

Total number of printed pages-15

14 (CHM-1) 101 N/O

2018

CHEMISTRY

Paper : CH 101

(Inorganic Chemistry-I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Determine the polyhedral geometry of B_5H_9 using Wade's rules. 1
2. Answer the following questions : **(any two)** 2×2=4
 - a) What is hydroboration reaction ? Write an equation to show how it can be used to prepare an organoborane compound. 2
 - b) Write a brief note on lanthanum hexaboride highlighting the importance of this boride. 2

Contd.

c) Comment on the similarities and differences between boron nitride and graphite. 2

3. Suggest a cost effective method for preparing trialkylaluminium. Draw the structure of the compound and cite *one* important application of this organoaluminium compound. 3

Or

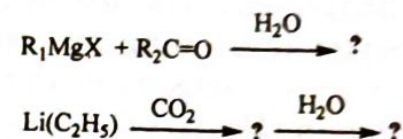
Tl^{201} finds application as a nuclear medicine in cardiac stress test. Indicate which aspect of the chemistry of this element makes this medical application possible. Also explain why at higher doses compounds of Tl are highly toxic.

4. Answer the following questions : (*any two*)
2×4=8

- a) What are fullerenes and fullerides? Comment on the electrical conductivity shown by fullerides based on buckminsterfullerene. 2+2
- b) What are phosphazenes and what are their various types? Write briefly about polyphosphazenes and their potentially useful properties. 2+2

c) Give a brief overview of the various types of metal-oxo compounds formed due to the versatile coordination ability of the oxide ion as a ligand. 4

5. Write down the products in the following reactions : 1+2



Or

Give a method for the synthesis of methylberyllium. Describe its structure in the solid state.

6. Answer the following questions : (*any two*)
2×4=8

- a) The compound Na_2IrCl_6 reacts with triphenylphosphine in diethylene glycol under an atmosphere of CO to give A, known as Vaska's compound. Excess of CO with 'A' produces a five-coordinate species 'B' which on treatment with $NaBH_4$ in ethanol gives 'C'. Name the three complexes A, B and C with structures. 4

b) What is Creutz-Taube complex? Explain briefly why studies on this and related complexes are of importance. 4

c) Explain the structure and bonding in $[Re_2Cl_8]^{2-}$ with the help of molecular orbital theory. Use the molecular orbital energy level diagram for the above species to determine the Mo-Mo bond order in $Mo_2(\mu-O_2CCH_3)_4$. 3+1

7. Answer the following questions : (any three) 3×3=9

a) In a crystalline solid, anions(B) are arranged in a cubic close packing. Cations(A) are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the solid? 3

b) What is an alloy? Write a short note on steel as an important example of alloys. 3

c) What are p-type and n-type semiconductors? Which one of the following statements is always true regarding conductors and semiconductors? 2+1

i) Semiconductors are half as good as conductors when comparing their electron mobility.

ii) Conductors have large band gaps and semiconductors have small band gaps.

iii) Conductors and semiconductors do not conduct electricity at high temperature.

iv) None of the above statements are true.

d) An element occurs in the BCC structure with cell edge of 288 pm. The density of the element is 7.2 g/cm^3 . How many atoms of the element does 208g of the element contain? 3

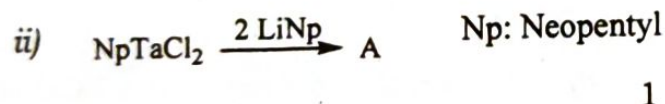
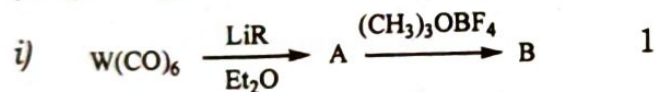
e) What are layered solids? Give two examples of such species and suggest a method for the convenient characterization of such solids. 2+1

8. Describe the steps involved in chemical vapour deposition method for the synthesis of solid state compounds. Write down the major advantages and disadvantages associated with this method. 4

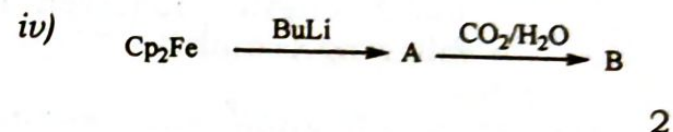
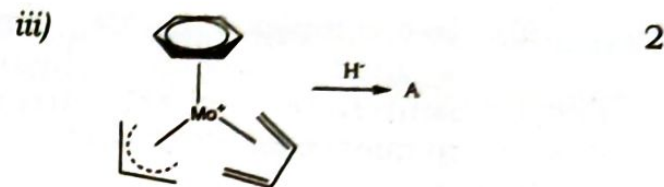
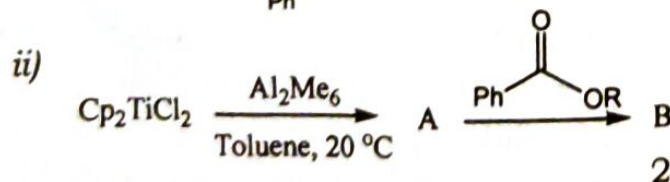
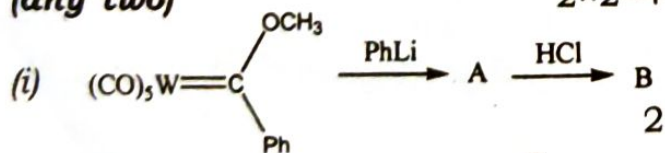
Or

Explain band theory of solids. Discuss how this theory may be used. Describe electrical conductivity of solids.

9. a) Identify A and B as applicable :
(any two) $2 \times 1 = 2$



- b) Identify A and B as applicable :
(any two) $2 \times 2 = 4$



- c) Write the Total Electron Count (TEC) and the Skeletal Electron Count (SEC) of $\text{Ru}_5\text{C(CO)}_{15}$. Draw its structure. 3

Or

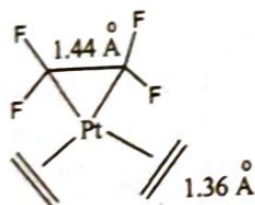
Total Electron Count (TEC) for main group element cluster to have a close structure is $4n + 2$, while that of transition metal cluster is $14n + 2$. Why is that difference?

- d) Answer the following questions :
(any two) $2 \times 2 = 4$

- i) How many stretching frequencies are observed in the IR spectra of M(CO)_6 and M(CO)_5 ? Point groups of M(CO)_6 and M(CO)_5 are O_h and D_{3h} , respectively. 2

ii) In a complex $L_nM(CO)_m$, how does a good pi-acceptor ligand (L) influence on the stretching frequency of CO? 2

iii) Comment on the differences in bond lengths observed in the following complex:



In what condition, an alkene bonding to a transition metal can increase the oxidation state of the metal? 2

e) Answer the following questions :
(any two) 2×1=2

i) The HOMO of CO has bigger lobes on the side of carbon atom — YES/NO.

ii) The LUMO of CO has bigger lobes on the side of carbon atom — YES/NO.

iii) CO can stabilize the negative oxidation states of some metals — YES/NO.

iv) CO is a poor pi-acceptor ligand — YES/NO.

f) Answer the following questions :
(any two) 2×1=2

i) Write a reaction to show that ferrocene is more stable than cobaltocene.

ii) Why is the d_z^2 orbital of iron in ferrocene almost non-bonding?

iii) Why is not Cp_2Sn perfectly sandwich as ferrocene?

iv) What is the difference between Cp_2Mg and Cp_2Fe from their bonding aspect?

g) Draw the catalytic cycle of $Co_2(CO)_8$ catalysed hydroformylation reaction.

3

OR

Why is $(Et_3P)_3RhCl$ inactive whereas $(Ph_3P)_3RhCl$ active for alkene hydrogenation reaction? What will happen when you replace Rh with Ir in Wilkinson's catalyst? What will happen when $(Ph_3P)RhCl_3$ is taken as catalyst?

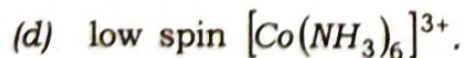
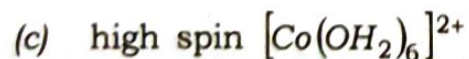
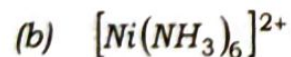
(Old Course)

1. Explain why the similarities in properties of $3d$ and $4d$ transition metals are less compared to similarities between the $4d$ and $5d$ transition metals. 2
2. Answer **any two** questions : $3 \times 2 = 6$
 - (i) Sketch the two structures that describe most four-coordinate complexes. In which structure are isomers possible for complexes of formula MA_2B_2 ? 3
 - (ii) Comment on the oxidation states shown by lanthanide elements. 3
 - (iii) Write a short note on 'chelate effect'. 3
3. Answer **any two** questions : $8 \times 2 = 16$
 - (i) Give a description of how an octahedral crystal field will split the set of five d orbitals of a transition metal ion. What are the various factors which determine the crystal field splitting parameter? $4 + 4 = 8$

(ii) What is 'ligand field theory' of coordination complexes and compare it with crystal field theory. Discuss the effect of an octahedral ligand (crystal) field on the ^3F term of d^2 .
3+5=8

(iii) State and explain Jahn-Teller effect. Identify the d electron configurations for which the octahedral complexes are likely to undergo Jahn-Teller distortion?
5+3=8

4. Calculate the crystal field stabilisation energies of :
1×4=4



Or

Construct the molecular orbital energy level diagram for the MnO_4^- ion. 4

5. What are the selection rules that govern electronic transitions in transition metal complexes? 2

6. Answer **any two** questions : 3×2=6

(i) What are the electron configurations for which ^2D is the free ion ground term? What is the total degeneracy of the ^2D term? 3

(ii) Predict the number of ligand field bands that will be expected in the electronic spectrum of $[V(OH_2)_6]^{2+}$ by drawing the relevant Orgel diagram. 3

(iii) $[CoF_6]^{3-}$ is colored while $[FeF_6]^{3-}$ is colorless. Explain. 3

7. Answer **any two** questions : 2×2=4

(i) Define what paramagnetic susceptibility is and write down how it is related to magnetic moment. 2

(ii) Calculate the spin-only magnetic moments of (a) $[Fe(OH_2)_6]^{2+}$ and (b) $[Ru(OH_2)_6]^{2+}$. 1+1=2

- (iii) Explain briefly what is quenching of orbital contribution to magnetic moment. 2

8. Answer **any two** questions : 3×2=6

- (i) Describe a method commonly used for the measurement of magnetic susceptibility. 3

- (ii) Write a brief note on temperature independent paramagnetism. 3

- (iii) Comment on the magnetic properties of compounds formed by the lanthanides. 3

9. Briefly explain what the half-life of a radionuclide is. 2

10. Answer **any three** questions : 4×3=12

- (i) Plutonium-239 has a half-life of 2.44×10^4 years. What fraction of plutonium-239 is left after 9.76×10^4 years? 4

- (ii) Cobalt-60 is a radionuclide which has medical use in cancer treatment. Give the nuclear reactions using which it can be prepared. 4

- (iii) In the technique known as 'radiocarbon dating', $^{14}_6\text{C}$ is used as the radioactive isotope which has a half-life of 5730 years. Explain the origin of this isotope of carbon in the plant and animal world and describe how radiocarbon dating is useful in the determination of age of fossilised matter. 4

- (iv) What are radioactive tracers? Comment on their use in the determination of mechanism of chemical reactions. 4

- (v) Discuss the method of analysis by isotope dilution analysis and throw light on some of its applications. 4