4$
- Q.11. The d- orbital will split under trigonal bipyramidal ligand field into:  
 (a) One level (b) Two level  
 (c) Three level (d) Four level
- Q.12. The Mulliken symbols for the spectroscopic states arising from the free-ion term F are:  
 (a)  $\text{T}_{2g} + \text{E}_g$  (b)  $\text{T}_{1g} + \text{T}_{2g} + \text{T}_{1u}$   
 (c)  $\text{T}_{1g} + \text{T}_{2g} + \text{A}_{2g}$  (d)  $\text{T}_{1g} + \text{A}_{1g} + \text{T}_{2g}$
- Q.13. Jahn-Teller effect is not observed in high spin complexes of.  
 (a)  $\text{d}^4$  (b)  $\text{d}^7$

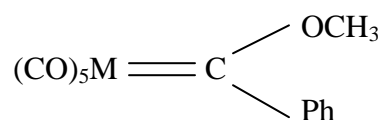
- (c)  $d^8$  (d)  $d^9$
- Q.14. For which of the following ion colour is NOT due to d-d transition?
- (a)  $\text{CrO}_4^{2-}$  (b)  $[\text{Cu}(\text{NH}_3)_4]^{+2}$   
 (c)  $[\text{Ti}(\text{H}_2\text{O})_6]^{+2}$  (d)  $\text{CoF}_6^{-3}$
- Q.15. The purple colour of iodine is due to:
- (a) d-d transition (b)  $\pi-\sigma^*$  transition  
 (c) Charge transfer transition (d)  $\pi^*-\sigma^*$  transition
- Q.16. Jahn-Teller effect is not observed in the high spin complexes of:
- (a)  $d^4$  (b)  $d^7$   
 (c)  $d^{10}$  (d)  $d^9$
- Q.17. Silica gel contains  $[\text{CoCl}_4]^{2-}$  as an indicator. When activated silica gel becomes dark blue while upon absorption of moisture, its color changes to pale pink. This is because:
- (a) Co(II) changes its coordination from tetrahedral to octahedral.  
 (b) Co(II) changes its oxidation state to Co(III).  
 (c) Tetrahedral crystal field splitting is NOT equal to octahedral field splitting.  
 (d) Co(II) forms kinetically labile CO(III) forms kinetically inert complexes
- Q.18. Among the following complexes, optical activity is possible in:
- (a)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]$  (b)  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)\text{Cl}]^+$   
 (c)  $[\text{Co}(\text{CN})_5\text{NC}]^-$  (d)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
- Q.19. For the complex ion  $[\text{Cu}(\text{NH}_3)_6]^{+2}$ , the number of possible d-d transitions will be:
- (a) 1 (b) 2  
 (c) 3 (d) 4
- Q.20. The compound which shows MLCT is:
- (a)  $\text{Ni}(\text{CO})_4$  (b)  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c)  $\text{HgO}$  (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$
- Q.21. Coordinated water molecules of Cd(II) complex can be successively replaced by  $\text{Br}^-$  finally to result in  $[\text{CdBr}_4]^{2-}$ . In this process the fourth equilibrium constant is observed which is higher than one because:
- (a) Equilibrium for the last step is always the highest.  
 (b) Three molecules of water are released during the fourth step.  
 (c) The aqua-Cd(II) species is octahedral.  
 (d) The  $\text{Br}^-$  anion replaces a neutral  $\text{H}_2\text{O}$  molecule from the coordination sphere.
- Q.22. The bands in the electronic spectrum of  $[\text{Cr}(\text{NH}_3)_6]^{+3}$  are due to the following transition:
- (A)  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  (B)  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  (C)  ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$
- Identify the correct statement about them:
- (a) Intensity of A is lowest (b) Intensity of C is lowest  
 (c) Intensities of A, B and C are similar (d) Intensities of B and C are similar.
- Q.23. The complexes  $[\text{Co}(\text{NH}_3)_3\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$  are example of
- (a) Linkage isomers (b) Ionization isomers  
 (c) Geometrical isomers (d) Co-ordination isomers

- Q.24. Jahn-Teller distortion of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  acts to:
- Raise symmetry.
  - Remove an electronic degeneracy.
  - Cause loss of  $\text{H}_2\text{O}$  ligand.
  - Promote a d-electron to an anti-bonding molecular orbital.
- Q.25. The pale colour of  $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$  is due to:
- Spin forbidden d-d transition
  - Metal to ligand charge transfer
  - Ligand to metal charge transfer
  - Inter ligand excitation
- Q.26. The experimental magnetic moment of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is  $2.3 \mu_B$  and is attributed to the:
- Spin only value of low spin Fe
  - Spin only value of high spin Fe
  - Low spin Fe with orbital contribution.
  - High spin Fe with orbital contribution.
- Q.27. The no. of possible isomers for  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  is (bpy = 2,2'-bipyridine)
- 2
  - 3
  - 4
  - 5
- Q.28. Ziese's salt is:
- $\text{K}^+[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$
  - $\text{K}_2[\text{PtCl}_3-\eta^1-\text{C}_3\text{H}_6]$
  - $\text{K}^+[\text{PtCl}_3-\eta^2-\text{C}_2\text{H}_4]^-$
  - $\text{K}^+[\text{PtCl}_3-\eta^2-\text{C}_3\text{H}_6]\text{Cl}^-$
- Q.29. The ground state term symbol of  $\text{Ni}^{+2}$  ion is:
- $^3\text{F}$
  - $^3\text{A}$
  - $^3\text{P}$
  - $^3\text{E}$
- Q.30. The possible J values for  $^3\text{D}$  term symbol are:
- 2
  - 3
  - 4
  - 5
- Q.31.  $\text{CrO}_3$  is bright in color due to:
- d-d transition
  - CT transition
  - both (a) and (b)
  - None of these
- Q.32. Complex in which organic ligand is having only  $\sigma$ - bond with metal is:
- $\text{W}(\text{CH}_3)$
  - $(\eta^5-\text{C}_5\text{H}_5)_2\text{Fe}$
  - $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$
  - $(\eta^6-\text{C}_6\text{H}_6)_2\text{Ru}$
- Q.33. Jahn-Teller effect is in the field of:
- Nuclear Physics
  - Vibronic interaction
  - Thermodynamics
  - Kinetic theory of gases
- Q.34. The lowest energy state of the  $1s^2 2s^1 3s^1$  configuration of Be is:
- $^1\text{S}_0$
  - $^1\text{D}_2$
  - $^3\text{S}_1$
  - $^3\text{P}_1$
- Q.35. The number of microstates in term  $^1\text{G}$  is:
- 9
  - 6
  - 7
  - 15

- Q.36. The complex compound used in the chemotherapy of cancer is:  
 (a) *cis* -  $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$  (b) *cis* -  $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_4]$   
 (c) *cis* -  $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$  (c) *trans* -  $[\text{Pt}^{\text{II}}(\text{NH}_3)_4\text{Cl}_2]$
- Q.37.  $[\text{Ni}(\text{CN})_4]^{-2}$  and  $[\text{NiCl}_4]^{-2}$  complex ions are:  
 (a) Both diamagnetic.  
 (b) Both paramagnetic.  
 (c) Diamagnetic and paramagnetic respectively.  
 (d) Anti-ferromagnetic and diamagnetic respectively.
- Q.38. In  $\text{TeCl}_4$ , the central atom tellurium involves:  
 (a)  $\text{sp}^3$  hybridisation (b)  $\text{sp}^3\text{d}$  hybridisation  
 (c)  $\text{sp}^3\text{d}^2$  hybridisation (d)  $\text{sp}^3\text{d}^3$  hybridisation
- Q.39. Unlike d-d transition, f-f transitions  
 (a) Do not change much with the change in ligand.  
 (b) Change significantly with change in ligand.  
 (c) Appear at low energies, i.e. at the near-IR region.  
 (d) Appears as broad band.
- Q.40. Which of the following show charge transfer band?  
 (a) Lanthanum Nitrates (b) Ceric Ammonium Nitrate  
 (c) Manganese(II) acetate (d) Copper(II) sulphate pentahydrate
- Q.41. Hemoglobin, a complex containing iron, is a constituent of blood. The oxidation state of Iron in the complex is:  
 (a) 0 (b) +1  
 (c) +2 (d) +3
- Q.42. According to crystal field theory,  $\text{Ni}^{+2}$  can have two unpaired electrons in:  
 (a) Octahedral geometry only (b) Square-planar geometry only  
 (c) Tetrahedral geometry only  
 (d) Both octahedral and tetrahedral geometries
- Q.43. In trigonal bipyramidal crystal field, the d- orbital with the highest energy is :  
 (a)  $d_{xy}$  (b)  $d_{yz}$   
 (c)  $d_{x^2-y^2}$  (d)  $d_{z^2}$
- Q.44. The electronic transition responsible for the colour of the transition metal ions is:  
 (a)  $d_\pi \rightarrow d_\sigma$  (b)  $d_\pi \rightarrow d_{\sigma^*}$   
 (c)  $d_\pi \rightarrow d_{\pi^*}$  (d)  $d_\sigma \rightarrow d_{\pi^*}$
- Q.45. The number of microstates for  $d^5$  electronic configuration is:  
 (a)  $21 \times 6^3$  (b)  $14 \times 6^3$   
 (c)  $7 \times 6^2$  (d)  $28 \times 6^3$
- Q.46. The self-indicating silica gel (impregnated with cobalt chloride) turns pink on absorbing moisture and becomes blue on heating. The pink and blue color is respectively due to  
 (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  and  $[\text{CoCl}_4]^{-2}$   
 (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  and  $\text{Co}_2\text{O}_3$



- (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{+3}$   
 (d)  $\text{Co}^{+2}$  and  $\text{Co}^{+3}$
- Q.47. In the solid state the  $\text{CuCl}_5^{-3}$  ion has two types of bonds. These are  
 (a) Three long and two short (b) Two long and three short  
 (c) One long and four short (d) Four long and one short.
- Q.48. For the metal olefin complex  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$  and  $[\text{PtCl}_3(\text{C}_2\text{F}_4)]^-$  the correct statement is :  
 (a) C-C bond length is same in both (i) and (ii)  
 (b) C-C bond length in (i) is smaller than (ii)  
 (c) C-C bond length in (i) is larger compared to that of (ii)  
 (d) A metallocycle is formed in each complex.
- Q.49. The octahedral ion which shows both facial and meridional isomers are:  
 (a) Triglycinatocobalt(III) (b) Tris ethylenediamine cobalt(III)  
 (c) Dichloro diglycinatocobalt(III) (d) Trioxalatocobaltate(III).
- Q.50. The existence of two different coloured complexes of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  is due to:  
 (a) Optical isomerism (b) Linkage isomerism  
 (c) Geometrical isomerism (d) Coordination isomerism
- Q.51.  $[\text{NiX}_4]^{-2}$ ,  $[\text{CoX}_4]^{-2}$  and  $[\text{MnX}_4]^{-2}$  are (where X is a halogen):  
 (a) Coloured (b) Coloured due to  $\text{L} \rightarrow \text{MCT}$   
 (c) Colourless (d) Coloured due to  $\text{M} \rightarrow \text{LCT}$
- Q.52. Which of the following has zero field stabilization energy in octahedral complexes?  
 (a)  $\text{Fe}^{+3}$  (low spin) (b)  $\text{Fe}^{+3}$  (high spin)  
 (c)  $\text{Cr}^{+3}$  (high spin) (d)  $\text{Co}^{+2}$  (low spin)
- Q.53. The molecule



Obey 18-electron rule. The two 'M' satisfying the condition are:

- (a) Cr,  $\text{Re}^+$  (b) Mo, V  
 (c) V,  $\text{Re}^+$  (d) Cr, V
- Q.54. The number of possible isomers for the square planar mononuclear complex  $[(\text{NH}_3)_2\text{M}(\text{CN})_2]$  of a metal M is :  
 (a) 2 (b) 4  
 (c) 6 (d) 3
- Q.55. The ligand that exhibits linkage isomerism in its transition metal complexes is:  
 (a)  $[\text{SO}_3]^{-2}$  (b)  $[\text{SO}_4]^{-2}$   
 (c)  $[\text{NO}_3]^{-1}$  (d)  $[\text{ClO}_4]^-$
- Q.56. Which of following metal fragments  $d^n - \text{ML}_m$  is isolobal with CH?  
 (a)  $d^7 - \text{ML}_5$  (b)  $d^9 - \text{ML}_3$   
 (c)  $d^8 - \text{ML}_4$  (d)  $d^5 - \text{ML}_6$

- Q.57. What is the IUPAC name of  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)\text{Cl}(\text{CN})]$  compound?
- Chloro cyano nitro triamine cobalt (III)
  - Triamine chloro cyano nitro cobalt (III)
  - Cyano chloro nitro triamine cobalt (III)
  - Nitro chloro cyano triamine cobalt (III)
- Q.58. The asymmetric nature of visible absorption band of  $[\text{Ti}(\text{H}_2\text{O})_6]^{+2}$  is due to:
- Laporte's allowed transition
  - Laporte's forbidden transition
  - Dynamic Jahn-Teller distortion
  - Intensity stealing transition
- Q.59. The number of stereo isomers of  $\text{trans-}[\text{CoCl}_2(\text{triethylenetetramine})]\text{Cl}$  are:
- 1
  - 2
  - 3
  - 4
- Q.60. The number of possible isomers of  $[\text{Ru}(\text{PPh}_3)_2(\text{acac})_2]$  (acac=acetylacetonate) is:
- 2
  - 3
  - 4
  - 5
- Q.61. Jahn-Teller distortion affects the geometry of
- $[\text{Cu}(\text{NH}_3)_4]^{+2}$
  - $[\text{MnCl}_4]^{-2}$
  - $[\text{Ni}(\text{NH}_3)_4]^{+2}$
  - None of these
- Q.62. The correct d- electron configuration showing spin-orbit coupling is:
- $t_{2g}^4 e_g^2$
  - $t_{2g}^6 e_g^0$
  - $t_{2g}^4 e_g^0$
  - $t_{2g}^3 e_g^2$
- Q.63. The correct spinel structure of  $\text{Co}_3\text{O}_4$  is:
- $(\text{Co}^{+2})_t(2\text{Co}^{+3})_{\text{oct}}\text{O}_4$
  - $(\text{Co}^{+2})_t(2\text{Co}^{+3}\text{Co}^{+3})_{\text{oct}}\text{O}_4$
  - $(\text{Co}^{+2}\text{Co}^{+3})_t(\text{Co}^{+3})_{\text{oct}}\text{O}_4$
  - $(2\text{Co}^{+3})_t(\text{Co}^{+2})_{\text{oct}}\text{O}_4$
- Q.64. The metal ion which is most likely to show the low spin-high spin equilibrium in its complexes has the electronic configuration:
- $d^3$
  - $d^4$
  - $d^6$
  - $d^8$
- Q.65. The effective magnetic moment is maximum for:
- $\text{K}_4\text{Mn}(\text{CN})_6$
  - $\text{K}_2\text{MnO}_4$
  - $\text{K}_2\text{MnCl}_4$
  - $\text{KMnO}_4$
- Q.66. The purple color of  $\text{KMnO}_4$  is due to the transition:
- CT ( $L \rightarrow M$ )
  - CT ( $M \rightarrow L$ )
  - p-d transition
  - d-d transition
- Q.67. The substitution of Cp group with nitric oxide is the easiest for:
- $\eta^2 - \text{Cp}_2\text{Fe}$
  - $\eta^2 - \text{Cp}_2\text{CoCl}$
  - $\eta^2 - \text{Cp}_2\text{Ni}$
  - $\eta^2 - \text{Cp}_2\text{Co}$
- Q.68. The oxidation state of iron in met- haemoglobin is:
- +3
  - +2
  - +4
  - 0
- Q.69. The electric dipole allowed transition in  $d^2$  atomic system is
- $^3F \rightarrow ^1D$
  - $^3F \rightarrow ^1P$
  - $^3F \rightarrow ^3D$
  - $^3F \rightarrow ^3P$

- Q.70. For a valence electron in a  $^2D$  state, the possible J-values are:  
 (a)  $5/2$  and  $1/2$  (b)  $5/2$  and  $3/2$   
 (c)  $3/2$  and  $1/2$  (d)  $3/2$  and  $0$
- Q.71. "Any non-linear molecular system in a degenerate electronic state will undergo some kind of distortion which will lower its symmetry, thereby removing degeneracy".  
 This statement is:  
 (a) Crystal field effect (b) Jahn-Teller effect  
 (c) Ligand-field effect (d) Tetrahedral distortion effect
- Q.72. Among the following the strongest oxidizing agent is:  
 (a)  $[WO_4]^{-2}$  (b)  $[CrO_4]^{-2}$   
 (c)  $[MoO_4]^{-2}$  (d)  $[ReO_4]^{-1}$
- Q.73. The total no. of Cu-O bonds present in the crystalline copper(II) acetate monohydrate are:  
 (a) 10 (b) 6  
 (c) 8 (d) 4
- Q.74. The magnetic property of  $Hg[Co(NCS)_4]$  at  $25^\circ C$  is:  
 (a) Diamagnetic (b) Paramagnetic  
 (c) Ferromagnetic (d) Anti-ferromagnetic
- Q.75. The spin-only ( $\mu_s$ ) and spin plus orbital ( $\mu_{s+L}$ ) magnetic moments of  $[CrCl_6]^{-3}$  are  
 (a) 3.87 BM and 5.20 BM (b) 2.84 BM and 5.20 BM  
 (c) 3.87 BM and 6.34 BM (d) 3.87 BM and 6.34 BM
- Q.76. The lowest energy d-d transition in Cr (+3) a complex varies in the order:  
 (a)  $CrCl_6^{-6} < Cr(H_2O)_6^{+3} < Cr(en)_3^{+3} < Cr(CN)_6^{-3}$   
 (b)  $CrCl_6^{-6} < Cr(en)_3^{+3} < Cr(H_2O)_6^{+3} < Cr(CN)_6^{-3}$   
 (c)  $Cr(CN)_6^{-3} < CrCl_6^{-6} < Cr(H_2O)_6^{+3} < Cr(en)_3^{+3}$   
 (d)  $Cr(H_2O)_6^{+3} < Cr(en)_3^{+3} < CrCl_6^{-6} < Cr(CN)_6^{-3}$
- Q.77. The light pink color of  $[Co(H_2O)_6]^{+2}$  and the deep blue color of  $[CoCl_4]^{-2}$  are due to:  
 (a) MLCT transition in first and d-d transition in second.  
 (b) LMCT transition in both.  
 (c) d-d transition in both.  
 (d) d-d transition in first and MLCT transition in second.
- Q.78. In  $[Mo_2(S_2)_6]^{-2}$  cluster the no. of bridging  $S_2^{-2}$  and coordination no. of Mo respectively are:  
 (a) 2 and 8 (b) 2 and 6  
 (c) 1 and 8 (d) 1 and 6
- Q.79. The spin-only magnetic moment and the spectroscopic ground state term symbol of manganese centre in  $[MnF_6]^{-3}$  are  
 (a) 4.9 BM and  $^5D$  (b) 3.9 BM and  $^4F$   
 (c) 3.9 BM and  $^3D$  (d) 4.9 BM and  $^3F$
- Q.80.  $[CoCl_4]^{-2}$  shows a deep blue colour because of :  
 (a) Metal to ligand CT transition  
 (b) Ligand to metal CT transition

- (c) Spin allowed and Laporte forbidden d-d transition  
 (d) Spin allowed and Laporte allowed d-d transition
- Q.81. Among the complexes  $K_4[Cr(CN)_6]$  (A),  $K_4[Fe(CN)_6]$  (B),  $K_3[Co(CN)_6]$  (C),  $K_4[Mn(CN)_6]$  (D), Jahn-Teller distortion is shown by  
 (a) A, B and C (b) B, C and D  
 (c) A and D (d) B and C
- Q.82. Which of the following does not obey EAN rule?  
 (a)  $Fe(CO)_5$  (b)  $V(CO)_6$   
 (c)  $K_4[Fe(CN)_6]$  (d)  $Mn_2(CO)_{10}$
- Q.83. The no. of spin-allowed ligand field transitions for Ni(II) complexes with  $^3A_{2g}$  ground state are:  
 (a) 2 (b) 3  
 (c) 1 (d) 4
- Q.84. The complex  $[Fe(phen)_2(NCS)_2]$  (phen = 1,10 phenanthroline) shows spin cross-over behavior. CFSE and  $\mu_{eff}$  at 250 and 150 K, respectively are:  
 (a)  $0.4 \Delta_o$ , 4.90 BM and  $2.4 \Delta_o$ , 0.00 BM  
 (b)  $2.4 \Delta_o$ , 2.90 BM and  $0.4 \Delta_o$ , 1.77 BM  
 (c)  $2.4 \Delta_o$ , 0.00 BM and  $0.4 \Delta_o$ , 4.90 BM  
 (d)  $1.2 \Delta_o$ , 4.90 BM and  $2.4 \Delta_o$ , 0.00 BM
- Q.85. Match the action of  $H_2O_2$  in aqueous medium given in column A with the oxidation/reduction listed in column B

A: action of $H_2O_2$	B: type of reaction
I: Oxidation in acid	(A) $[Fe(CN)_6]^{-3} \rightarrow [Fe(CN)_6]^{-4}$
II: Oxidation in base	(B) $[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$
III: Reduction in acid	(C) $MnO_4^- \rightarrow Mn^{+2}$
IV: Reduction in base	(D) $Mn^{+4} \rightarrow Mn^{+2}$

The correct answer is:

- (a) I - (A), II - (B), III - (C), IV - (D)  
 (b) I - (B), II - (D), III - (C), IV - (A)  
 (c) I - (C), II - (B), III - (D), IV - (A)  
 (d) I - (D), II - (A), III - (C), IV - (B)

**Answers**

1 - (b)	2- (c)	3- (d)	4- (a)	5- (c)	6- (c)
7 - (c)	8 - (d)	9 - (c)	10- (a)	11 - (c)	12 - (c)
13- (c)	14- (a)	15- (b)	16- (c)	17- (a)	18- (a)
19- (a)	20- (a)	21- (b)	22- (b)	23- (a)	24- (b)
25- (a)	26- (c)	27- (b)	28- (c)	29- (a)	30- (b)
31- (b)	32- (a)	33- (b)	34- (c)	35- (a)	36- (c)
37- (c)	38- (b)	39- (a)	40- (b)	41- (c)	42- (d)
43- (d)	44- (b)	45- (c)	46- (a)	47- (b)	48- (a)
49- (a)	50- (c)	51- (a)	52- (b)	53- (a)	54- (c)
55- (a)	56- (b)	57- (b)	58- (b)	59- (c)	60- (b)
61- (a)	62- (c)	63- (a)	64- (c)	65- (c)	66- (a)
67- (c)	68- (a)	69- (c)	70- (b)	71- (b)	72- (b)
73- (a)	74- (a)	75- (a)	76- (a)	77- (c)	78- (a)
79- (a)	80- (c)	81- (c)	82- (b)	83- (b)	84- (a)
85- (c)					

## Chapter 6

### Metal Carbonyls

(Contributed by: Dr. Dinkar Malik, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- In metal carbonyls metal generally exhibit zero oxidation state and metal carbonyls are generally covalent in nature.
- The no. of metal-metal bonds in dimers  $[\text{CpFe}(\text{CO})(\text{NO})]_2$  and  $[\text{CpMo}(\text{CO})_3]_2$  are zero and one respectively.
- In metal carbonyls  $\sigma$ -bond as well as  $\pi$ -bonds are formed between metal and carbon atoms.
- Wilkinson's catalyst is used for hydrogenation.
- The tendency to retain cluster of metal atoms will predominate in those metals which have large energies of atomization.
- Wilkinson's catalyst is  $(\text{Ph}_3\text{P})_3\text{RhCl}$ .
- Linear NO is neutral and it donates 3 electrons, bent NO is also neutral but it donates 1 electron.

$\eta^3$ -NO	-	linear
$\eta^1$ -NO	-	bent

1- Polyhedral electron count (PEC) =  $(\text{TVE} - n \times 12) / 2$

$n$  = no. of metal atoms.

TVE = total valence electron

$n-1$  = super hyper closo

$n$  = hyper closo

$n + 1$  = closo

$n + 2$  = nido

$n + 3$  = arachano

$n + 4$  = hypo

$n + 5$  = conjuncto

- Except  $\text{Fe}(\text{CO})_5$  and  $\text{V}(\text{CO})_6$  all other mononuclear carbonyls are colorless.
- Among mononuclear carbonyl  $\text{Fe}(\text{CO})_5$  is yellow and  $\text{V}(\text{CO})_6$  is black.
- CO, NO,  $\text{CN}^-$  etc. behaves as  $\sigma$ -donor as well as  $\pi$ -acceptor ligand.
- Ziegler-Natta Catalyst is  $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ .
- Wilkinson's Catalyst is  $[\text{RhCl}(\text{PPh}_3)_3]$  and it contains 16 valence electrons.
- $\text{Fe}(\text{CO})_5 + 3\text{NaOH} \longrightarrow \text{Na}[\text{HFe}(\text{CO})_4] + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
- $\text{V}(\text{CO})_6$  is paramagnetic due to the presence of unpaired electrons (17 electrons in valence shell).
- Favorable conditions for a ligand to be  $\pi$ -acceptor are availability of vacant d-orbital, low oxidation state of metal and high electron density of metal.

- In solid form  $\text{Co}_2(\text{CO})_8$  has two bridging CO groups. While in solution form it has no bridging CO groups, solid form converts into liquid form by heating.
- $\text{Fe}_2(\text{CO})_9 + 4\text{Na} \longrightarrow 2\text{Na}_2[\text{Fe}(\text{CO})_4] + \text{CO}$
- $[\text{IrCl}(\text{Ph}_3\text{P})_3] + \text{Cl}_2 \longrightarrow [\text{IrCl}_3(\text{Ph}_3\text{P})_3]$
- $\text{Co}_6(\text{CO})_{16}$ ,  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{Ir}_6(\text{CO})_{16}$  are paramagnetic in nature and do not follow 18 electron rule.
- A metal cluster may be defined as a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms.
- Poly nuclear carbonyls, nitrolyls and related compounds exist in lower oxidation states
- In trigonal bipyramidal complexes the two ligands lie on z- axis and there is xy plane somewhere between the axis. In xy plane there are four electrons and on z-axis there is only one electron in  $d_{z^2}$  orbital:

$$d_{xz} = d_{yz} < d_{xy} = d_{x^2-y^2} < d_{z^2}$$

- There will be no distortion if  $e_g$  and  $t_{2g}$  or both are symmetrical.
- $\text{Fe}(\text{CO})_5 \xrightarrow{\text{U.V. Light}} \text{Fe}_2(\text{CO})_9 + \text{CO}$
- $\text{Fe}(\text{CO})_5 \xrightarrow{140^\circ \text{C}} \text{Fe} + 5\text{CO}$
- $\text{Fe}(\text{CO})_5 \xrightarrow{70^\circ \text{C}} \text{Fe}_2(\text{CO})_9 + \text{Fe}_3(\text{CO})_{12}$
- In  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  all the CO groups are Terminal.
- Jahn Teller distortion will be large if  $e_g$  is unsymmetrical however Jahn Teller distortion will be small if  $t_{2g}$  is unsymmetrical.

## Multiple Choice Questions

- Q.1. The no. of metal-metal bonds in dimers  $[\text{CpFe}(\text{CO})(\text{NO})]_2$  and  $[\text{CpMo}(\text{CO})_3]_2$  respectively are:  
 (a) 2 and 2 (b) 2 and 3  
 (c) 1 and 2 (d) 0 and 1
- Q.2. Which of the following has NOT three bridging carbonyl group?  
 (a)  $\text{Fe}_2(\text{CO})_9$  (b)  $\text{Co}_4(\text{CO})_{12}$   
 (c)  $\text{Rh}_4(\text{CO})_{12}$  (d)  $\text{Fe}_3(\text{CO})_{12}$
- Q.3. An example of species having quadrupole bond is :  
 (a)  $\text{Mn}_2(\text{CO})_9$  (b)  $\text{Cr}_2\text{O}_7^{2-}$   
 (c)  $[\text{Re}_2\text{Cl}_8]^{2-}$  (d)  $\text{Hg}_2(\text{CH}_3\text{COO})_2$
- Q.4. (A)  $[\text{Cp}_2\text{Zr}(\text{CO})(\text{Cl})]^+$  (B)  $[\text{Cp}_2\text{Zr}(\text{CO})_2]$   
 Which of the following statement is correct?  
 (a)  $\nu_{\text{C-O}}$  of A is greater than that of B  
 (b)  $\nu_{\text{C-O}}$  of B is greater than that of A  
 (c)  $\nu_{\text{C-O}}$  of A is equal to  $\nu_{\text{C-O}}$  of B  
 (d) The metal Zr having +4 oxidation state in (A) whereas in (B) Zr is present in Zero oxidation state.
- Q.5. Which of the following complex has highest  $\nu_{\text{C-O}}$  stretching frequency?  
 (a)  $\text{Fe}(\text{CO})_4(\text{PF}_3)$  (b)  $\text{Fe}(\text{CO})_4(\text{PCl}_3)$   
 (c)  $\text{Fe}(\text{CO})_4(\text{PMe}_3)$  (d)  $\text{Fe}(\text{CO})_4\text{P}(\text{OMe})_3$
- Q.6. On reducing  $\text{Fe}_3(\text{CO})_{12}$  with an excess of Na, a carbonylate ion is formed. The Iron is isoelectronic with:  
 (a)  $[\text{Mn}(\text{CO})_5]^-$  (b)  $[\text{Ni}(\text{CO})_4]$   
 (c)  $[\text{Mn}(\text{CO})_5]^-$  (d)  $[\text{V}(\text{CO})_6]^-$
- Q.7. Which of the following oxidation state stabilizes the metal atom in carbonyl compounds?  
 (a) 1 (b) 2  
 (c) 3 (d) 0
- Q.8. Which of the following statement is false about ferrocene?  
 (a) It obeys 18-electron rule. (b) It is diamagnetic.  
 (c) It is an Orange solid. (d) It resists electrophilic reaction.
- Q.9. Arrange the following in increasing order of  $\nu_{\text{C-O}}$  stretching frequency:  
 (I)  $[\text{Mo}(\text{CO})_3(\text{PF}_3)_3]$  (II)  $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$   
 (III)  $[\text{Mo}(\text{CO})_3\text{P}\{\text{Cl}(\text{Ph})_2\}_3]$  (IV)  $[\text{Mo}(\text{CO})_3(\text{PMe}_3)_3]$   
 (a)  $\text{IV} < \text{III} < \text{II} < \text{I}$  (b)  $\text{III} < \text{IV} < \text{II} < \text{I}$   
 (c)  $\text{I} < \text{II} < \text{III} < \text{IV}$  (d)  $\text{II} < \text{III} < \text{I} < \text{IV}$
- Q.10. The complex having highest  $\nu_{\text{M-C}}$  frequency:  
 (a)  $\text{Mo}(\text{CO})_6$  (b)  $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$



- (c)  $\text{Mo(CO)}_4(\text{P(OMe)}_3)_2$  (d)  $\text{Mo(CO)}_4(\text{PF}_3)_2$
- Q.11. The cluster having arachano type structure:
- (a)  $[\text{Os}_3(\text{CO})_{16}]$  (b)  $[\text{Os}_3(\text{CO})_{12}]$   
 (c)  $[\text{Ir}_4(\text{CO})_{12}]$  (d)  $[\text{Rh}_6(\text{CO})_{16}]$
- Q.12. Which of the following statement is incorrect about metal carbonyls?
- (a) In metal carbonyls metal present in zero oxidation state.  
 (b) In metal carbonyls  $\sigma$ -bond as well as  $\pi$ -bonds are formed between metal and carbon atoms.  
 (c) In metal carbonyl CO act as a neutral ligand.  
 (d) Only  $\sigma$ -bond is formed between metal atom and carbon atom.
- Q.13. Which of the following has lowest stretching frequency?
- (a)  $\text{V(CO)}_6^+$  (b)  $\text{Co(CO)}_4^-$   
 (c)  $\text{Ni(CO)}_4$  (d)  $\text{Fe(CO)}_4^{-2}$
- Q.14. Wilkinson's catalyst is used for:
- (a) Hydrogenation (b) Epoxidation  
 (c) Polymerization (d) Metathesis reaction
- Q.15. Which of the following is most easily reduced?
- (a)  $\text{V(CO)}_6$  (b)  $\text{Cr(CO)}_6$   
 (c)  $\text{Fe(CO)}_5$  (d)  $\text{Ni(CO)}_4$
- Q.16. Reaction of  $\text{Fe(CO)}_5$  with  $\text{OH}^-$  leads to a complex A which on oxidation with  $\text{MnO}_2$  gives B. Compound A and B respectively are:
- (a)  $[\text{HFe(CO)}_4]^-$  and  $\text{Fe}_3(\text{CO})_{12}$  (b)  $[\text{Fe(CO)}_5(\text{OH})]^-$  and  $\text{Fe}_2(\text{CO})_9$   
 (c)  $[\text{Fe(CO)}_4]^{-2}$  and  $\text{Mn}_2(\text{CO})_{10}$  (d)  $[\text{HFe(CO)}_4]^-$  and  $\text{Fe}_2\text{O}_3$
- Q.17. Which of the following metal carbonyls cannot be formed by the direct combination with CO ?
- (a)  $\text{Cr(CO)}_6$  (b)  $\text{Mn}_2(\text{CO})_{10}$   
 (c)  $\text{Fe(CO)}_5$  (d)  $\text{Co}_2(\text{CO})_8$
- Q.18. Wilkinson's catalyst is:
- (a)  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (b)  $(\text{Ph}_3\text{P})\text{RhCl}$   
 (c)  $\text{Ph}_3\text{P}_3\text{RhCl}$  (d)  $(\text{Ph}_3\text{P})_2\text{RhCl}_2$
- Q.19. Which of the following IR frequencies is the closest to that of the triply bridged CO group?
- (a)  $1700\text{ cm}^{-1}$  (b)  $1810\text{ cm}^{-1}$   
 (c)  $1920\text{ cm}^{-1}$  (d)  $2140\text{ cm}^{-1}$
- Q.20. Which of the following does not obey 18  $e^-$  rules?
- (a)  $\text{Cr(CO)}_6$  (b)  $\text{Mn}_2(\text{CO})_{10}$   
 (c)  $\text{Fe(CO)}_5$  (d)  $\text{V(CO)}_6$
- Q.21. For the reaction,  
 $\text{trans- [IrCl(CO)(PPh}_3)_2] + \text{Cl}_2 \longrightarrow \text{trans- [IrCl}_3(\text{CO})(\text{PPh}_3)_2]$ ,  
 the correct observations:

- (a)  $\nu_{\text{CO}}(\text{product}) > \nu_{\text{CO}}(\text{reactant})$  (b)  $\nu_{\text{CO}}(\text{product}) < \nu_{\text{CO}}(\text{reactant})$   
 (c)  $\nu_{\text{CO}}(\text{product}) = \nu_{\text{CO}}(\text{reactant})$  (d)  $\nu_{\text{CO}}(\text{product}) = \nu_{\text{CO}}(\text{Free CO})$
- Q.22. In the reaction,  
 $4\text{C}_6\text{H}_5\text{MgBr} + \text{CrCl}_3 + 2\text{CO} \longrightarrow \text{A}(\text{unstable}) \xrightarrow{(\text{H}^+)} \text{Cr}(\text{CO})_6 + 2\text{Cr}^{+3} + 12\text{C}_6\text{H}_5^- + 3\text{H}_2$   
 The unstable intermediate formed is:  
 (a)  $\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5)_4$  (b)  $\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_5)_3$   
 (c)  $\text{Cr}(\text{CO})_4(\text{C}_6\text{H}_5)_2$  (d)  $\text{Cr}(\text{CO})(\text{C}_6\text{H}_5)_5$
- Q.23. Which of the following compounds show normal spinel structure?  
 (a)  $\text{NaCr}_2\text{O}_4$  (b)  $\text{ZnO}$   
 (c)  $\text{Fe}_3\text{O}_4$  (d)  $\text{Fe}(\text{CO})_5$
- Q.24. Metal-Metal quadruple bonds are well known for metal:  
 (a) Ni (b) Co  
 (c) Fe (d) Re
- Q.25. The no. of Metal-Metal bonds present in  $\text{Ir}_4(\text{CO})_{12}$  are:  
 (a) 4 (b) 5  
 (c) 6 (d) 8
- Q.26. Na in liq.  $\text{NH}_3$  reacts with  $\text{Fe}_2(\text{CO})_9$  to give:  
 (a)  $[\text{Fe}(\text{CO})_5]$  (b)  $[\text{HFe}(\text{CO})_4]^-$   
 (c)  $[\text{H}_2\text{Fe}(\text{CO})_4]^-$  (d)  $[\text{Fe}(\text{CO})_4]^{-2}$
- Q.27. The correct statement regarding terminal/ bridging CO groups in solid  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  is:  
 (a) Both have equal no. of bridging CO groups.  
 (b) Number of bridging CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 4.  
 (c) The no. of terminal CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 8.  
 (d) The no. bridging CO groups in  $\text{Ir}_4(\text{CO})_{12}$  is 0.
- Q.28. Which of the following is paramagnetic in nature?  
 (a)  $\text{Cr}(\text{CO})_6$  (b)  $\text{V}(\text{CO})_6$   
 (c)  $\text{Fe}(\text{CO})_5$  (d)  $\text{Ni}(\text{CO})_4$
- Q.29. Regarding the catalytic cycle of hydrogenation of alkenes involving  $(\text{Ph}_3\text{P})_3\text{RhCl}$  as the catalyst, the correct statements is:  
 (a) Only 18-electron Rh complex is involved.  
 (b) 14-, 16- and 18- electron Rh complexes are involved.  
 (c) 14- and 16- electron Rh complexes are involved.  
 (d) 16- and 18- electron Rh complexes are involved.
- Q.30. The value of x in  $\text{Fe}_3(\text{CO})_x$  is:  
 (a) 8 (b) 9  
 (c) 10 (d) 12
- Q.31. Mention the incorrect statement about poly nuclear carbonyls:  
 (a) They have the general formula  $\text{M}_x(\text{CO})_y$ .  
 (b) These are generally insoluble in organic solvent.  
 (c) They decompose at or below their melting point.

- (d) These carbonyls are more volatile than the others.
- Q.32.  $[\text{Co}(\text{CO})_4]$  is isolobal with:
- (a)  $\text{CH}_4$  (b)  $\text{CH}_3$   
(c)  $\text{CH}_2$  (d)  $\text{CH}$
- Q.33. The final product of the reaction  $[\text{Mn}(\text{CO})_6] + \text{MeLi} \rightarrow$  is:
- (a)  $[\text{Mn}(\text{CO})_6]^+\text{Me}^-$  (b)  $[\text{Mn}(\text{CO})_5\text{Me}]$   
(c)  $[\text{Mn}(\text{CO})_6]$  (d)  $[(\text{MeCO})\text{Mn}(\text{CO})_5]$
- Q.34. The oxidative addition and reductive elimination are favored by:
- (a) Electron rich metal centre.  
(b) Electron deficient metal centre.  
(c) Electron deficient and electron rich metal centers respectively.  
(d) Electron rich and electron deficient metal centers respectively.
- Q.35. The hapticities 'x' and 'y' of the arenes moieties in the diamagnetic complex  $[(\eta^x\text{-C}_6\text{H}_6)\text{Ru}(\eta^y\text{-C}_6\text{H}_6)]$  are:
- (a) 6 and 6 (b) 4 and 4  
(c) 4 and 6 (d) 6 and 2
- Q.36. Arrange the following in increasing order of CO stretching frequencies :
- I.  $\text{Cr}(\text{CO})_6$  II.  $[\text{V}(\text{CO})_6]^-$  III.  $[\text{Mo}(\text{CO})_6]^+$  IV. CO
- (a)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (b)  $\text{II} < \text{I} < \text{III} < \text{IV}$   
(c)  $\text{IV} < \text{I} < \text{II} < \text{III}$  (d)  $\text{I} < \text{III} < \text{IV} < \text{II}$
- Q.37. What are the favorable conditions for a ligand to be pi-acceptor?
- (a) The ligand must have vacant orbital.  
(b) The metal atom should be of low oxidation state.  
(c) The electron density should be high on metal atom.  
(d) All are correct.
- Q.38. Intense band generally observed for a carbonyl group in the IR spectrum is due to:
- (a) The force constant of CO bond is large.  
(b) The force constant of CO bond is small.  
(c) There is no change in dipole moment for CO bond stretching.  
(d) The dipole moment changes due to CO bond stretching is large.
- Q.39. The product of the reaction of propene, CO and  $\text{H}_2$  in presence of  $\text{Co}_2(\text{CO})_8$  is:
- (a) Butanoic acid (b) Butanal  
(c) 2-butanone (d) Methyl propanoate
- Q.40. Among the metals Mn, Fe, Co and Ni the one those would react in its native form directly with CO giving metal carbonyl compound are:
- (a) Co and Mn (b) Mn and Fe  
(c) Fe and Ni (d) Ni and Co
- Q.41. Carbonylate ions are formed by the action of:
- (a) Reaction of Lewis acid such as  $\text{AlCl}_3$  with CO and carbonyl halide.  
(b) Reaction of Halogen with  $\text{Fe}(\text{CO})_5$ .

- (c) Reaction of alkali with simple Carbonyl.  
 (d) By reduction of carbonyls with alkali metals.
- Q.42. Total number of vertices in metal clusters  $[\text{Ru}_6(\text{C})(\text{CO})_{17}]$ ,  $[\text{Os}_5(\text{C})(\text{CO})_{15}]$  and  $[\text{Ru}_5(\text{C})(\text{CO})_{16}]$  are 6, 5 and 5 respectively. The predicted structures of these complexes respectively are:  
 (a) Closo, nido and nido (b) Closo, nido and arachano  
 (c) Arachano, closo and nido (d) Arachano, nido and closo
- Q.43. Which of the following is an example of poly nuclear carbonyl?  
 (a)  $\text{Cr}(\text{CO})_6$  (b)  $\text{Fe}(\text{CO})_5$   
 (c)  $\text{W}(\text{CO})_6$  (d)  $\text{Fe}_2(\text{CO})_9$
- Q.44. The no. of Metal-Metal bonds in the dimers,  $[\text{CpFe}(\text{CO})(\text{NO})]_2$  and  $[\text{CpMo}(\text{CO})_3]_2$  respectively are  
 (a) 2 and 2 (b) 2 and 3  
 (c) 1 and 2 (d) 0 and 1
- Q.45. In the hydroformylation reaction, the intermediate  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Co}(\text{CO})_4$ :  
 (a) Forms acyl intermediate  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Co}(\text{CO})_3$   
 (b) Forms an adduct with an olefin reagent.  
 (c) Reacts with  $\text{H}_2$   
 (d) Eliminates propane.
- Q.46. Oxidation occurs very easily in case of:  
 (a)  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{Fe}$  (b)  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{Co}$   
 (c)  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{Ru}$  (d)  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{Co}^+$
- Q.47. The color of  $\text{Fe}(\text{CO})_5$  is:  
 (a) White (b) Black  
 (c) Yellow (d) Brown
- Q.48. The no. of anti bonding electrons in NO and CO according to molecular orbital theory are:  
 (a) 1, 0 (b) 2, 2  
 (c) 3, 2 (d) 2, 3
- Q.49. The no. of terminal CO groups present in  $\text{Fe}_2(\text{CO})_9$  is  
 (a) 2 (b) 5  
 (c) 6 (d) 3
- Q.50. What are the oxidation states of metal ion in the following compounds?  
 1.  $\text{PdCl}_2$  2.  $\text{Pd}(\text{PPh}_3)_4$  3.  $\text{Pd}(\text{OAc})_2$  4.  $\text{Pd}(\text{Ar})\text{Br}$   
 (a) 2, 4, 2, 2, (b) 2, 0, 2, 1  
 (c) 2, 0, 2, 2, (d) 0, 0, 0, 2
- Q.51. The refluxing of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with an excess of  $\text{PPh}_3$  in ethanol gives a complex A. Complex A and valence electron count on Rhodium are, respectively,  
 (a)  $[\text{RhCl}(\text{PPh}_3)_3]$ , 16 (b)  $[\text{RhCl}(\text{PPh}_3)_5]$ , 16  
 (c)  $[\text{RhCl}(\text{PPh}_3)_3]$ , 18 (d)  $[\text{RhCl}(\text{PPh}_3)_5]$ , 18

Q.52. Which is the correct statement about metal carbonyls?

- (a) The C atom of CO molecule donates its electron pair to the metal atom.
- (b) The O atom of CO molecule donates its electron pair to the metal atom.
- (c) Both C and O atoms of CO molecule donate its electron pair to the metal atom.
- (d) None of these.

Q.53. Match the following-

	Carbonyl Cluster	Total Valence Electron
1.	$\text{Rh}_6(\text{CO})_{16}$	(A) 72
2.	$\text{Os}_5(\text{CO})_{16}$	(B) 74
3.	$[\text{Fe}_4\text{C}(\text{CO})_{12}]^{-2}$	(C) 86
4.	$\text{Os}_5(\text{CO})_{15}\text{C}$	(D) 62

	1	2	3	4
(a)	C	A	D	B
(b)	B	A	C	D
(c)	D	C	A	B
(d)	A	C	D	B

Q.54. An efficient catalyst for hydrogenation of alkenes is  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ . However  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$  does not catalyze this reaction because:

- (a)  $\text{PPh}_3$  binds stronger to Ir than Rh
- (b) Cl binds stronger to Ir than Rh
- (c)  $\text{PPh}_3$  binds stronger to Rh than Ir
- (d) Cl binds stronger to Rh than Ir

Q.55. Reductive elimination step in hydrogenation of alkenes by Wilkinson's catalyst results in (neglecting solvent in coordination sphere of Rh):

- |   |   |
|---|---|
| (a) T-shaped $[\text{RhCl}(\text{PPh}_3)_2]$ ,                  | (b) Trigonal-Planar $[\text{RhCl}(\text{PPh}_3)_2]^{+2}$ ,            |
| (c) T-shaped $[\text{Rh}(\text{H})(\text{PPh}_3)\text{Cl}]^+$ , | (d) Trigonal-Planar $[\text{Rh}(\text{H})\text{I}(\text{PPh}_3)_2]$ , |

Q.56. In the trans-  $\text{PtCl}_2\text{L}(\text{CO})$  complex, the CO stretching frequency for  $\text{L} = \text{NH}_3$ , pyridine,  $\text{NMe}_3$  decreases in the order:

- |   |   |
|---|---|
| (a) Pyridine > $\text{NH}_3$ > $\text{NMe}_3$ | (b) $\text{NH}_3$ > Pyridine > $\text{NMe}_3$ |
| (c) $\text{NMe}_3$ > $\text{NH}_3$ > Pyridine | (d) Pyridine > $\text{NMe}_3$ > $\text{NH}_3$ |

Q.57. Consider the following statements about metal carbonyls:

- 1- Generally mononuclear carbonyls are colorless while other is colored.
- 2- They are covalent in nature.
- 3- They are poor conductor of electricity.
- 4- They are generally paramagnetic in nature.

Which of the following statements given above is/are correct?

- |               |                 |
|---------------|-----------------|
| (a) 2 and 4   | (b) 1 and 4     |
| (c) 1,2 and 3 | (d) 1,2,3 and 4 |

Q.58. Mention the incorrect statement about mononuclear carbonyls:

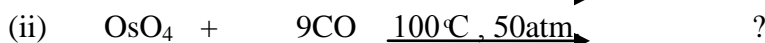
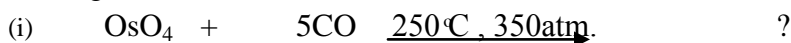
- (a) These are readily soluble in organic solvent.

- (b) These can be vaporized without decomposition.  
 (c) These carbonyls are more volatile than the others.  
 (d) They have specific color.
- Q.59. Though cyclobutadiene ( $C_4H_4$ ) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because  
 (a) Its engages in long-range interaction with transition metals.  
 (b) It gains stability due to formation of  $(C_4H_4)^{-2}$  on binding to transition metals.  
 (c) Its polymerization ability reduces in the presence of transition metal.  
 (d) It becomes stable in presence of transition metals due to formation of  $(C_4H_4)^{-2}$
- Q.60. The structure of carborane with formula,  $C_2B_{10}H_{12}$  is formally derived from:  
 (a) Closo-borane (b) Nido-borane  
 (c) Arachano-borane (d) Conjuncto-boranes
- Q.61. The product of the following reaction is:  

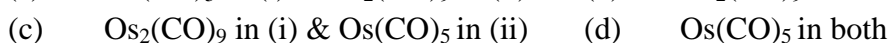
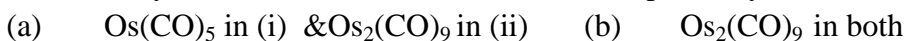
$$Fe(CO)_5 \xrightarrow{\text{U.V. Light}}$$
  
 (a) Fe and CO (b)  $Fe_2(CO)_9$  and CO  
 (c)  $Fe_3(CO)_{12}$  (d) None of the above.
- Q.62. The correct combination of metal, number of CO ligands and charge for a metal carbonyl complex  $[M(CO)_x]^z$  that satisfies 18-electron rule is:  
 (a)  $M = Ti, x = 6, z = 1$  (b)  $M = V, x = 6, z = 1$   
 (c)  $M = Co, x = 4, z = 2$  (d)  $M = Mo, x = 5, z = 1$
- Q.63. Which of the following compound has three bridging carbonyl group?  
 (a)  $Co_2(CO)_8$  (b)  $Fe_2(CO)_9$   
 (c)  $Mn_2(CO)_{10}$  (d) None of these
- Q.64. Which of the following is NOT suitable as catalyst for hydroformylation?  
 (a)  $HCo(CO)_4$  (b)  $HCo(CO)_3PPh_3$   
 (c)  $HRh(CO)(PPh_3)_3$  (d)  $H_2Rh(PPh_3)_2Cl$
- Q.65. The bond order of the metal-metal bond in the dimeric complex  $[Re_2Cl_4(PMe_2Ph)_4]^+$  is:  
 (a) 4.0 (b) 3.5  
 (c) 3.0 (d) 2.5
- Q.66. Solid  $Co_2(CO)_8$  shows infrared CO stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and  $2112\text{ cm}^{-1}$ . When dissolved in hexane, the carbonyl bands at 1887 and  $1856\text{ cm}^{-1}$  disappears. These changes in infrared spectrum are due to:  
 (a) Loss of terminal CO  
 (b) Structural changes of  $Co_2(CO)_8$  involving conversion of terminal CO to bridging CO.  
 (c) Dissociation of  $Co_2(CO)_8$  to  $Co(CO)_4$ .  
 (d) Structural changes of  $Co_2(CO)_8$  involving conversion of bridging CO to terminal CO.
- Q.67. The binding modes of NO in 18 electron compound  $[Co(CO)_3(NO)]$  and  $[Ni(\eta^5Cp)(NO)]$ , respectively, are:

- (a) Linear and bent (b) Bent and linear  
(c) Linear and linear (d) Bent and bent
- Q.68. Wacker's process uses the catalyst:  
(a) Wilkinson's catalyst (b) Ziese's salt  
(c) Ziegler's-Natta catalyst (d) Potash salt
- Q.69. The correct statement regarding terminal/bridging CO groups in solid  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  is:  
(a) Both have equal no. of bridging CO groups.  
(b) No. of bridging CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 4.  
(c) The no. of terminal CO groups in  $\text{Co}_4(\text{CO})_{12}$  is 8.  
(d) The no. of bridging CO groups in  $\text{Ir}_4(\text{CO})_{12}$  is 0.
- Q.70. How many isomers are possible for  $\text{C}_2\text{B}_2\text{H}_{12}$ ?  
(a) Three (b) Two  
(c) One (d) Four
- Q.71.  $\text{Rh}_6(\text{CO})_{16}$  has :  
(a) All terminal CO groups.  
(b) 10 terminal and 6 bridged CO groups.  
(c) 4 bridged and 12 terminal CO groups.  
(d) 8 bridging and 8 terminal CO groups.
- Q.72. Match the following:
- | List-1 |   |   |   | List-2                  |
|--------|---|---|---|-------------------------|
| (A)    | $\text{Fe}_3(\text{CO})_{12}$   |   |   | 1. Tetrahedral          |
| (B)    | $\text{Ni}(\text{CO})_4$  |   |   | 2. Octahedral           |
| (C)    | $\text{Fe}(\text{CO})_5$  |   |   | 3. Trigonal Bipyramidal |
| (D)    | $[\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})(\text{NO})\text{Cl}]^+$ |   |   | 4. Square Pyramidal     |
|        | A   | B | C | D                       |
| (a)    | 1   | 2 | 4 | 3                       |
| (b)    | 2   | 1 | 3 | 4                       |
| (c)    | 1   | 2 | 3 | 4                       |
| (d)    | 3   | 2 | 1 | 4                       |
- Q.73. In  $\text{H}_2\text{Ru}_6(\text{CO})_{18}$  cluster, containing 8 co-ordinate Ru centers, the hydrogen atoms are:  
(a) Both terminal (b) One terminal and other bridging  
(c) Both bridging between two Ru (d) Both bridging between three Ru
- Q.74. The sandwich complex  $\eta\text{-CpCoC}_n\text{H}_n$  is an 18 electron species, when 'n' is:  
(a) 6 (b) 4  
(c) 3 (d) 5
- Q.75. On reducing  $\text{Fe}_3(\text{CO})_{12}$  with an excess of sodium, a carbonylate ion is formed. The ion is isoelectronic with  
(a)  $[\text{Mn}(\text{CO})_5]^-$  (b)  $[\text{Ni}(\text{CO})_4]$   
(c)  $[\text{Mn}(\text{CO})_5]^-$  (d)  $[\text{V}(\text{CO})_6]^-$

Q.76. In the given reactions,



The carbonyl formed in both the reactions are, respectively:



Q.77. Complex  $\text{Mo}(\text{py})_2(\text{CO})_4$  has two forms. Which of the statement about these forms is true?

(a) Cis- form will give single band around  $2000\text{ cm}^{-1}$  in IR and Trans-form will give 4 bands.

(b) Cis- form will give 4 bands and Trans-form will give single band around  $2000\text{ cm}^{-1}$  in IR.

(c) Both Cis and Trans-form will give 4 bands.

(d) Both Cis and Trans-form will give single bands at  $2000\text{ cm}^{-1}$ .

Q.78. The HOMO in CO is:

(a)  $\pi$ -bonding

(b)  $\sigma$ -bonding

(c)  $\pi$ - antibonding

(d)  $\sigma$ -antibonding

Q.79. the oxidation state of Fe in the complex  $[\text{CpFe}(\text{CO})_2]_2$  is:

(a) +2

(b) +1

(c) 0

(d) -1

Q.80. In metal carbonyl complexes, as more electron density moves from the metal d-orbital's to CO  $\pi^*$  orbitals, the CO stretching frequency :

(a) Increases

(b) Decreases

(c) Remains same

(d) Disappears

Q. 81. Which metal carbonyls do not obey 18- electron rule:

1-  $\text{Co}_6(\text{CO})_{16}$

2-  $\text{Ir}_6(\text{CO})_{16}$

3-  $\text{Co}_4(\text{CO})_{12}$

4-  $\text{V}(\text{CO})_6$

(a) 3 and 4

(b) 2 and 3

(c) 1,2 and 4

(d) 1,2,3 and 4

Q.82. The neutral complex which follows 18- electron rule is:

(a)  $(\eta^5 - \text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2$

(b)  $(\eta^5 - \text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3$

(c)  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{Co}$

(d)  $(\eta^5 - \text{C}_5\text{H}_5)\text{Re}(\eta^6 - \text{C}_6\text{H}_6)$

Q.83. Which of the following metal carbonyls is NOT found in liquid form at ordinary temperature?

(a)  $\text{Ni}(\text{CO})_4$

(b)  $\text{Fe}(\text{CO})_5$

(c)  $\text{Os}(\text{CO})_5$

(d)  $\text{Mn}_2(\text{CO})_{10}$

Q.84. The hapticity of cyclo hepta 1,3,5-triene in  $(\text{C}_7\text{H}_8)\text{Fe}(\text{CO})_3$  is:

(a) 2

(b) 4

(c) 6

(d) 7

Q.85. The oxidation state of Fe in  $[\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2][\text{BF}_4]$  is:

(a) +1

(b) +2

(c) +3

(d) +4



- Q.86. An example of metal cluster with no bridging ligand:
- (a)  $\text{Mn}_2(\text{CO})_{10}$  (b)  $\text{Co}_2(\text{CO})_8$   
 (c)  $\text{Fe}_2(\text{CO})_9$  (d)  $\text{Fe}_3(\text{CO})_{12}$
- Q.87. In Ziegler-Natta Catalysis the commonly used catalyst is:
- (a)  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{TiCl}_4$  (b)  $(\eta^5\text{-Cp})_2\text{TiCl}_2$ ,  $\text{Al}(\text{OH})_3$   
 (c)  $\text{VO}(\text{acac})_2$ ,  $\text{Al}_2(\text{CH}_3)_6$  (d)  $\text{TiCl}_4$ ,  $\text{BF}_3$
- Q.88. The square planar complex  $[\text{IrCl}(\text{Ph}_3\text{P})_3]$  undergoes oxidative addition of  $\text{Cl}_2$  to give two products:
- (a) *fac* and *mer* (b) *cis* and *trans*  
 (c) Enantiomers (d) Linkage isomers
- Q.89. The most unstable species among the following is:
- (a)  $\text{Ti}(\text{C}_2\text{H}_5)_4$  (b)  $\text{Ti}(\text{CH}_2\text{Ph})_4$   
 (c)  $\text{Pb}(\text{CH}_3)_4$  (d)  $\text{Pb}(\text{C}_2\text{H}_5)_4$
- Q.90. CO bond order is lowest in:
- (a) Uncoordinated CO (b) CO bonded to one metal  
 (c) CO bridging Two metals (d) CO bridging Three metals
- Q.91. An aqueous solution of NaOH reacts with  $\text{Fe}(\text{CO})_5$  to form:
- (a)  $[\text{HFe}(\text{CO})_4]^-$  (b)  $[\text{HFe}_2(\text{CO})_4]^-$   
 (c)  $[\text{H}_2\text{Fe}(\text{CO})_4]^-$  (d) None of these.
- Q.92. Arrange the following in increasing order of CO stretching frequencies:
- I. CO      II.  $\text{Mo}(\text{CO})_3(\text{NH}_3)_3$       III.  $\text{Mo}(\text{CO})_6$       IV.  $\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$
- (a)  $\text{IV} < \text{III} < \text{II} < \text{I}$  (b)  $\text{III} < \text{IV} < \text{II} < \text{I}$   
 (c)  $\text{II} < \text{III} < \text{IV} < \text{I}$  (d)  $\text{I} > \text{II} > \text{III} > \text{IV}$
- Q.93. The compound formed by the reaction of NO and metals are called:
- (a) Nitrite (b) Nitrates  
 (c) Nitrosyls (d) None of these.
- Q.94. The oxidation state of Mn in  $[\text{Mn}(\text{NO})_3(\text{CO})]$  is:
- (a) -1 (b) -2  
 (c) -3 (d) 0

**Answers**

1- (d)	2- (d)	3- (b)	4- (a)	5- (a)	6- (b)
7 - (d)	8 - (d)	9 - (a)	10 - (b)	11 - (b)	12 - (d)
13- (d)	14- (a)	15- (a)	16 (a)	17- (b)	18- (a)
19- (a)	20- (d)	21- (a)	22- (a)	23- (a)	24- (d)
25- (c)	26- (d)	27- (d)	28- (b)	29- (d)	30- (d)
31- (d)	32- (b)	33- (d)	34- (d)	35- (c)	36- (b)
37- (d)	38- (d)	39- (b)	40- (c)	41- (d)	42- (b)
43- (d)	44- (d)	45- (a)	46- (b)	47- (c)	48- (a)
49- (c)	50- (c)	51- (a)	52- (a)	53- (a)	54- (c)
55- (a)	56- (a)	57- (c)	58- (d)	59- (b)	60- (c)
61- (b)	62- (b)	63- (b)	64- (d)	65- (b)	66- (d)
67- (c)	68- (c)	69- (d)	70- (b)	71- (c)	72- (b)
73- (c)	74- (b)	75- (b)	76- (d)	77- (b)	78- (a)
79- (b)	80- (b)	81- (c)	82- (d)	83- (d)	84- (b)
85- (c)	86- (a)	87- (a)	88- (a)	89- (a)	90- (d)
91- (a)	92- (c)	93- (c)	94- (d)		

## Chapter 7

### Reaction Mechanism of Transition Metal Complexes

(Contributed by: Dr. Dinkar Malik, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- 5-co-ordinated and 8-co-ordinated complexes are generally fluxional even at low temperature.
- Fluxional molecules undergo deformational rearrangements in which the atom actually interchanges their places with one another e.g.  $\text{PF}_5$ .
- The non-rigid molecules in which two or more configurations are chemically equivalent and such non-rigid molecules are called fluxional.
- In an outer sphere redox reaction electron transfer occurs through the intact co-ordination shells of the metal ions.
- The octahedral complexes, in general, are not fluxional.
- In  $\text{S}_{\text{N}}1$  mechanism the co-ordination no. of the complex is decreased from 6 to 5.
- $\text{S}_{\text{N}}1\text{CB}$  mechanism stands for substitution, nucleophilic, unimolecular, conjugate base.
- Strong field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^7, d^9$  and  $d^{10}$  configuration are labile (-ve CFAE).
- Strong field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^7, d^9$  and  $d^{10}$  configuration have positive value of CFAE (inert complexes).
- A class of fluxional molecule of great importance is those with trigonal bipyramidal configuration. When all the five appended groups are identical single atoms, as in  $\text{AB}_5$ , the symmetry of the molecule is  $\text{D}_{3h}$ .
- Trans- effect is explained by polarization theory.
- The arrangement of stabilities of high spin complexes of the ions between  $\text{Mn}^{+2}$  and  $\text{Zn}^{+2}$  with a ligand is known as Irving-William order of stability-  

$$\text{Mn}^{+2} < \text{Fe}^{+2} < \text{Co}^{+2} < \text{Ni}^{+2} < \text{Cu}^{+2} < \text{Zn}^{+2}$$
- With the increase in trans- effect of ligands, the rate of reaction also increases.
- The non-rigid molecules in which two or more configurations are not chemically equivalent and the process of inter conversion is called isomerism or tautomerism.
- Most of the inorganic reactions are ionic in nature
- In the dissociative mechanism of octahedral complexes, the more stable intermediate formed is square pyramidal.
- $\text{S}_{\text{N}}1$  mechanism is favored when oxidation state of metal atom is less.
- Fluxional molecules undergo deformational rearrangements in which the atom actually interchanges their places with one another e.g.  $\text{PF}_5$ .
- Metal Complexes having low ( -ve) or zero value of CFAE are labile complexes.
- Metal Complexes having high ( +ve) value of CFAE are inert complexes.

- Cis- and trans- isomers of the complexes can be detected by Kurnakov's test.
- CFAE is equal to the difference between CFSE of reactant and intermediate.
- In  $S_N1$  mechanism, the rate determining slowest step is metal-ligand bond breaking step.
- For inner sphere mechanism electron transfer reactions, one complex should be inert and other should be labile.
- For outer sphere mechanism electron transfer reactions, both the complexes should be labile.
- The process in which one of the more symmetrical forms (TBP for the 5-co-ordinated complex) changes to another (square pyramidal) and then back to an equivalent form in which the interchange of the ligands take place is called polytonal arrangement.
- In an inner sphere redox reaction the two metal ions are connected in the activated complex through a bridging ligand common to both co-ordination shells.
- For inner sphere mechanism, the inert complex should have a ligand capable of forming bridge between the two complexes.
- Weak field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9, d^{10}$  are labile (-ve CFAE).
- In  $S_N2$  mechanism pentagonal bi pyramidal (PBP) intermediate is formed, while octahedral wedge intermediate is more common.
- All non-transition metals complexes are labile in nature.

## Multiple Choice Questions

- Q.1. Electron transfer is fast if the conductivity of the ligand is:  
 (a) Zero (b) Low  
 (c) High (d) None of these
- Q.2. Which one of the following statement is incorrect?  
 (a) Most of the inorganic reactions are ionic.  
 (b) Reactions of transition metal complexes are slow.  
 (c) It is possible to study the mechanism of transition metal complexes.  
 (d) It is possible to study the mechanism of ionic reaction.
- Q.3. The reaction of  $\text{PtCl}_4^{-2}$  with two equivalents of  $\text{NH}_3$  produces:  
 (a)  $\text{Cis-Pt}(\text{NH}_3)_2\text{Cl}_2$  (b)  $\text{Trans-Pt}(\text{NH}_3)_2\text{Cl}_2$   
 (c) Both (a) & (b) (d)  $\text{Cis-[Pt}(\text{NH}_3)_2\text{Cl}_4]^{-2}$
- Q.4. Electron transfer is fast if:  
 (a) The electron belongs to  $t_{2g}$  orbital.  
 (b) The electron spins of the two complex ions are the same.  
 (c) The concentration of the cations in the solution is high.  
 (d) All of the above
- Q.5. Which of the following statement is true for the following reaction?  

$$\text{x} + \text{y-z} \longrightarrow \text{x---y---z} \longrightarrow \text{x-y} + \text{z}$$
  
 (a) The energy of  $\text{x---y---z}$  is lowest. (b)  $\text{x---y---z}$  is very stable.  
 (c)  $\text{x---y---z}$  has a long life. (d)  $\text{x---y---z}$  cannot be isolated.
- Q.6. Mention the correct statement about electron transfer reactions:  
 (a) Electron transfer reaction occurring through inner sphere mechanism are faster than outer sphere mechanism.  
 (b) Electron transfer reaction occurring through outer sphere mechanism are faster if Ligands are  $\pi$ - acceptor.  
 (c) Electron transfer reaction occurring through outer sphere mechanism are faster if the conductivity of ligand is high.  
 (d) All are correct.
- Q.7. The ability of a group to direct the entering ligand to occupy trans-position with respect to the group is called:  
 (a) Steric effect (b) Peroxide effect  
 (c) Inductive effect (d) Trans effect
- Q.8. The reaction is an example of:  

$$[\text{Co}(\text{NH}_3)_5\text{Cl}]^+ + \text{Hg}^{+2} \longrightarrow [\text{Hg}(\text{NH}_3)_5\text{Cl}]^+ + \text{Co}^{+2}$$
  
 (a) Electrophilic substitution reaction.  
 (b) Nucleophilic substitution reaction.  
 (c) Electrophilic addition reaction.  
 (d) Nucleophilic addition reaction.
- Q.9. Mention the correct statement about inner sphere mechanism:  
 (a) The inert complex should have a ligand capable of forming bridge between the two complexes.  
 (b) The labile complex should have a bridging ligand.  
 (c) Both the complexes should have a bridging ligand.

- (d) None of the complexes should have a bridging ligand.
- Q.10. The final product containing chromium in the reaction between  $[\text{CoCl}(\text{NH}_3)_5]^{+2}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$  and  $\text{H}_3\text{O}^+$  is:
- (a)  $[\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_4\text{Cl}]^{+2}$  (b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$   
 (c)  $[\text{CrCl}(\text{NH}_3)_5]^{+2}$  (d)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{+2}$
- Q.11. In the dissociative mechanism of octahedral complexes, the more stable intermediate formed is:
- (a) Square planar (b) Square pyramidal  
 (c) Prismatic (d) Trigonal pyramidal
- Q.12. For outer sphere mechanism electron transfer reactions:
- (a) Both the complexes should be inert.  
 (b) Both the complexes should be labile.  
 (c) One should be inert and other should be labile.  
 (d) Electron transfer is slow if the ligands are pi-acceptor.
- Q.13. Electron transfer from  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$  to  $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$  is likely to occur via:
- (a) d-d transition (b) Inner sphere electron transfer  
 (c)  $\text{S}_{\text{N}}1$  mechanism (d) Outer sphere mechanism
- Q.14. Which of the following statement is/are correct about  $\text{S}_{\text{N}}1$  mechanism of octahedral complexes:
- (i) It is also known as dissociative mechanism.  
 (ii) It generally occurs through TBP intermediate.  
 (iii) It occurs in a single step.  
 (iv) The rate depends on the concentration of the reactant only.
- (a) (i) only (b) (i) & (iv)  
 (c) (ii) & (iii) (d) (i), (ii), (iii) & (iv)
- Q.15. For inner sphere mechanism electron transfer reactions:
- (a) Both the complexes should be inert  
 (b) Both the complexes should be labile  
 (c) One should be inert and other should be labile  
 (d) The rate of reaction decreases with increase in nucleophilic character of bridging ligand.
- Q.16. The rate of exchange of cyanide ligands in the complexes
- (i)  $[\text{Ni}(\text{CN})_4]^{-2}$  (ii)  $[\text{Mn}(\text{CN})_6]^{-3}$  (iii)  $[\text{Cr}(\text{CN})_6]^{-3}$   
 (a) (ii) > (i) > (iii) (b) (iii) > (i) > (ii)  
 (c) (i) > (iii) > (ii) (d) (i) > (ii) > (iii)
- Q.17. Which of the following conditions is favorable for  $\text{S}_{\text{N}}1$  mechanism?
- (a) Smaller size of the metal ion.  
 (b) Higher charge on metal ion.  
 (c) Larger size of the leaving group.  
 (d) Absence of chelating group in the complexes.
- Q.18. For aquation reaction, the favorable condition is:
- (a)  $\text{pH} < 3$  (b)  $\text{pH} < 7$   
 (c)  $\text{pH} > 7$  (d)  $\text{pH} > 12$
- Q.19. The substitutionally inert complex ion amongst the following is:
- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$   
 (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$  (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$

- Q.20. Which of the following condition is favorable for  $S_N2$  mechanism?
- (a) Large size of the metal ion. (b) Lower charge on the metal ion.  
 (c) Larger size of the incoming group. (c) Smaller size of the leaving group.
- Q.21. Trans effect is not shown by:
- (a)  $[\text{PtCl}_4]^{-2}$  (b)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{+1}$   
 (c) Cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (d) Trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- Q.22. CFSE of transition metal complexes can be determined by:
- (a) UV-visible spectroscopy (b) IR spectroscopy  
 (c) Microwave spectroscopy (d) NMR spectroscopy
- Q.23. Which of the following statements is/are true about  $S_N1$  reactions?
- (i) In  $S_N1$  mechanism, the rate determining slowest step is metal-ligand bond breaking step.  
 (ii) In  $S_N1$  mechanism, the rate determining slowest step is metal-ligand bond making step.  
 (iii) In  $S_N1$  mechanism the co-ordination no. of the complex is decreased from 6 to 5.  
 (iv) In  $S_N2$  mechanism the co-ordination no. of the complex is decreased from 6 to 5.  
 (a) (i) & (ii) (b) (i) & (iii)  
 (c) (i),(ii) & (iii) (d) (i),(ii) & (iv)
- Q.24.  $[\text{Co}(\text{NH}_3)_5\text{X}]^{+2} + \text{H}_2\text{O} \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3} + \text{X}^-$   
 Mention the correct statement about the above reaction-
- (a) It is found to be of second order  
 (b) It is found to be of zero order.  
 (c)  $\text{H}_2\text{O}$  is involved in rate determining step.  
 (d)  $\text{H}_2\text{O}$  does not affect the rate of reaction.
- Q.25. In the inner sphere reduction of  $[\text{CoCl}(\text{NH}_3)_5]^{+2}$  with  $[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$ , the chloride:
- (a) Bridges the metal centre only.  
 (b) Mediates electron transfer only.  
 (c) Bridges and mediates electron transfer both.  
 (d) Does not play any role.
- Q.26. Mention the correct statement:
- (a) In  $S_N1$  mechanism the rate,  $r = k[\text{ML}_5\text{X}][\text{Y}]$   
 (b) In  $S_N2$  mechanism the rate,  $r = k[\text{ML}_5\text{X}]$   
 (c) In  $S_N1$  mechanism the rate,  $r = k[\text{ML}_5\text{X}]^2$   
 (d) In  $S_N2$  mechanism the rate,  $r = k[\text{ML}_5\text{X}][\text{Y}]$
- Q.27. With the increase in trans effect of ligands, the rate of reaction:
- (a) Decrease (b) Increase  
 (c) Neither increase nor decrease (d) May slightly increase or decrease.
- Q.28.  $[\text{Cr}(\text{H}_2\text{O})_6]^{+2} + [\text{CoCl}(\text{NH}_3)_5]^{+3} \longrightarrow [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+2} + [\text{CrCl}(\text{H}_2\text{O})_5]^{+3}$   
 The correct statement regarding the above reaction is that:
- (a) It follows outer sphere mechanism  
 (b) It follows inner sphere mechanism with  $\text{NH}_3$  acting as the bridging ligand.  
 (c) It follows inner sphere mechanism with  $\text{Cl}^-$  acting as the bridging ligand.  
 (d) It is not an electron transfer reaction.
- Q.29. Mention the correct statement about  $S_N2$  mechanism:
- (a) It is also known as dissociative mechanism.  
 (b) In this mechanism the intermediate formed has co-ordination no. less than the

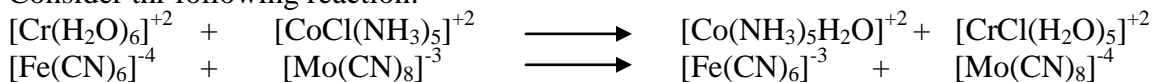
- co-ordination no. of initial complex.
- (c) It is also known as inter ligand associative mechanism ( $I_a$ ).
- (d) In this mechanism pentagonal bi pyramidal (PBP) intermediate is formed, while octahedral wedge intermediate is more common.
- Q.30. Trans effect is explained by:
- (a) Polarization theory (b) Mulliken theory
- (c) Pauling theory (d) Magnetic theory
- Q.31. The Cr(III) species formed soon after electron transfer between  $\text{IrCl}_6^{-2}$  and  $\text{Cr}(\text{H}_2\text{O})_6^{+2}$  is:
- (a)  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  (b)  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$
- (c)  $\text{CrCl}_6^{-3}$  (d)  $\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3$
- Q.32. Mention the correct statement about inert and labile complexes:
- (a)  $[\text{Ni}(\text{CN})_4]^{-2}$  is thermodynamically unstable but kinetically stable.
- (b)  $[\text{Co}(\text{NH}_3)_6]^{-2}$  is thermodynamically stable but kinetically labile.
- (c) Labile complexes are those in which ligand substitution takes place easily.
- (d) The terms inert and labile are thermodynamic terms.
- Q.33.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{OH})]^{+2} + \text{Cl}^-$
- (i) The rate of above reaction depends upon the concentration of nucleophile.
- (ii) When the concentration of  $\text{OH}^-$  is high it follows first order rate law.
- (iii) It follows second order mechanism.
- (iv) It involves two steps in its mechanism.
- Which of the following statements is/are correct?
- (a) (i) only (b) (i) & (ii)
- (c) (iii) & (iv) (d) All are correct.
- Q.34. The correct order of rate of exchange of water molecules between the co-ordination sphere and bulk is:
- (a)  $\text{Cr}^{+3} < \text{Al}^{+3} < \text{Cr}^{+2} < \text{Ni}^{+2}$  (b)  $\text{Cr}^{+3} < \text{Al}^{+3} < \text{Ni}^{+2} < \text{Cr}^{+2}$
- (c)  $\text{Cr}^{+3} < \text{Ni}^{+2} < \text{Cr}^{+2} < \text{Al}^{+3}$  (d)  $\text{Cr}^{+3} < \text{Cr}^{+2} < \text{Al}^{+3} < \text{Ni}^{+2}$
- Q.35. Mention the correct statement about complexes:
- (a) Outer orbital complexes of Ni(II) are labile.
- (b) Outer orbital complexes of Cr(III) are inert.
- (c) Inner orbital complexes of Sc(III) are inert.
- (d) Outer orbital complexes of Zn (II) are labile.
- Q.36.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{OH})]^{+2} + \text{Cl}^-$
- The above reaction follows:
- (a)  $\text{S}_{\text{N}}1$  mechanism (b)  $\text{S}_{\text{N}}2$  mechanism
- (c)  $\text{S}_{\text{N}}1\text{CB}$  mechanism (d)  $\text{S}_{\text{N}}\text{i}$  mechanism
- Q.37. Lability of the ions  $\text{Cr}^{+2}$ ,  $\text{Mn}^{+2}$  and  $\text{V}^{+2}$  should follow the order:
- (a)  $\text{Cr}^{+2} > \text{Mn}^{+2} > \text{V}^{+2}$  (b)  $\text{Mn}^{+2} > \text{Cr}^{+2} > \text{V}^{+2}$
- (c)  $\text{Mn}^{+2} > \text{V}^{+2} > \text{Cr}^{+2}$  (d)  $\text{V}^{+2} > \text{Cr}^{+2} > \text{Mn}^{+2}$
- Q.38. Mention the correct statement:
- (a) Complexes having  $\text{sp}^3\text{d}^2$  hybridization have strong bonds than the complexes having  $\text{d}^2\text{sp}^3$ .
- (b) Complexes having  $\text{d}^2\text{sp}^3$  hybridization have strong bonds than the complexes having  $\text{sp}^3\text{d}^2$ .
- (c) Both have equal bond strength.
- (d) It cannot be decided.



Q.39. The correct order of Trans effect is:

- (a)  $\text{H}^+ > \text{SCN}^- > \text{Br}^- > \text{H}_2\text{O}$  (b)  $\text{CO} > \text{Py} > \text{H}_2\text{O} > \text{CH}_3^-$   
 (c)  $\text{C}_6\text{H}_5^- > \text{I}^- > \text{Py} > \text{OH}^-$  (d)  $\text{CO} > \text{H}_2\text{O} > \text{CH}_3^- > \text{Py}$

Q.40. Consider the following reaction:



Which one of the following is the correct statement?

- (a) Both involve an inner sphere mechanism.  
 (b) Both involve an outer sphere mechanism.  
 (c) Reaction 1 follows an inner sphere and reaction 2 follows outer sphere mechanism.  
 (d) Reaction 1 follows an outer sphere and reaction 2 follows inner sphere mechanism.

Q.41. CFAE is also known as:

- (a) The difference between CFSE of reactant and product.  
 (b) The difference between CFSE of reactant and intermediate.  
 (c) The difference between CFSE of product and intermediate.  
 (d) The CFSE of reactant only.

Q.42. Which of the following is the theory of Trans effect:

- (a) Mulliken theory (b) Huckel theory  
 (c) pi-bonding theory (d) Sigma-bonding theory

Q.43. Mention the correct statement:

- (i) Complexes having low (-ve) CFAE are labile.  
 (ii) Complexes having zero CFAE are labile.  
 (iii) Complexes having high (+ve) CFAE are inert.  
 (iv) Complexes having zero CFAE are inert.  
 (a) (iv) only (b) (i) & (ii)  
 (c) (ii) & (iii) (d) (i), (ii) & (iii)

Q.44. The reaction of  $\text{PtCl}_4^{2-}$  with  $\text{NH}_3$  gives product A while its reaction with  $[\text{NO}_2]^{-2}$  followed by  $\text{NH}_3$  gives product B. The A and B respectively, are:

- (a) Trans-  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and trans-  $[\text{Pt}(\text{NH}_3)\text{Cl}_2(\text{NO}_2)]^-$   
 (b) Cis-  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and trans-  $[\text{Pt}(\text{NH}_3)\text{Cl}_2(\text{NO}_2)]^-$   
 (c) Cis-  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and cis-  $[\text{Pt}(\text{NH}_3)\text{Cl}_2(\text{NO}_2)]^-$   
 (d) Trans-  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and cis-  $[\text{Pt}(\text{NH}_3)\text{Cl}_2(\text{NO}_2)]^-$

Q.45. Electrostatic polarization theory was proposed by:

- (a) Guldberg (b) Einstein  
 (c) Gringberg (d) Chatt

Q.46. Mention the incorrect statement about  $\text{S}_{\text{N}}1$  reactions which are occurring through square pyramidal intermediate-

- (a) Weak field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9, d^{10}$  are labile.  
 (b) Weak field octahedral complexes of metal ions with  $d^3$  or  $d^8$  configurations have -ve CFAE.  
 (c) Strong field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^7, d^9$  and  $d^{10}$  configuration are labile.  
 (d) Strong field octahedral complexes of metal ions with  $d^0, d^1, d^2, d^7, d^9$  and  $d^{10}$

configuration have negative value of CFAE.

- Q.47. Cis- and trans- isomers are detected by:
- |                   |                     |
|-------------------|---------------------|
| (a) Lucas test    | (b) Kurnakov's test |
| (c) Mulliken test | (d) Ring test       |
- Q.48. The order of reactivity of ligands  $\text{NMe}_3$ ,  $\text{PMe}_3$ , and  $\text{CO}$  with complexes  $\text{MeTiCl}_3$  and  $(\text{CO})_5\text{Mo(Ph)}$  are:
- |   |
|---|
| (a) $\text{CO} > \text{PMe}_3 > \text{NMe}_3$ and $\text{CO} > \text{NMe}_3 > \text{PMe}_3$ |
| (b) $\text{PMe}_3 > \text{CO} > \text{NMe}_3$ and $\text{NMe}_3 > \text{CO} > \text{PMe}_3$ |
| (c) $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$ and $\text{CO} > \text{PMe}_3 > \text{NMe}_3$ |
| (d) $\text{NMe}_3 > \text{CO} > \text{PMe}_3$ and $\text{PMe}_3 > \text{NMe}_3 > \text{CO}$ |
- Q.49.  $[\text{Co}(\text{NH}_3)_5\text{X}]^{+2} + \text{H}_2\text{O} \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3} + \text{X}^-$   
is an example of:
- |                      |                     |
|----------------------|---------------------|
| (a) Acid hydrolysis  | (b) Base hydrolysis |
| (c) Anation reaction | (d) None of these   |
- Q.50. Pi-bond in tetrahedral complexes is formed by the following symmetry:
- |           |                   |
|-----------|-------------------|
| (a) $t_1$ | (b) $t_2$         |
| (c) e     | (d) None of these |
- Q.51. The platinum complex of  $\text{NH}_3$  and  $\text{Cl}^-$  ligands is an anti-tumour agent. The correct isomeric formula of the complex and its precursor are:
- |  |  |
|--|--|
| (a) Cis- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{PtCl}_4^{-2}$            | (b) Trans- $(\text{NH}_3)_2\text{Cl}_2$ and $\text{PtCl}_4^{-2}$                     |
| (c) Cis- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_4^{+2}$ | (d) Trans- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_4^{-2}$ |
- Q.52.  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3} + \text{X}^- \longrightarrow [\text{Co}(\text{NH}_3)_5\text{X}]^{+2} + \text{H}_2\text{O}$   
is an example of-
- |                      |                     |
|----------------------|---------------------|
| (a) Acid hydrolysis  | (b) Base hydrolysis |
| (c) Anation reaction | (d) None of these   |
- Q.53. In an octahedral complex, non-bonding orbital's are:
- |                              |                                 |
|------------------------------|---------------------------------|
| (a) 4s                       | (b) $4p_x, 4p_y, 4p_z$          |
| (c) $3d_{x^2-y^2}, 3d_{z^2}$ | (d) $3d_{xy}, 3d_{yz}, 3d_{zx}$ |
- Q.54. The reactions of  $\text{Ni}(\text{CO})_4$  with the ligands ( $\text{L}=\text{PMe}_3$  or  $\text{P(OMe)}_3$ ) yields  $\text{Ni}(\text{CO})_3\text{L}$ . The reaction is:
- |                                  |                                  |
|----------------------------------|----------------------------------|
| (a) Associative                  | (b) Dissociative                 |
| (c) Interchange ( $\text{I}_a$ ) | (d) Interchange ( $\text{I}_d$ ) |
- Q.55. Which of the following ligand orbital form pi-bond in octahedral complexes?
- |                              |                   |
|------------------------------|-------------------|
| (a) $d_{x^2-y^2}$            | (b) $d_{z^2}$     |
| (c) $d_{xy}, d_{yz}, d_{zx}$ | (d) None of these |
- Q.56. MOT is also known as:
- |         |                   |
|---------|-------------------|
| (a) VBT | (b) LFT           |
| (c) CFT | (d) None of these |
- Q.57. Which of the following metal orbital does not take part in sigma bonding?
- |              |                            |
|--------------|----------------------------|
| (a) $d_{xy}$ | (b) $d_{yz}$               |
| (c) $d_{zx}$ | (d) $d_{x^2-y^2}, d_{z^2}$ |

**Answers**

1 - (c)	2- (d)	3- (a)	4- (d)	5- (d)	6- (d)
7 - (d)	8 - (a)	9 - (a)	10- (d)	11 - (b)	12 - (a)
13- (d)	14- (b)	15- (c)	16- (a)	17- (c)	18- (a)
19- (a)	20- (a)	21- (a)	22- (a)	23- (b)	24- (d)
25- (c)	26- (d)	27- (b)	28- (c)	29- (d)	30- (a)
31- (a)	32- (c)	33- (d)	34- (c)	35- (b)	36- (c)
37- (a)	38- (b)	39- (a)	40- (c)	41- (b)	42- (c)
43- (d)	44- (b)	45- (c)	46- (b)	47- (b)	48- (c)
49- (a)	50- (c)	51- (a)	52- (c)	53- (d)	54- (b)
55- (c)	56- (b)	57- (d)			

## Chapter 8

### p- Block Elements

(Contributed by: Dr. Punam Yadav, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- The type of force that holds the layers of C atoms in graphite together is Vander Waal forces.
- The Compound having an S-S bond is  $\text{H}_2\text{S}_2\text{O}_3$ .
- Alkali metals possess metallic luster when freshly cut because they contain loosely bound electrons which absorb the photons and then re-emit.
- The atomicity and the total number of bonds in the elemental white phosphorus molecule is 4 and 6 respectively.
- Boron has highly symmetrical Icosahedral structure.
- When  $\text{NaNO}_2$  is treated with Na,  $\text{Na}_2\text{O}$  and  $\text{N}_2$  are formed.
- Temporary hardness of water is due to calcium bicarbonate can be removed by adding  $\text{Ca}(\text{OH})_2$ .
- Calcium is obtained by electrolysis of molten  $\text{CaCl}_2$ .
- The metallic lustre exhibited by sodium metal is due to oscillation of loose electron.
- KF combines with HF to form  $\text{KHF}_2$  which exists as  $\text{K}^+$  and  $[\text{HF}_2]^-$ .
- The geometries of  $\text{Ni}(\text{CO})_4$  and  $[\text{NiCl}_4]^{2-}$  are tetrahedral and tetrahedral respectively.
- The hybridization of xenon atom in  $\text{XeF}_4$  is  $\text{sp}^3\text{d}^2$ .
- The main products of the reaction of equi molar quantities of  $\text{XeF}_6$  with  $\text{NaNO}_3$  are  $\text{XeOF}_4$ ,  $\text{NaF}$  and  $\text{NO}_2\text{F}$ .
- Bromine can be liberated from KBr solution by the action of chlorine water.
- The perxenate is  $\text{XeO}_4^{4-}$  can be prepared by hydrolysis of  $\text{XeF}_6$  in basic medium.
- The xenon fluoride which is excellent fluorinating agent of aromatic compound, in the presence of Lewis acid  $\text{XeF}_4$ .
- Chlorine acts as a bleaching agent only in presence of moisture.
- In polymeric  $(\text{BeCl}_2)_n$  3c-2e bonds are present.
- A solution of sodium metal in liquid ammonia is strongly reducing due to presence of solvated electron.
- The material used in solar cells contains silicon.
- In basic beryllium acetate the co-ordination of Be is four.
- The co-ordination number of Li in  $\text{LiCH}_3$  is seven.
- The most abundant element in earth's crust is oxygen.
- Egyptian blue  $\text{CaCuSi}_4\text{O}_{10}$  is an example of sheet silicate.
- A Sodalite cage in zeolites is a truncated octahedron.
- Silicates with 3D frame work are phyllo silicate.
- The formula of pyrosilicate ion is  $\text{Si}_2\text{O}_7^{6-}$ .

- Black phosphorus is thermodynamically most stable.
- The percentage of p-character in the orbitals forming P-P bonds in  $P_4$  is 75 percent.
- The product formed in the reaction of  $SOCl_2$  with white phosphorus is  $PCl_5$ .
- $N_2O$  is used as propellant for whipping creams.
- Ammonia gas can be dried by quick lime.

## Multiple Choice Questions

- Q.1. The atomicity and the total number of bonds in the elemental white phosphorus molecule is respectively:  
(a) 4 and 6 (b) 6 and 4  
(c) 4 and 4 (d) 6 and 6
- Q.2. The product formed on heating  $\text{S}_2\text{Cl}_2$  and  $\text{NH}_3$  over solid  $\text{NH}_4\text{Cl}$  is:  
(a)  $(\text{SN})_x$  (b)  $\text{S}_3\text{N}_3\text{Cl}_3$   
(c)  $\text{S}_8\text{Cl}_2$  (d)  $\text{S}_4\text{N}_4$
- Q.3. The Compound having an S-S bond is:  
(a)  $\text{H}_2\text{S}_2\text{O}_3$  (b)  $\text{H}_2\text{S}_2\text{O}_4$   
(c)  $\text{H}_2\text{S}_2\text{O}_7$  (d)  $\text{H}_2\text{S}_2\text{O}_8$
- Q.4. Which of the following oxides is neutral?  
(a) CO (b)  $\text{SnO}_2$   
(c) ZnO (d)  $\text{SiO}_2$
- Q.5. Ammonia gas can be dried by:  
(a) Conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{P}_2\text{O}_5$   
(c)  $\text{CaCl}_2$  (d) Quick lime
- Q.6. Which of the following is used as propellant for whipping creams?  
(a)  $\text{N}_2\text{O}$  (b) NO  
(c)  $\text{N}_2\text{O}_3$  (d)  $\text{N}_2\text{O}_5$
- Q.7. There is no S-S bond in:  
(a)  $\text{S}_2\text{O}_4^{-2}$  (b)  $\text{S}_2\text{O}_5^{-2}$   
(c)  $\text{S}_2\text{O}_3^{-2}$  (d)  $\text{S}_2\text{O}_7^{-2}$
- Q.8. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorus is:  
(a)  $\text{PCl}_3$  (b)  $\text{SOCl}_2$   
(c)  $\text{SCl}_2$  (d)  $\text{POCl}_3$
- Q.9. Which among the following is the strongest base?  
(a)  $\text{AsH}_3$  (b)  $\text{NH}_3$   
(c)  $\text{PH}_3$  (d)  $\text{SbH}_3$
- Q.10. Which of the following has O-O linkage?  
(a)  $\text{H}_2\text{S}_2\text{O}_6$  (b)  $\text{H}_2\text{S}_2\text{O}_8$   
(c)  $\text{H}_2\text{S}_2\text{O}_3$  (d)  $\text{H}_2\text{S}_4\text{O}_6$
- Q.11. Which of the following oxides of nitrogen is a colored gas?  
(a)  $\text{N}_2\text{O}$  (b) NO  
(c)  $\text{N}_2\text{O}_4$  (d)  $\text{NO}_2$
- Q.12. Among the trihalides of nitrogen, which one is least basic?  
(a)  $\text{NF}_3$  (b)  $\text{NCl}_3$   
(c)  $\text{NBr}_3$  (d)  $\text{NI}_3$
- Q.13. The percentage of p-character in the orbitals forming P-P bonds in  $\text{P}_4$  is:

- (a) 25 (b) 33  
(c) 50 (d) 75
- Q.14. Which one of the following properties is not shown by NO?
- (a) It is diamagnetic in gaseous state.  
(b) It is a neutral oxide.  
(c) It combines with oxygen to form nitrogen dioxide.  
(d) Its bond order is 2.5.
- Q.15. Which of the following isomers of phosphorus is thermodynamically most stable?
- (a) Red (b) White  
(c) Black (d) Yellow
- Q.16. Which of the following compounds on strong heating evolves ammonia gas?
- (a)  $(\text{NH}_4)_2\text{SO}_4$  (b)  $\text{HNO}_3$   
(c)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (d)  $\text{NH}_3\text{NO}_3$
- Q.17. The formula of pyrosilicate ion is:
- (a)  $\text{SiO}_4^{-4}$  (b)  $\text{Si}_2\text{O}_7^{-6}$   
(c)  $\text{Si}_3\text{O}_9^{-6}$  (d)  $\text{Si}_6\text{O}_{18}^{-12}$
- Q.18. The gaseous product of the reaction of boron trifluoride with tetrahydroborate ion is:
- (a)  $\text{F}_2$  (b)  $\text{HF}$   
(c)  $\text{H}_2$  (d)  $\text{B}_2\text{H}_6$
- Q.19. Which of the following has smallest bond enthalpy?
- (a) Si - H (b) C - H  
(c) Ge - H (d) Pb - H
- Q.20. Silicates with 3D frame work are:
- (a) Niso-silicate (b) Soro-silicate  
(c) Phyllo-silicate (d) Tecto-silicate
- Q.21. A Sodalite cage in zeolites is:
- (a) a truncated tetrahedron (b) an icosahedron  
(c) a truncated octahedron (d) a dodecahedron
- Q.22. Moderate electrical conductivity is shown by:
- (a) Silica (b) Graphite  
(c) Diamond (d) None of these
- Q.23. What is the nature of silicon-oxygen bond in silica?
- (a) Polar covalent (b) Ionic  
(c) Non polar covalent (d) Coordinate Covalent
- Q.24. Which of the following is least stable and has doubtful existence?
- (a)  $\text{CCl}_4$  (b)  $\text{GeI}_4$   
(c)  $\text{SnI}_4$  (d)  $\text{PbI}_4$
- Q.25. Boric acid does not have:
- (a) exists in polymeric form due to inter molecular hydrogen-bonding.  
(b) is used in manufacturing of optical glasses.

- (c) is a tribasic acid.  
(d) with borax, it is used in preparation of a buffer solution.
- Q.26. Name the structure of silicates in which three oxygen atoms of  $[\text{SiO}_4]^{-2}$  are shared is  
(a) Pyrosilicate (b) Sheet-silicate  
(c) Linear chain-silicate (d) Three dimensional-silicate
- Q.27. Egyptian blue  $\text{CaCuSi}_4\text{O}_{10}$  is an example of:  
(a) Sheet-silicate (b) Cyclic-silicate  
(c) Pyrosilicate (d) Chain-silicate
- Q.28. Among the following substituted silanes, the one that gives cross-linked silicone polymer upon hydrolysis is:  
(a)  $(\text{CH}_3)_4\text{Si}$  (b)  $\text{CH}_3\text{SiCl}_3$   
(c)  $(\text{CH}_3)_2\text{SiCl}_2$  (d)  $(\text{CH}_3)_3\text{SiCl}$
- Q.29. The correct statement regarding closo- $\{\text{B}_n\text{H}_n\}$  species is:  
(a) it always has -2 charge.  
(b) it always has +2 charge.  
(c) it is neutral species.  
(d) it is more reactive than nido-, arachno- and hypo-boranes.
- Q.30. The most abundant element in earth's crust is:  
(a) Al (b) Fe  
(c) Si (d) O
- Q.31. Which of the following molecules exists as a monomer under ambient conditions?  
(a) Trimethylaluminium (b) Triethylaluminium  
(c) Triphenylaluminium (d) Trimesitylaluminium
- Q.32. In  $[\text{B}_4\text{O}_5(\text{OH})_4]^{-2}$ , the number of boron atoms having an octet of electrons is :  
(a) 0 (b) 1  
(c) 2 (d) 4
- Q.33. The  $\text{K}_2\text{CO}_3$  is a diamagnetic sesquioxide, and then which is incorrect?  
(a) It is a paramagnetic.  
(b) It is a diamagnetic.  
(c) It has a mixture of peroxide and superoxide.  
(d) It is colored.
- Q.34. In basic beryllium acetate the co-ordination of Be is:  
(a) 4 (b) 3  
(c) 2 (d) 5
- Q.35. The co-ordination number of Li in  $\text{LiCH}_3$  is:  
(a) 7 (b) 6  
(c) 4 (d) 5
- Q.36. In bicyclic cryptands form 1:1 metal complex, which conformation of cryptand is most likely present?



- (a) exo - exo (b) exo - endo  
(c) endo - endo (d) endo - exo
- Q.37. The material used in solar cells contains:  
(a) Cs (b) Si  
(c) Sn (d) Ti
- Q.38. Nitrogen dioxide cannot be prepared by heating:  
(a)  $\text{KNO}_3$  (b)  $\text{Pb}(\text{NO}_3)_2$   
(c)  $\text{Cu}(\text{NO}_3)_2$  (d)  $\text{AgNO}_3$
- Q.39. A solution of sodium metal in liquid ammonia is strongly reducing due to presence of :  
(a) Na atoms (b) NaH  
(c)  $\text{NaNH}_2$  (d) Solvated electrons
- Q.40. In polymeric  $(\text{BeCl}_2)_n$ , there are:  
(a) 3c-2e bonds (b) 3c-3e bonds  
(c) 2c-3e bonds (d) 2c-2e bonds
- Q.41. A metal which does not react with nitrogen is:  
(a) Li (b) K  
(c) Ca (d) Mg
- Q.42. KOH is preferably used to absorb  $\text{CO}_2$  gas because:  
(a) KOH is more soluble than NaOH in water.  
(b) KOH is stronger base than NaOH.  
(c)  $\text{KHCO}_3$  is soluble in water and  $\text{NaHCO}_3$  is sparingly soluble in water.  
(d) KOH is cheaper than NaOH.
- Q.43. HBr and HI reduce sulphuric acid, HCl can reduce  $\text{KMnO}_4$  and HF can reduce:  
(a)  $\text{H}_2\text{SO}_4$  (b)  $\text{KMnO}_4$   
(c)  $\text{K}_2\text{Cr}_2\text{O}_7$  (d) None of these
- Q.44. Chlorine acts as a bleaching agent only in presence of:  
(a) Dry air (b) Moisture  
(c) Sunlight (d) Pure oxygen
- Q.45. The xenon fluoride which is excellent fluorinating agent of aromatic compound, in the presence of Lewis acid, is:  
(a)  $\text{XeF}_6$  (b)  $\text{XeF}_4$   
(c)  $\text{XeF}_2$  (d)  $\text{XeOF}_2$
- Q.46. Which of the following compounds formed by xenon has the same number of valence electron as  $\text{I}_3^-$  ?  
(a)  $\text{XeO}_4$  (b)  $\text{XeF}_4$   
(c)  $\text{XeF}_2$  (d)  $\text{XeO}_3$
- Q.47. The perxenate is  $\text{XeO}_4^{-4}$  can be prepared by:  
(a) Direct reaction of Xe with oxygen.  
(b) Reaction of  $\text{XeF}_6$  with oxygen.  
(c) Hydrolysis of  $\text{XeF}_6$  in acidic medium.

- (d) Hydrolysis of  $\text{XeF}_6$  in basic medium.
- Q.48. Which of the following is not a pseudo halide?  
 (a)  $\text{CNO}^-$  (b)  $\text{RCOO}^-$   
 (c)  $\text{OCN}^-$  (d)  $\text{N}_3^-$
- Q.49. Bromine can be liberated from KBr solution by the action of:  
 (a) Iodine solution (b) Chlorine water  
 (c) NaCl (d) KI
- Q.50. The main products of the reaction of equi molar quantities of  $\text{XeF}_6$  with  $\text{NaNO}_3$  are:  
 (a)  $\text{XeOF}_4$ , NaF and  $\text{NO}_2\text{F}$  (b)  $\text{XeO}_2\text{F}_2$ , NaF, NOF and  $\text{F}_2$   
 (c)  $\text{XeOF}_4$ ,  $\text{NaNO}_2$  and  $\text{F}_2$  (d)  $\text{XeF}_4$ ,  $\text{NaNO}_2$  and  $\text{F}_2\text{O}$
- Q.51. The hybridization of xenon atom in  $\text{XeF}_4$  is:  
 (a)  $\text{sp}^2$  (b)  $\text{sp}^3$   
 (c)  $\text{sp}^3\text{d}$  (d)  $\text{sp}^3\text{d}^2$
- Q.52. Which pair of ions forms the strongest ionic bond?  
 (a)  $\text{Na}^+$  and  $\text{I}^-$  (b)  $\text{Na}^+$  and  $\text{F}^-$   
 (c)  $\text{Na}^+$  and  $\text{Cl}^-$  (d)  $\text{K}^+$  and  $\text{I}^-$
- Q.53. Which of the following molecule has highest dipole moment?  
 (a)  $\text{BCl}_3$  (b)  $\text{CCl}_4$   
 (c)  $\text{NF}_3$  (d)  $\text{NH}_3$
- Q.54. The state of hybridization of Ni in  $\text{K}_2[\text{NiCl}_4]$  is:  
 (a)  $\text{dsp}^2$  (b)  $\text{sp}^3$   
 (c)  $\text{sp}^2\text{d}$  (d)  $\text{d}^3\text{s}$
- Q.55. Which of the following pair is isostructural?  
 (a)  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (b)  $\text{BF}_3$  and  $\text{H}_3\text{C}^+$   
 (c)  $\text{CCl}_4$  and  $\text{PtCl}_4$  (d)  $\text{NH}_3$  and  $\text{BF}_3$
- Q.56. Which of the following chemical species has highest bond order?  
 (a)  $\text{O}_2$  (b)  $\text{O}_2^+$   
 (c)  $\text{O}_2^-$  (d)  $\text{O}_2^{-2}$
- Q.57. Which of the following species is diamagnetic in the ground state?  
 (a)  $\text{O}_2^{-2}$  (b)  $\text{O}_2^-$   
 (c) NO (d)  $\text{O}_2^+$
- Q.58. Which of the following molecules has a dipole moment?  
 (a)  $\text{SF}_6$  (b)  $\text{PCl}_5$   
 (c)  $\text{BF}_3$  (d)  $\text{SF}_4$
- Q.59. In which of the following salt, cation and anion are iso-electronic?  
 (a) LiF (b) NaCl  
 (c) KCl (d) KBr
- Q.60. Which molecule has zero bond order?  
 (a)  $\text{H}_2^+$  (b)  $\text{H}_2$   
 (c) HeH (d)  $\text{He}_2$

- Q.61. Which of following molecules has square planar geometry?  
 (a)  $\text{XeO}_2\text{F}_2$  (b)  $\text{SF}_4$   
 (c)  $\text{BF}_4^-$  (d)  $\text{XeF}_4$
- Q.62. Among the following pentachlorides the one which does not exist due to 'inert pair effect'?  
 (a)  $\text{PCl}_5$  (b)  $\text{BiCl}_5$   
 (c)  $\text{SbCl}_5$  (d)  $\text{AsCl}_5$
- Q.63. The geometries of  $\text{Ni}(\text{CO})_4$  and  $[\text{NiCl}_4]^{2-}$  respectively, are:  
 (a) Tetrahedral and square planar (b) Square planar and tetrahedral  
 (c) Tetrahedral and tetrahedral (d) Square planar and square planar
- Q.64.  $\text{KF}$  combines with  $\text{HF}$  to form  $\text{KHF}_2$ . The compound contains the species :  
 (a)  $\text{K}^+$ ,  $\text{F}^-$  and  $\text{H}^+$  (b)  $\text{K}^+$ ,  $\text{F}^-$  and  $\text{HF}$   
 (c)  $\text{K}^+$  and  $[\text{HF}_2]^-$  (d)  $[\text{KHF}]^+$  and  $\text{F}^-$
- Q.65. Which of the following does not exist in solid state?  
 (i)  $\text{LiHCO}_3$  (ii)  $\text{Ca}(\text{HCO}_3)_2$  (iii)  $\text{Zn}(\text{HCO}_3)_2$  (iv)  $\text{AgHCO}_3$   
 (a) i, ii, iii and iv (b) i, ii, iii  
 (c) i, ii, and iv (d) ii, iii and iv
- Q.66. Melting point of a mixture of  $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$  mixture is:  
 (a) Higher than that of  $\text{Na}_2\text{CO}_3$ .  
 (b) Higher than that of  $\text{K}_2\text{CO}_3$ .  
 (c) Lower than that of both  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .  
 (d) Lower than that of both  $\text{K}_2\text{CO}_3$  only.
- Q.67.  $\text{Li}$  does not resemble with other alkali metals in following properties:  
 (a)  $\text{Li}_2\text{CO}_3$  decomposes into oxides while other alkali metal carbonates are thermally stable.  
 (b)  $\text{LiCl}$  is predominantly covalent.  
 (c)  $\text{Li}_3\text{N}$  is formed when  $\text{Li}$  is heated with  $\text{N}_2$  gas.  
 (d) All are correct.
- Q.68. Which one of the following properties is not shown by  $\text{NO}$ ?  
 (a) It is diamagnetic in gaseous state.  
 (b) It is a neutral oxide.  
 (c) It combines with oxygen to form nitrogen dioxide.  
 (d) Its bond order is 2.5.
- Q.69.  $\text{K}^+$  forms most stable complex with:  
 (a) crypt-221 (b) crypt-222  
 (c) dibenzo crown-6 (d) dicyclohexyl crown-6
- Q.70. The metallic lustre exhibited by sodium metal is explained by:  
 (a) Diffusion of sodium ions.  
 (b) Oscillation of loose electron.  
 (c) Excitation of free protons.

- (d) Existence of body centered cubic lattice.
- Q.71. Calcium is obtained by:
- (a) Electrolysis of molten  $\text{CaCl}_2$ .
  - (b) Electrolysis of solution of  $\text{CaCl}_2$  in water.
  - (c) Reduction of  $\text{CaCl}_2$  with carbon.
  - (d) Roasting of limestone.
- Q.72. The alkali metals which form normal oxide, peroxide as well as super oxides are:
- (a) Na, Li
  - (b) K, Li
  - (c) Li, Cs
  - (d) K, Rb
- Q.73. The compound which does not have -O-O- bond is:
- (a)  $\text{BaO}_2$
  - (b)  $\text{Na}_2\text{O}_2$
  - (c)  $\text{CrO}_5$
  - (d)  $\text{Fe}_2\text{O}_3$
- Q.74. Temporary hardness of water is due to calcium bicarbonate can be removed by adding:
- (a)  $\text{CaCO}_3$
  - (b)  $\text{Ca(OH)}_2$
  - (c)  $\text{CaCl}_2$
  - (d)  $\text{HCl}$
- Q.75. When  $\text{NaNO}_2$  is treated with Na:
- (a)  $\text{NaNO}_3$  is formed
  - (b)  $\text{Na}_2\text{O}$  and  $\text{N}_2$  are formed
  - (c)  $\text{Na}_2\text{O}_2$  and  $\text{N}_2$  are formed
  - (d)  $\text{Na}_2\text{O}$  and  $\text{Na}_3\text{N}$  are formed
- Q.76. To an acidified dichromate solution, a pinch of  $\text{Na}_2\text{O}_2$  is added and shaken. What is observed?
- (a) Blue color.
  - (b) Orange color changing to green directly.
  - (c) Copious evolution of oxygen.
  - (d) Bluish-Green precipitate.
- Q.77. Alkali metals possess metallic luster when freshly cut because:
- (a) They have a hard surface.
  - (b) Their crystal structure contains ordered arrangement of constituent atoms.
  - (c) They contain loosely bound electrons which absorb the photons and then re-emit.
  - (d) They are obtained from the minerals on which light has been falling for years.
- Q.78. Icosahedral structure is generally exhibited by
- (a) C
  - (b) Si
  - (c) Ge
  - (d) B
- Q.79. For borazine, which of the following statement is TRUE?
- (a) N atom is nucleophilic in nature.
  - (b) B atom is nucleophilic in nature.
  - (c) Bond between B and N is non-polar.
  - (d) N atom is electrophilic in nature.
- Q.80. The type of force that holds the layers of C atoms in graphite together is:
- (a) Ionic
  - (b) H-bonding
  - (c) Vander Waals
  - (d) Covalent

**Answers**

1 - (a)	2 - (d)	3 - (b)	4 - (a)	5 - (d)	6 - (a)
7 - (d)	8 - (a)	9 - (b)	10 - (b)	11 - (d)	12 - (a)
13 - (d)	14 - (a)	15 - (c)	16 - (a)	17 - (b)	18 - (d)
19 - (d)	20 - (d)	21 - (c)	22 - (b)	23 - (a)	24 - (d)
25 - (c)	26 - (b)	27 - (a)	28 - (b)	29 - (a)	30 - (d)
31 - (d)	32 - (c)	33 - (b)	34 - (a)	35 - (a)	36 - (c)
37 - (b)	38 - (a)	39 - (d)	40 - (a)	41 - (b)	42 - (c)
43 - (d)	44 - (b)	45 - (b)	46 - (c)	47 - (d)	48 - (b)
49 - (b)	50 - (a)	51 - (d)	52 - (b)	53 - (d)	54 - (b)
55 - (b)	56 - (b)	57 - (a)	58 - (d)	59 - (c)	60 - (d)
61 - (d)	62 - (b)	63 - (c)	64 - (c)	65 - (a)	66 - (c)
67 - (d)	68 - (a)	69 - (b)	70 - (b)	71 - (a)	72 - (d)
73 - (d)	74 - (b)	75 - (b)	76 - (a)	77 - (c)	78 - (d)
79 - (d)	80 - (c)				

## Chapter 9

### Chemical Bonding

(Contributed by: Dr. Punam Yadav, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- The molecules  $\text{NO}_2$  is paramagnetic while  $\text{N}_2\text{O}_4$  is diamagnetic.
- The bond energies of  $\text{H}_2$ ,  $\text{F}_2$  and  $\text{Cl}_2$  decrease in the following order:  

$$\text{H}_2 > \text{Cl}_2 > \text{F}_2$$
- $\text{NaCl}$  has ionic bonding and  $\text{Kr}$  has van der Waals interaction.
- The bond angle of  $\text{Cl}_2\text{O}$  is greater than that of  $\text{H}_2\text{O}$ .
- $\text{S}_2$  and  $\text{O}_2$  gases are paramagnetic in nature.
- $\text{BF}_3$  and  $\text{N}(\text{SiH}_3)_3$  show back donation.
- $\text{P}_2$  converts into  $\text{P}_4$  due to weak  $\text{P}_\pi\text{-P}_\pi$  bonding.
- Number of co-ordinate bonds in  $\text{BeH}_4^{2-}$  are two.
- The cyanide ion,  $\text{CN}^-$  and  $\text{N}_2$  are isoelectronic, but in contrast to  $\text{CN}^-$ ,  $\text{N}_2$  is chemically inert, because of the presence of more number of electrons in bonding orbital's.
- $\text{H}_2\text{O}_2$  contains both polar and non-polar bonds.
- $\text{CaC}_2$  contains one  $\sigma$  and two  $\pi$  bonds between the carbon atoms.
- The hybridization of sulphur in sulphur dioxide is  $\text{sp}^2$ .
- The  $\text{d}_\pi\text{-p}_\pi$  bond is possible in phosphate ion.
- $\text{I}_3^-$  ion is linear having and having  $\text{sp}^3\text{d}$  hybridization.
- Carbon and sulphur atoms form discrete polyatomic molecules in its elemental state.
- The  $\text{Si}-\text{O}-\text{Si}$  bond angle in  $\text{Me}_3\text{SiOSiMe}_3$  is  $180^\circ$ .
- According to VSEPR theory, sulphate ion has ideal tetrahedral shape.
- If  $\text{CH}_4$  is assumed to give two disubstituted products. Then the shape of  $\text{CH}_4$  will be square planar.
- Hybridization state of boron and oxygen in boric acid is  $\text{sp}^2$  and  $\text{sp}^3$  respectively.
- Bond angle in white phosphorous is  $60^\circ$ .
- Hybridization of  $\text{Si}$  in  $\text{Si}_4\text{O}_{11}^{6-}$  is  $\text{sp}^3$ .
- Hybridization and shape of  $\text{N}(\text{SiH}_3)_3$  is  $\text{sp}^2$  and planar.
- Shape of  $\text{O}_2\text{F}_2$  is similar to that of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{Cl}_2$ .
- Maximum number of bond pair can be held by  $\text{N}$  is four.
- $\text{P}_2$  converts into  $\text{P}_4$  due to weak  $\text{P}_\pi\text{-P}_\pi$  bonding.
- The bond angle of  $\text{Cl}_2\text{O}$  is greater than that of  $\text{H}_2\text{O}$ .

## Multiple Choice Questions

- Q.1. Among following species the iso-structural species are:  
 (I) BN (II)  $\text{CO}^{++}$  (III)  $\text{CN}^+$  (IV)  $\text{CN}_2^{2-}$   
 (a) I, II (b) I, II, III  
 (c) III, IV (d) I, II, III, IV
- Q.2. Correct order of bond angles is:  
 (a)  $\text{PF}_3 < \text{PH}_3$  (b)  $\text{AsH}_3 < \text{SbH}_3$   
 (c)  $\text{OH}_2 < \text{OF}_2$  (d)  $\text{OF}_2 > \text{OCl}_2$
- Q.3. The compound pair which show correct order of angle is:  
 (I)  $\text{NH}_3 > \text{PH}_3$  (II)  $\text{H}_2\text{S} < \text{H}_2\text{O}$  (III)  $\text{NO}_2^+ > \text{NO}_2$   
 (IV)  $\text{NO}_2^+ > \text{NO}_2^-$  (V)  $\text{NO}_2^- > \text{NO}_2^+$   
 (a) I, II, V (b) II, III, IV, V  
 (c) I > II, III, IV (d) I, II, III, IV
- Q.4. The  $X^*$  molecular orbital in ethane is:  
 (a) Symmetric under inversion and anti-symmetric under reflection about the plane of the molecule.  
 (b) Anti-symmetric under inversion and symmetric under reflection about the plane of the molecule.  
 (c) Symmetric under inversion and symmetric under reflection about the plane of the molecule.  
 (d) Anti-symmetric under inversion and anti-symmetric under reflection about the plane of the molecule.
- Q.5. The bond energies of  $\text{H}_2$ ,  $\text{F}_2$  and  $\text{Cl}_2$  decrease in the following order  
 (a)  $\text{H}_2 > \text{F}_2 > \text{Cl}_2$  (b)  $\text{Cl}_2 > \text{F}_2 > \text{H}_2$   
 (c)  $\text{F}_2 > \text{Cl}_2 > \text{H}_2$  (d)  $\text{H}_2 > \text{Cl}_2 > \text{F}_2$
- Q.6. Arrange the following molecules in order of increasing bond polarity  
 (1)  $\text{H}_2\text{O}$  (2)  $\text{NH}_3$  (3)  $\text{PH}_3$  (4)  $\text{H}_2\text{S}$   
 (a)  $1 < 2 < 3 < 4$  (b)  $4 < 3 < 2 < 1$   
 (c)  $3 < 4 < 2 < 1$  (d)  $3 < 4 < 1 < 2$
- Q.7. The element NaCl and Kr crystallize in a cubic structure. While NaCl is a solid at room temperature, Kr is a gas? The reason for this is:  
 (a) NaCl has covalent bonding and Kr has metallic bonding.  
 (b) NaCl has ionic bonding and Kr has covalent bonding.  
 (c) NaCl has ionic bonding and Kr has vander waals interaction.  
 (d) NaCl has ionic bonding and Kr has hydrogen bonding.
- Q.8. The molecules  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are respectively:  
 (a) Diamagnetic, paramagnetic  
 (b) Paramagnetic, paramagnetic  
 (c) Paramagnetic, diamagnetic  
 (d) Diamagnetic, diamagnetic
- Q.9. The bond angle of  $\text{Cl}_2\text{O}$  is:  
 (a) Smaller than that of  $\text{F}_2\text{O}$  (b) Smaller than that of  $\text{H}_2\text{O}$   
 (c) Greater than that of  $\text{H}_2\text{O}$  (d) Same as that of  $\text{F}_2\text{O}$
- Q.10. Which is/are paramagnetic among:  
 (I)  $\text{S}_2(\text{gas})$  (II)  $\text{O}_2$  (III)  $\text{NO}_2^+$  (IV)  $\text{CaH}_2$

- (a) I, II (b) I, II, III  
(c) II only (d) all
- Q.11. The molecule which show back donation is:  
(a)  $\text{BF}_3$  (b)  $\text{N}(\text{SiH}_3)_3$   
(c) Both (d) None
- Q.12.  $\text{P}_2$  converts into  $\text{P}_4$  due to:  
(a) Weak  $\text{P}_\pi\text{-P}_\pi$  bonding (b) Strong  $\text{P}_\pi\text{-P}_\pi$  bonding  
(c) Strong  $\text{P}_\pi\text{-d}_\pi$  bonding (d) Weak sigma bonding
- Q.13. Number of co-ordinate bonds in  $\text{BeH}_4^{2-}$  are:  
(a) 2 (b) 1  
(c) 3 (d) zero
- Q.14. Which has an exact angle of  $120^\circ$  among the following?  
(a)  $\text{C}_2\text{H}_4$  (b)  $\text{BF}_3$   
(c)  $\text{HCHO}$  (d) All
- Q.15. Maximum number of bond pair can be holded by N is:  
(a) 2 (b) 3  
(c) 4 (d) 5
- Q.16. Correct order of bond angle among the following molecules is:  
(a)  $\text{OCl}_2 > \text{OH}_2 > \text{OF}_2$  (b)  $\text{OCl}_2 < \text{OH}_2 < \text{OF}_2$   
(c)  $\text{OH}_2 < \text{OF}_2 < \text{OCl}_2$  (d)  $\text{OH}_2 < \text{OCl}_2 < \text{OF}_2$
- Q.17. Correct order of bond angle among the following molecules is:  
(a)  $\text{AsH}_3 < \text{AsF}_3 < \text{AsCl}_3$  (b)  $\text{AsH}_3 > \text{AsF}_3 > \text{AsCl}_3$   
(c)  $\text{AsH}_3 < \text{AsCl}_3 < \text{AsF}_3$  (d)  $\text{AsH}_3 > \text{AsCl}_3 > \text{AsF}_3$
- Q.18. Which of the following does not exist?  
(a)  $\text{PH}_5$  (b)  $\text{PCl}_5$   
(c)  $\text{NI}_3$  (d) A and C both
- Q.19. Which will have highest dipole moment?  
(a) o-Chloro Toluene (b) m-Chloro Toluene  
(c) p-Chloro Toluene (d) o-Dichloro Benzene
- Q.20. Which is most polar bond among the following?  
(a) S-Cl (b) Se-Cl  
(c) S-Br (d) Se-Br
- Q.21. Which will have zero dipole moment among the following molecule?  
(a)  $\text{O}_2\text{F}_2$  (b)  $\text{H}_2\text{O}_2$   
(c)  $\text{MnO}_4^-$  (d) All
- Q.22. Shape of  $\text{O}_2\text{F}_2$  is similar to that of:  
(a)  $\text{H}_2\text{O}_2$  (b)  $\text{S}_2\text{Cl}_2$   
(c)  $\text{CH}_3\text{-O-C}_6\text{H}_5\text{-OCH}_3$  (d) All
- Q.23. Which of the following molecule has highest dipole moment?  
(a)  $\text{CF}_4$  (b)  $\text{MnO}_4^-$   
(c)  $\text{CH}_3\text{OH}$  (d)  $\text{NCl}_3$
- Q.24. How many  $\pi$  bonds are present in  $\text{P}_2\text{O}_5$  molecule?  
(a) 4 (b) 2  
(c) 3 (d) Zero
- Q.25. Which of the following bond is least covalent in nature?  
(a) S-F in  $\text{SF}_2$  (b) S-F in  $\text{SF}_4$



- (c) S-F in  $\text{SF}_6$  (d) All have equally covalent nature
- Q.26. In which process the hybridization state of boron is not changed in the last product (adduct):  
 (a)  $\text{BF}_3 + \text{THF} \rightarrow \text{Adduct}$  (b)  $\text{BF}_3 + \text{H}_2\text{O} \rightarrow \text{Product}$   
 (c)  $\text{BF}_3 + \text{SbF}_5 \rightarrow \text{Product}$  (d)  $\text{H}_3\text{BO}_3 + \text{NaCO}_3 \rightarrow \text{Product}$
- Q.27. Which have trigonal planar geometry?  
 (a)  $\text{SF}_4$  (b)  $\text{XeO}_3$   
 (c)  $\text{BF}_3$  (d)  $\text{CO}_2$
- Q.28. Formula of a metal oxide is  $\text{MO}$ , formula of its phosphate will be:  
 (a)  $\text{M}_3(\text{PO}_4)_2$  (b)  $\text{MPO}_4$   
 (c)  $\text{M}_3(\text{H}_2\text{PO}_4)_2$  (d)  $\text{M}_2(\text{PO}_4)_3$
- Q.29. Correct order of bond angles among the following molecules are:  
 (a)  $\text{H}_2\text{S} < \text{NH}_3 < \text{SiH}_4 < \text{BF}_3$  (b)  $\text{NH}_3 < \text{H}_2\text{S} < \text{SiH}_4 < \text{BF}_3$   
 (c)  $\text{H}_2\text{S} < \text{SiH}_4 < \text{NH}_3 < \text{BF}_3$  (d)  $\text{H}_2\text{S} < \text{NH}_3 < \text{BF}_3 < \text{SiH}_4$
- Q.30. Hybridisation in  $\text{MnO}_4^-$  is:  
 (a)  $sd^3$  (b)  $sp^3$   
 (c)  $p^3d$  (d)  $dsp^3$
- Q.31. Angles in  $\text{XeO}_3\text{F}_2$  are equal with which molecule:  
 (a)  $\text{PBr}_3\text{F}_2$  (b)  $\text{XeO}_2\text{F}_2$   
 (c)  $\text{BrF}_3$  (d) All
- Q.32. For hybridization which statement is incorrect?  
 (a) Different orbitals are mixed. (b) Hybrid from sigma bonds only.  
 (c) Hybrid orbitals are lower in energy than atomic orbitals  
 (d) Hybridization can be shown experimentally.
- Q.33. Hybridization in boron is  $\text{BF}_3$ - ether mixture is:  
 (a)  $sp^3$  (b)  $sp^2$   
 (c)  $sp$  (d)  $sp^3d$
- Q.34. Maximum number of atoms in same central plane in  $\text{PCl}_5$  is:  
 (a) 4 (b) 3  
 (c) 2 (d) 6
- Q.35. Hybridization on anionic carbon in allyl anion is:  
 (a)  $sp^2$  (b)  $sp^3$   
 (c)  $sp$  (d)  $sp^3d$
- Q.36. Hybridization and shape of  $\text{N}(\text{SiH}_3)_3$  is:  
 (a)  $sp^3$ , tetrahedral (b)  $sp^2$ , planar  
 (c)  $sp^3$ , planar (d)  $sp^2$ , angular
- Q.37. Hybridization in  $(\text{C}_6\text{H}_5)_3\text{C}^-$  (on negative carbon) is:  
 (a)  $sp^2$  (b)  $sp^3$   
 (c)  $sp$  (d)  $sp^3d$
- Q.38. Hybridization in carbon suboxide ( $\text{C}_3\text{O}_2$ ) and  $\text{CO}_2$  are:  
 (a)  $sp$  in both (b)  $sp$  and  $sp^2$   
 (c)  $sp^2$  and  $sp$  (d)  $sp^3$  and  $sp$
- Q.39. Hybridization on central atom in  $\text{SOF}_4$  is:  
 (a)  $sp^2$  (b)  $sp^3$   
 (c)  $dsp^3$  (d)  $sp^3d$
- Q.40. Hybridization on central atom in  $\text{Be}_2\text{C}$  is:

- (a)  $sp^2$  (b)  $sp^3$   
(c)  $sp$  (d) None
- Q.41. Hybridization of central atom in  $O_2^-H_3$  is:  
(a)  $sp^2$  (b)  $sp^3$   
(c)  $dsp^2$  (d)  $sp^3d$
- Q.42. Hybridization of Si in  $Si_4O_{11}^{6-}$  is:  
(a)  $sp^2$  (b)  $sp^3$   
(c)  $sp^3d^2$  (d)  $sp^3d$
- Q.43. Number of singlet linkages in  $TeBr_4$  are:  
(a) 2 (b) 3  
(c) 1 (d) 4
- Q.44. In a regular octahedral molecule  $MX_6$  the No. of X-M-X bonds at  $180^\circ$  is:  
(a) 2 (b) 3  
(c) 6 (d) 4
- Q.45. In octahedral structure the pair of d-orbital's involved is:  
(a)  $d_{xy}$  and  $d_{yz}$  (b)  $d_{x^2-y^2}$  and  $d_z^2$   
(c)  $d_{xy}$  and  $d_{x^2-y^2}$  (d)  $d_z^2$  and  $d_{xy}$
- Q.46. The ONO angle is maximum in:  
(a)  $NO_3^-$  (b)  $NO_2^-$   
(c)  $NO_2$  (d)  $NO_2^+$
- Q.47. The number of H-C-H bond angles in  $CH_4$  are:  
(a) 4 (b) 2  
(c) 1 (d) 6
- Q.48. Bond angle in white phosphorous is:  
(a)  $60^\circ$  (b)  $90^\circ$   
(c)  $109^\circ 28'$  (d) Zero
- Q.49. Hybridization state of boron and oxygen in boric acid is:  
(a)  $sp^3, sp^2$  (b)  $sp^2, sp^3$   
(c)  $sp^2, sp^2$  (d)  $sp^3, sp^3$
- Q.50. Which is correct order of bond angle:  
(a)  $CCl_4 > BF_3 > NO_2^+$  (b)  $NH_3 > NCl_3 > NBr_3$   
(c)  $Br_2O > Cl_2O > OF_2$  (d)  $PCl_3 > PBr_3 > PI_3$
- Q.51. If  $CH_4$  is assumed to give two disubstituted products. Then the shape of  $CH_4$  will be:  
(a) Tetrahedral (b) Square planar  
(c) Trigonal bi pyramidal (d) Pyramidal
- Q.52. Which is not paramagnetic among the following molecules?  
(a)  $B_2$  (b)  $C_2$   
(c)  $O_2$  (d) None
- Q.53. Structure of  $SbF_4^-$  is similar with:  
(a)  $SF_4$  (b)  $XeOF_4$   
(c)  $ClF_4$  (d)  $XeO_4$
- Q.54. The correct non-linear and iso-structural pair is:  
(a)  $SCl_2$  and  $I_3$  (b)  $SCl_2$  and  $I_3^+$   
(c)  $SCl_2$  and  $ClF_2^-$  (d)  $I_3^+$  and  $ClF_2^-$
- Q.55. According to VSEPR theory, the molecule having ideal tetrahedral shape is:  
(a)  $SF_4$  (b)  $SO_4^{2-}$

- (c)  $\text{S}_2\text{Cl}_2$  (d)  $\text{SO}_2\text{Cl}_2$
- Q.56. The Si – O – Si bond angle in  $\text{Me}_3\text{SiOSiMe}_3$  is:  
 (a)  $\sim 120^\circ$  (b)  $\sim 180^\circ$   
 (c)  $\sim 90^\circ$  (d)  $\sim 109^\circ$
- Q.57. Among the following pairs in which the two species are not isostructural is:  
 (a)  $\text{IO}_3^-$  and  $\text{XeO}_3$  (b)  $\text{BH}_4^-$  and  $\text{NH}_4^+$   
 (c)  $\text{PF}_6^-$  and  $\text{SF}_6$  (d)  $\text{SiF}_4$  and  $\text{SF}_4$
- Q.58. The atoms that form discrete polyatomic molecule in its elemental state are:  
 (a) C and S (b) C and O  
 (c) N and S (d) C and F
- Q.59. Which of the following species has two nonbonded electron pairs on the central atom?  
 (a)  $\text{TeCl}_4$  (b)  $\text{ClF}_3$   
 (c)  $\text{ICl}_2^-$  (d)  $\text{PCl}_3$
- Q.60.  $\text{I}_3^-$  ion is linear having the hybridization:  
 (a) sp (b)  $\text{sp}^2$   
 (c)  $\text{sp}^3\text{d}$  (d)  $\text{sp}^3$
- Q.61. Among the molecular ions the  $\text{d}_\pi\text{-p}_\pi$  bond is possible in:  
 (a)  $\text{NO}_3^-$  (b)  $\text{PO}_4^{3-}$   
 (c)  $\text{CO}_3^{2-}$  (d)  $\text{NO}_2^-$
- Q.62. Which of the following compound is covalent?  
 (a)  $\text{H}_2$  (b)  $\text{CaO}$   
 (c)  $\text{KCl}$  (d)  $\text{Na}_2\text{S}$
- Q.63. If a molecule  $\text{MX}_3$  has zero dipole moment, the sigma bonding orbital's used by M (atomic number < 21) are:  
 (a) Pure p (b) sp hybridized  
 (c)  $\text{sp}^2$  hybridized (d)  $\text{sp}^3$  hybridized
- Q.64. The ion that is isoelectronic with CO is:  
 (a)  $\text{CN}^-$  (b)  $\text{O}_2^+$   
 (c)  $\text{O}_2^-$  (d)  $\text{N}_2^+$
- Q.65. Which one among the following does not have the hydrogen bond?  
 (a) Phenol (b) Liquid  $\text{NH}_3$   
 (c) Water (d)  $\text{HCl}$
- Q.66. The hybridization of sulphur in sulphur dioxide is:  
 (a) sp (b)  $\text{sp}^3$   
 (c)  $\text{sp}^2$  (d)  $\text{dsp}^2$
- Q.67. The species in which the central atom uses  $\text{sp}^2$ - hybrid orbital's in its bonding is:  
 (a)  $\text{PH}_3$  (b)  $\text{NH}_3$   
 (c)  $\text{CH}_3^+$  (d)  $\text{SbH}_3$
- Q.68. The molecule that has linear structure is:  
 (a)  $\text{CO}_2$  (b)  $\text{NO}_2$   
 (c)  $\text{SO}_2$  (d)  $\text{SiO}_2$
- Q.69. The molecule which has zero dipole moment is:  
 (a)  $\text{CH}_2\text{Cl}_2$  (b)  $\text{BF}_3$   
 (c)  $\text{NF}_3$  (d)  $\text{ClO}_2$
- Q.70. The molecule which has pyramidal shape is:  
 (a)  $\text{PCl}_3$  (b)  $\text{SO}_3$

- (c)  $\text{CO}_3^{2-}$  (d)  $\text{NO}_3^-$
- Q.71. The type of hybrid orbital's used by the chlorine atom in  $\text{ClO}_2^-$  is:  
 (a)  $\text{sp}^3$  (b)  $\text{sp}^2$   
 (c)  $\text{sp}$  (d) None of these
- Q.72. Which one of the following molecules is planar?  
 (a)  $\text{NF}_3$  (b)  $\text{NCl}_3$   
 (c)  $\text{PH}_3$  (d)  $\text{BF}_3$
- Q.73. The number and type of bonds between two carbon atoms in  $\text{CaC}_2$  are:  
 (a) One sigma and one pi bond (b) One sigma and two pi bonds  
 (c) One sigma and one half pi bonds (d) One sigma bond
- Q.74. Arrange the following compounds in order of increasing dipole moment, toluene(I), m-dichlorobenzene(II), o-dichlorobenzene(III), p-dichlorobenzene(IV):  
 (a)  $\text{I} < \text{IV} < \text{II} < \text{III}$  (b)  $\text{IV} < \text{I} < \text{II} < \text{III}$   
 (c)  $\text{IV} < \text{I} < \text{III} < \text{II}$  (d)  $\text{IV} < \text{II} < \text{I} < \text{III}$
- Q.75. The cyanide ion,  $\text{CN}^-$  and  $\text{N}_2$  are isoelectronic, but in contrast to  $\text{CN}^-$ ,  $\text{N}_2$  is chemically inert, because of:  
 (a) Low bond energy. (b) Absence of bond polarity.  
 (c) Unsymmetrical electron distribution.  
 (d) Presence of more number of electrons in bonding orbital's.
- Q.76. Among  $\text{KO}_2$ ,  $\text{AlO}_2^-$ ,  $\text{BaO}_2$  and  $\text{NO}_2^+$  unpaired electron is present in:  
 (a)  $\text{NO}_2^+$  and  $\text{BaO}_2$  (b)  $\text{KO}_2$  and  $\text{AlO}_2^-$   
 (c)  $\text{KO}_2$  only (d)  $\text{BaO}_2$  only
- Q.77. Which contain both polar and non-polar bonds?  
 (a)  $\text{NH}_4\text{Cl}$  (b)  $\text{HCN}$   
 (c)  $\text{H}_2\text{O}_2$  (d)  $\text{CH}_4$
- Q.78. Which one of the following compounds has  $\text{sp}^2$ - hybridization?  
 (a)  $\text{CO}_2$  (b)  $\text{SO}_2$   
 (c)  $\text{N}_2\text{O}$  (d)  $\text{CO}$
- Q.79. The geometry and the type of hybrid orbital present about the central atom in  $\text{BF}_3$  is:  
 (a) Linear,  $\text{sp}$  (b) Trigonal planar,  $\text{sp}^2$   
 (c) Tetrahedral,  $\text{sp}^3$  (d) Pyramidal,  $\text{sp}^3$
- Q.80. In compounds of type  $\text{ECl}_3$ , where  $\text{E}=\text{B}, \text{P}, \text{As}$  or  $\text{Bi}$  the angles  $\text{Cl-E-Cl}$  are:  
 (a)  $\text{B} > \text{P} = \text{As} = \text{Bi}$  (b)  $\text{B} > \text{P} > \text{As} > \text{Bi}$   
 (c)  $\text{B} < \text{P} = \text{As} = \text{Bi}$  (d)  $\text{B} < \text{P} < \text{As} < \text{Bi}$

**Answers**

1 - (d)	2- (c)	3- (c)	4- (a)	5- (d)	6- (c)
7 - (c)	8 - (c)	9 - (c)	10- (a)	11 - (c)	12 - (a)
13- (a)	14- (b)	15- (c)	16- (a)	17- (a)	18- (d)
19- (a)	20- (b)	21- (c)	22- (d)	23- (c)	24- (c)
25- (a)	26- (d)	27- (c)	28- (a)	29- (a)	30- (b)
31- (a)	32- (d)	33- (a)	34- (a)	35- (a)	36- (b)
37- (a)	38- (a)	39- (d)	40- (a)	41- (b)	42- (b)
43- (a)	44- (b)	45- (b)	46- (d)	47- (d)	48- (a)
49- (b)	50- (c)	51- (b)	52- (b)	53- (a)	54- (b)
55- (b)	56- (b)	57- (d)	58- (a)	59- (b)	60- (c)
61- (b)	62- (a)	63- (c)	64- (a)	65- (d)	66- (c)
67- (c)	68- (a)	69- (b)	70- (a)	71- (a)	72- (d)
73- (b)	74- (b)	75- (d)	76- (c)	77- (c)	78- (b)
79- (b)	80- (b)				

## Chapter 10

### Periodicity

(Contributed by: Dr. Punam Yadav, Department of Chemistry, M. S. College, Saharanpur)

#### Critical Points:

- Chromium and lead can exhibit more than one oxidation states in compounds.
- The basic anhydride of  $\text{Ba(OH)}_2$  is  $\text{BaO}$ .
- $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}$  etc oxides are neutral in nature.
- Seventeenth group elements have maximum electron affinity in the periodic table.
- Eighteenth group elements have maximum ionization energy in the periodic table.
- Electron affinity of eighteenth group elements is zero.
- Electron gain enthalpy of eighteenth group elements is a positive value because energy has to be supplied for the addition of electron to a inert electronic configuration.
- Second electron gain enthalpy of all the elements is a positive value because energy has to be supplied for the addition of electron to a negatively charged ion.
- The properties of elements are the periodic function of their atomic numbers.
- Non metallic elements are lesser in number than metallic elements.
- The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
- The electron affinity of the members of oxygen family of the periodic table follows the sequence:  
$$\text{S} > \text{O} < \text{Se}$$
- The correct order of second ionization potential of C, N, O and F is:  
$$\text{O} > \text{F} > \text{N} > \text{C}$$
- The first ionization potential in electron volts of nitrogen and oxygen atoms are 14.6 and 13.6 eV respectively.
- In the periodic table on moving from left to right along a period the first ionization potential of the elements increases.
- In the periodic table on moving from left to right along a period the atomic and ionic radii of the elements decreases.
- In the periodic table on moving from left to right along a period the electron affinity of the elements increases.
- The size of isoelectronic species  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{Na}^+$  is affected by

## Multiple Choice Questions

- Q.1. The statement that is not correct for the periodic classification of elements is:
- The properties of elements are the periodic function of their atomic numbers.
  - Non metallic elements are lesser in number than metallic elements.
  - The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
  - For transition elements the d subshells are filled electrons monotonically with increase in atomic number.
- Q.2. Which has maximum polarizing power of cation?
- $\text{Li}^+$
  - $\text{Mg}^{2+}$
  - $\text{Al}^{3+}$
  - $\text{O}^{2-}$
- Q.3. The size of the following species increase in the order:
- $\text{Mg}^{+2} < \text{Na}^+ < \text{F}^- < \text{Ar}$
  - $\text{F}^- < \text{Ar} < \text{Na}^+ < \text{Mg}^{+2}$
  - $\text{Ar} < \text{Mg}^{+2} < \text{F}^- < \text{Na}^+$
  - $\text{Na}^+ < \text{Ar} < \text{F}^- < \text{Mg}^{+2}$
- Q.4. The element in which maximum ionization energy of the following Electronic Configuration would be:
- $[\text{Ne}]3s^2 3p^1$
  - $[\text{Ne}]3s^2 3p^2$
  - $[\text{Ne}]3s^2 3p^3$
  - $[\text{Ar}]3d^{10} 4s^2 4p^3$
- Q.5. The outermost electronic configuration of most electronegative element is:
- $ns^2 np^1$
  - $ns^2 np^4$
  - $ns^2 np^5$
  - $ns^2 np^6$
- Q.6. The electron affinity of the members of oxygen family of the periodic table follows the sequence:
- $\text{O} > \text{S} > \text{Se}$
  - $\text{S} > \text{O} < \text{Se}$
  - $\text{O} < \text{S} > \text{Se}$
  - $\text{Se} > \text{O} > \text{S}$
- Q.7. The process that requires absorption of energy is:
- $\text{F} \rightarrow \text{F}^-$
  - $\text{Cl} \rightarrow \text{Cl}^-$
  - $\text{O}^- \rightarrow \text{O}^{2-}$
  - $\text{H} \rightarrow \text{H}^-$
- Q.8. In the following which configuration has maximum electro-negativity?
- $1s^2 2s^2 2p^5$
  - $1s^2 2s^2 2p^6$
  - $1s^2 2s^2 2p^4$
  - $1s^2 2s^2 2p^6 3s^2 3p^3$
- Q.9. Highest size will be of:
- $\text{Br}^-$
  - I
  - I<sup>-</sup>
  - I<sup>+</sup>
- Q.10. The correct order of second ionization potential of C, N, O and F is:
- $\text{C} > \text{N} > \text{O} > \text{F}$
  - $\text{O} > \text{N} > \text{F} > \text{C}$
  - $\text{O} > \text{F} > \text{N} > \text{C}$
  - $\text{F} > \text{O} > \text{N} > \text{C}$
- Q.11. Decreasing ionization potential for K, Ca and Ba is:
- $\text{Ba} > \text{K} > \text{Ca}$
  - $\text{Ca} > \text{Ba} > \text{K}$

- (c)  $K > Ba > Ca$  (d)  $Ca > K > Ba$
- Q.12. Element Hg has two oxidation states  $Hg^{+1}$  and  $Hg^{+2}$  the right order of radii of these ions is:  
 (a)  $Hg^{+1} < Hg^{+2}$  (b)  $Hg^{+2} < Hg^{+1}$   
 (c)  $Hg^{+1} = Hg^{+2}$  (d) None
- Q.13. The ionization energy will be maximum for the process:  
 (a)  $Ba \rightarrow Ba^{++}$  (b)  $Be \rightarrow Be^{++}$   
 (c)  $Cs \rightarrow Cs^{+}$  (d)  $Li \rightarrow Li^{+}$
- Q.14. The first ionization potential of Na, Mg, Al and Si are in the order:  
 (a)  $Na < Mg > Al < Si$  (b)  $Na > Mg > Al > Si$   
 (c)  $Na < Mg < Al > Si$  (d)  $Na > Mg > Al < Si$
- Q.15. Electron affinity is positive when  
 (a)  $O^{-}$  is formed from O (b)  $O^{2-}$  is formed from  $O^{-}$   
 (c)  $O^{+}$  is formed from O (d)  $Na^{+} + e \rightarrow Na$
- Q.16. Which of the following elements has the highest value of electron affinity?  
 (a) O (b) S  
 (c) Se (d) Te
- Q.17. The outer most electronic configuration of the most electronegative element is:  
 (a)  $ns^2 np^3$  (b)  $ns^2 np^4$   
 (c)  $ns^2 np^5$  (d)  $ns^2 np^6$
- Q.18. Which of the following represent the correct order of electron affinities?  
 (a)  $Cl > Br > I > F$  (b)  $Cl > F < Br < I$   
 (c)  $F > Cl > Br > I$  (d)  $Cl > F > Br > I$
- Q.19. The correct order of increasing first ionization energy is:  
 (a)  $C > B > Be > Li$  (b)  $C > Be > B > Li$   
 (c)  $B > C > Be > Li$  (d)  $Be > Li > B > C$
- Q.20. The set representing correct order of first ionization potential is:  
 (a)  $K > Na > Li$  (b)  $Be > Mg > Ca$   
 (c)  $B > C > N$  (d)  $Ge > Si > C$
- Q.21. Which of the following does not reflect the periodicity of elements?  
 (a) Bonding behavior (b) Electronegativity  
 (c) Ionization potential (d) Neutron/proton ratio
- Q.22. Which of the following ions has highest value of ionic radius?  
 (a)  $Li^{+}$  (b)  $B^{3+}$   
 (c)  $O^{2-}$  (d)  $F^{-}$
- Q.23. The correct order of first ionization potential among following elements is:  
 (a)  $B < Be < C < O < N$  (b)  $B < Be < C < N < O$   
 (c)  $Be < B < C < N < O$  (d)  $Be < B < C < O < N$
- Q.24. The decreasing order of the first ionization energy of the following element is:  
 (a)  $Xe > Be > As > Al$  (b)  $Xe > As > Al > Be$   
 (c)  $Xe > As > Be > Al$  (d)  $Xe > Be > Al > As$
- Q.25. Which of the following configuration is expected to have maximum difference in second and third ionization energies:  
 (a)  $1s^2 2s^2 2p^6$  (b)  $1s^2 2s^2 2p^6 3s^1$   
 (c)  $1s^2 2s^2 2p^6 3s^2$  (d)  $1s^2 2s^2 2p^1$
- Q.26. The correct order of second ionization potential of carbon, nitrogen, oxygen and Fluorine is:



- (a)  $C > N > O > F$  (b)  $O > N > F > C$   
 (c)  $O > F > N > C$  (d)  $F > O > N > C$
- Q.27. The element with the highest first ionization potential is:  
 (a) Boron (b) Carbon  
 (c) Nitrogen (d) Oxygen
- Q.28. The hydration energy of  $Mg^{2+}$  is larger than that of:  
 (a)  $Al^{3+}$  (b)  $Na^+$   
 (c)  $Be^{2+}$  (d)  $Mg^{3+}$
- Q.29. The first ionization potential in electron volts of nitrogen and oxygen atoms are respectively given by:  
 (a) 14.6, 13.6 (b) 13.6, 14.6  
 (c) 13.6, 13.6 (d) 14.6, 14.6
- Q.30. The electro negativity of the following elements increases in the order:  
 (a) C, N, Si, P (b) N, Si, C, P  
 (c) Si, P, C, N (d) P, Si, N, C
- Q.31. Which one of the following is the smallest in size?  
 (a)  $N^{3-}$  (b)  $O^{2-}$   
 (c)  $F^-$  (d)  $Na^+$
- Q.32. The ions  $O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}$  are isoelectronic. Their ionic radii show:  
 (a) A significant decrease from  $O^{2-}$  to  $Al^{3+}$ .  
 (b) An increase from  $O^{2-}$  to  $F^-$  and then decrease from  $Na^+$  to  $Al^{3+}$ .  
 (c) A decrease from  $O^{2-}$  to  $F^-$  and then increase from  $Na^+$  to  $Al^{3+}$ .  
 (d) A significant increase from  $O^{2-}$  to  $Al^{3+}$ .
- Q.33. Which of the following oxide is neutral?  
 (a) CO (b)  $SnO_2$   
 (c) ZnO (d)  $SiO_2$
- Q.34. Which one of the following is correct:  
 (a)  $Ti^{4+} < Mn^{7+}$  (b)  $^{35}_{17}Cl < ^{37}_{17}Cl$   
 (c)  $K^+ > Cl^-$  (d)  $P^{3+} < P^{5+}$
- Q.35. 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)  $K_2O > CaO > MgO$
- Q.36. The set representing the correct order of first ionization potential is:  
 (a)  $K > Na > Li$  (b)  $Be > Mg > Ca$   
 (c)  $B > C > N$  (d)  $Ge > Si > C$
- Q.37. Identify the correct order of acidic strength  
 (a)  $CaO < CuO < H_2O < CO_2$  (b)  $H_2O < CuO < CaO < CO_2$   
 (c)  $CaO < H_2O < CuO < CO_2$  (d)  $H_2O < CO_2 < CaO < CuO$
- Q.38. The series with the correct order of decreasing ionic size is:  
 (a)  $K^+ > Ca^{2+} > S^{2-} > Cl^-$  (b)  $S^{2-} > Cl^- > K^+ > Ca^{2+}$   
 (c)  $K^+ > Cl^- > Ca^{2+} > S^{2-}$  (d)  $Cl^- > K^+ > S^{2-} > Ca^{2+}$
- Q.39. Among lithium, nitrogen, carbon and oxygen which element has the highest first ionization potential?  
 (a) Lithium (b) Nitrogen

- (c) Carbon (d) Oxygen
- Q.40. Identify the correct option:  
In the periodic table on moving from left to right along a period:
- The atomic size of the elements increase.
  - The first ionization potential of the elements decreases.
  - The oxide of the element becomes less basic.
  - The oxide of the element becomes more basic.
- Q.41. The decreasing order of the first ionization energy of the following elements is:
- He > H > Be > B
  - Be > B > H > He
  - H > He > Be > B
  - B > Be > He > H
- Q.42. The degree of hydration is expected to be maximum for:
- Mg<sup>2+</sup>
  - Na<sup>+</sup>
  - Ba<sup>2+</sup>
  - K<sup>+</sup>
- Q.43. Anything that influences the valence electrons will affect the chemistry of the element. Which of the following factors does not affect the valence shell?
- Valence principal quantum number
  - Nuclear charge
  - Nuclear mass
  - Number of core electrons
- Q.44. The size of isoelectronic species F<sup>-</sup>, Ne, Na<sup>+</sup> is affected by:
- Nuclear charge
  - Valence principal quantum number
  - Electron-electron interactions in the outer orbital
  - None of the factors because their size is the same
- Q.45. Which of the following statement is incorrect in relation with ionization enthalpy?
- Ionization enthalpy increases for each successive electron.
  - The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.
  - End of valence electron is marked by a big jump in ionization enthalpy.
  - Removal of electron from orbital bearing lower n value is easier from orbital having higher n value.
- Q.46. Considering the elements B, C, N, F, Si the correct order of their metallic character is:
- B > Al > Mg > K
  - Si > B > C > N > F
  - F > N > C > B > Si
  - F > N > C > Si > B
- Q.47. Considering the elements F, Cl, O and N the correct order of their chemical reactivity in terms of oxidizing properties is:
- F > Cl > O > N
  - F > O > Cl > N
  - Cl > F > O > N
  - O > F > N > Cl
- Q.48. The correct order of increasing radius to the given elements is:
- Si, Al, P, Na
  - P, Si, Al, Na
  - Al, Si, P, Na
  - Al, P, Si, Na
- Q.49. Which of the following series of elements have nearly the same atomic radii?
- F, Cl, Br, I
  - Na, K, Rb, Cs
  - Li, Be, B, C
  - Fe, Co, Ni, Cu
- Q.50. In which of the following pair is the second atom larger than the first?
- Br, Cl
  - Na, Mg
  - Sr, Ca
  - N, P

- Q.51. Which of the following compounds can one expect to show strong ionic character?  
 (a)  $\text{BaCl}_2$  (b)  $\text{CsCl}$   
 (c)  $\text{CaCl}_2$  (d)  $\text{SrCl}_2$
- Q.52. The order of increasing electron affinity of the electronic configurations:  
 (i)  $1s^2 2s^2 2p^6 3s^2 3p^5$  (ii)  $1s^2 2s^2 2p^3$  (iii)  $1s^2 2s^2 2p^5$  (iv)  $1s^2 2s^2 2p^6 3s^1$   
 (a) ii, iv, iii, i (b) i, ii, iii, iv  
 (c) i, iii, ii, iv (d) iv, iii, iii, i
- Q.53. Which of the following electronic configurations represents the elements with maximum electron affinity?  
 (a)  $1s^2 2s^2 2p^6$  (b)  $1s^2 2s^2 2p^5$   
 (c)  $1s^2 2s^2 2p^6 3s^1$  (d)  $1s^2 2s^2 2p^6 3s^2 3p^5$
- Q.54. Which of the following oxides is neutral?  
 (a)  $\text{SnO}_2$  (b)  $\text{CO}$   
 (c)  $\text{Al}_2\text{O}_3$  (d)  $\text{Na}_2\text{O}$
- Q.55. The electronegativity of the following elements increases in the order:  
 (a)  $\text{C} < \text{N} < \text{Si} < \text{P}$  (b)  $\text{Si} < \text{P} < \text{C} < \text{N}$   
 (c)  $\text{N} < \text{C} < \text{P} < \text{Si}$  (d)  $\text{C} < \text{Si} < \text{N} < \text{P}$
- Q.56. Which of the following is arranged in increasing order of atomic radii?  
 (a)  $\text{K}^+ < \text{Na}^+ < \text{Li}^+$  (b)  $\text{K}^+ < \text{Li} < \text{Na}^+$   
 (c)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  (d)  $\text{Na}^+ < \text{Li}^+ < \text{K}^+$
- Q.57. The third ionization energy is maximum for:  
 (a) Nitrogen (b) Phosphorus  
 (c) Aluminium (d) Boron
- Q.58. Which of the following arrangements shows the correct order of decreasing paramagnetic behavior?  
 (a)  $\text{Na} > \text{Al} > \text{O} > \text{Ca}$  (b)  $\text{N} > \text{O} > \text{Al} > \text{Ca}$   
 (c)  $\text{O} > \text{N} > \text{Al} > \text{Ca}$  (d)  $\text{O} > \text{Na} > \text{Ca} > \text{Al}$
- Q.59. Which of the following is arranged in order of increasing density?  
 (a)  $\text{Ag} < \text{Au} < \text{Fe} < \text{Cu}$  (b)  $\text{Cu} < \text{Au} < \text{Ag} < \text{Fe}$   
 (c)  $\text{Fe} < \text{Cu} < \text{Ag} < \text{Au}$  (d)  $\text{Au} < \text{Ag} < \text{Cu} < \text{Fe}$
- Q.60. Which of the following is arranged in decreasing order of size?  
 (a)  $\text{Mg}^{2+} > \text{Al}^{3+} > \text{O}^{2-}$  (b)  $\text{O}^{2-} > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (c)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{O}^{2-}$  (d)  $\text{Mg}^{2+} = \text{Al}^{3+} > \text{O}^{2-}$
- Q.61. Which of the following is arranged in order of increasing second ionization energy?  
 (a)  $\text{C} < \text{N} < \text{O} < \text{F}$  (b)  $\text{F} < \text{C} < \text{N} < \text{O}$   
 (c)  $\text{C} < \text{N} < \text{F} < \text{O}$  (d)  $\text{F} < \text{O} < \text{N} < \text{C}$
- Q.62. The order of increasing ionic radius of the following is:  
 (a)  $\text{K}^+ < \text{Li}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  (b)  $\text{K}^+ < \text{Mg}^{2+} < \text{Li}^+ < \text{Al}^{3+}$   
 (c)  $\text{Li}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  (d)  $\text{Al}^{3+} < \text{Li}^+ < \text{Mg}^{2+} < \text{K}^+$
- Q.63. Arrange the following in order of decreasing electron affinity:  
 (a)  $\text{S} > \text{O} > \text{N}$  (b)  $\text{O} > \text{S} > \text{N}$   
 (c)  $\text{N} > \text{O} > \text{S}$  (d)  $\text{S} > \text{N} > \text{O}$
- Q.64. The basicity of the hydroxides of the following alkali metals is of the order:  
 (a)  $\text{Li} > \text{Na} > \text{Rb} > \text{Cs}$  (b)  $\text{Na} > \text{Li} > \text{Rb} > \text{Cs}$   
 (c)  $\text{Cs} > \text{Rb} > \text{Na} > \text{Li}$  (d)  $\text{Rb} > \text{Cs} > \text{Na} > \text{Li}$

- Q.65. Which electronic configuration of neutral atom will have the highest first ionization potential?
- (a)  $1s^2 2s^2 2p^1$  (b)  $1s^2 2s^2 2p^3$   
 (c)  $1s^2 2s^2 2p^2$  (d)  $1s^2 2s^2 2p^4$
- Q.66. The increasing order of first ionization enthalpy of the following element is:
- (a)  $F < S < P < B$  (b)  $P < S < B < F$   
 (c)  $B < P < S < F$  (d)  $B < S < P < F$
- Q.67. The ionization energy will be maximum for the process:
- (a)  $F \rightarrow F^-$  (b)  $Be \rightarrow Be^+$   
 (c)  $Cl \rightarrow Cl^-$  (d)  $O \rightarrow O^-$
- Q.68. The ionization energy will be maximum for the electronic configuration:
- (a)  $1s^2 2s^2 2p^2$  (b)  $1s^2 2s^2 2p^6 3s^1$   
 (c)  $1s^2 2s^2 2p^6 3s^2$  (d)  $1s^2 2s^2 2p^1$
- Q.69. The element which is strongly electropositive in nature is:
- (a) Cu (b) Cs  
 (c) Cr (d) Ba
- Q.70. Which is correct order for electron gain enthalpy?
- (a)  $S < O < Cl < F$  (b)  $O < S < F < Cl$   
 (c)  $Cl < F < S < O$  (d)  $F < Cl < O < S$
- Q.71. The order of Ionic radii is correct in which of the following pairs:
- (a)  $Ti^{4+} < Mn^{2+}$  (b)  $Cr^{6+} > Cr^{3+}$   
 (c)  $K^+ > Cl^-$  (d)  $P^{3+} > P^{5+}$
- Q.72. The first ionization energy of four consecutive elements present in the second period of periodic table are 8.3, 11.3, 14.5 and 13.6 eV respectively. Which one of the following is first ionization enthalpy of nitrogen?
- (a) 13.6 (b) 14.5  
 (c) 11.3 (d) 8.3
- Q.73. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^3$ . What is the atomic number of the element which is just below the above element in the periodic table?
- (a) 34 (b) 49  
 (c) 33 (d) 31
- Q.74. Which of the following species has highest electron gain enthalpy?
- (a)  $F^-$  (b) O  
 (c)  $O^-$  (d)  $Na^+$
- Q.75. Which pair follows the correct hydration energy order?
- (a)  $Fe^{2+} > Fe^{3+}$  (b)  $Cu^{2+} < Cu^+$   
 (c)  $K^+ > Cs^+$  (d)  $F^- < Br^-$
- Q.76. Select the correct ionic radius order among the following:
- (a)  $P^{3-} < P^{2-}$  (b)  $P^{3-} < S^{3-}$   
 (c)  $Na^+ > Mg^{2+}$  (d)  $S^{2-} < Ca^{2+}$
- Q.77. In which of the following process maximum amount of energy is evolved:
- (a)  $Cl \rightarrow Cl^-$  (b)  $Br^- \rightarrow Br$   
 (c)  $F \rightarrow F^-$  (d)  $I^- \rightarrow I$
- Q.78. Which element can exhibit more than one oxidation states in compounds?
- (i) Cr (ii) Pb (iii) Sr  
 (a) (i) only (b) (i) and (ii) only

- (c) (ii) and (iii) only (d) (i), (ii) and (iii) only
- Q.79. Which set of the orbital's is listed in the correct sequential order of filling electrons in an atom?
- (a) 3s 3p 3d (b) 3d 4s 4p  
(c) 3d 4p 5s (d) 4p 4d 5s
- Q.80. Which equation shows exothermic reaction for the formation of NaF(s)?
- (i)  $\text{Na (g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$  (ii)  $\text{F(g)} + \text{e}^- \rightarrow \text{F}^-(\text{g})$   
(iii)  $\text{Na}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{NaF(s)}$
- (a) (i) only (b) (ii) only  
(c) (i) and (iii) only (d) (ii) and (iii)
- Q.81. Select the correct order of ionic radii:
- (a)  $\text{O}^{2-} > \text{S}^{2-} > \text{Se}^{2-} > \text{Te}^{2-}$  (b)  $\text{Te}^{2-} > \text{S}^{2-} > \text{O}^{2-} > \text{Se}^{2-}$   
(c)  $\text{O}^{2-} > \text{Te}^{2-} > \text{S}^{2-} > \text{Se}^{2-}$  (d)  $\text{Te}^{2-} > \text{Se}^{2-} > \text{S}^{2-} > \text{O}^{2-}$
- Q.82. The formation of oxide ion  $\text{O}^{2-}(\text{g})$  requires first an exothermic and then endothermic step as shown below:
- $\text{O(g)} + \text{e}^- \rightarrow \text{O}^-(\text{g}) \quad \Delta H = -142 \text{ kJ/mol}$   
 $\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g}) \quad \Delta H = 844 \text{ kJ/mol}$
- This is because:
- (a)  $\text{O}^-$  ion has comparatively large size than oxygen atom.  
 (b) Oxygen has high electronegativity.  
 (c)  $\text{O}^-$  ion will tend to resist the addition of another electron.  
 (d) Oxygen has high ionization enthalpy.
- Q.83. What is the formula for the basic anhydride of  $\text{Ba(OH)}_2$ ?
- (a)  $\text{Ba}_2\text{O}$  (b)  $\text{BaO}$   
(c)  $\text{BaO}_2$  (d)  $\text{Ba}$

**Answers**

1 - (d)	2- (c)	3- (a)	4- (c)	5- (c)	6- (c)
7 - (c)	8 - (a)	9 - (c)	10- (c)	11 - (d)	12 - (b)
13- (b)	14- (a)	15- (b)	16- (b)	17- (c)	18- (d)
19- (b)	20- (b)	21- (d)	22- (c)	23- (a)	24- (d)
25- (c)	26- (c)	27- (c)	28- (b)	29- (a)	30- (c)
31- (d)	32- (a)	33- (a)	34- (b)	35- (a)	36- (b)
37- (a)	38- (b)	39- (b)	40- (c)	41- (c)	42- (a)
43- (c)	44- (a)	45- (d)	46- (b)	47- (b)	48- (a)
49- (d)	50- (d)	51- (b)	52- (a)	53- (d)	54- (b)
55- (b)	56- (c)	57- (a)	58- (b)	59- (c)	60- (b)
61- (c)	62- (d)	63- (ca	64- (c)	65- (b)	66- (d)
67- (b)	68- (a)	69- (b)	70- (b)	71- (d)	72- (d)
73- (c)	74- (b)	75- (c)	76- (c)	77- (a)	78- (b)
79- (c)	80- (d)	81- (d)	82- (c)	83- (b)	

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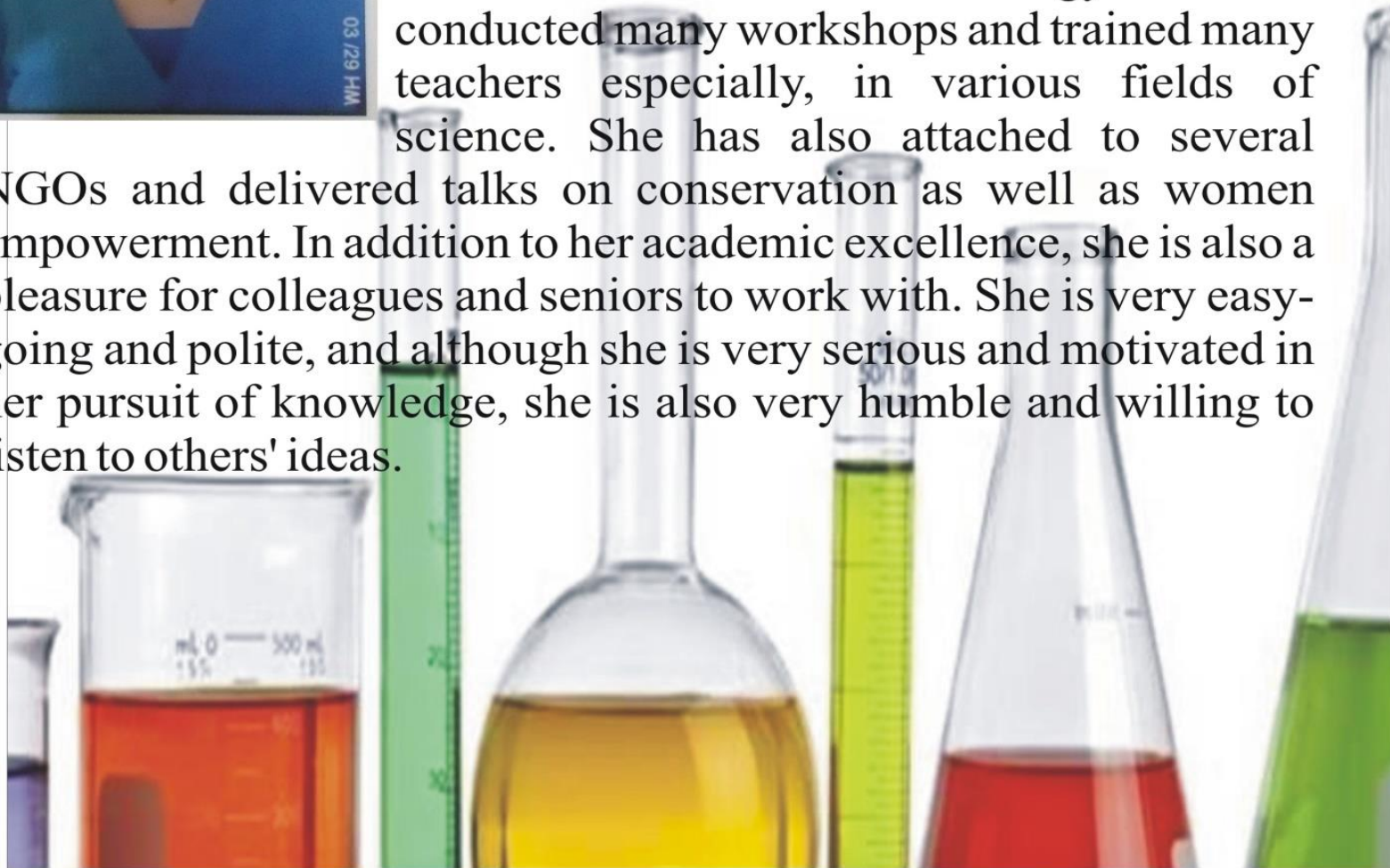


# ABOUT THE EDITOR



Babita Malik, Principal, K.L.G Public School, Saharanpur is highly learned and reputed member in the society. She awarded a prize for excellent work in the field of education by SOF society. She has contributed to a number of high-end academic platforms and gathering masters in various fields of science and technology. She has conducted many workshops and trained many teachers especially, in various fields of science. She has also attached to several

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