

Total number of printed pages-12

14 (CHM-2) CH 201

2018

CHEMISTRY

Paper : CH-201

(Inorganic Chemistry 2)

Full Marks : 80

Time : Three hours

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

1. Draw the structure of methyllithium.

1

2. Answer **any two** of the following **three** questions :

2×5=10

- (i) Explain what is meant by Polyhedral Skeletal Electron Pair Theory (PSEPT). Apply rules of PSEPT to determine the skeletal structure of the $B_6H_6^{2-}$ anion.

3+2=5

Contd.

- (ii) Several lower boranes were isolated and characterized by Alfred Stock in Germany in the first half of the last century. What were the challenges faced by these early investigators of borane chemistry and how were the synthetic problems addressed to successfully prepare and characterize the numerous neutral boranes that are known today? Give a method using which diborane can be prepared in the laboratory. Also, suggest a synthetic route to polyhedral borane anions such as $B_{12}H_{12}^{2-}$ from diborane.

3+1+1=5

- (iii) What are zeolites and why was the term 'molecular sieves' given to dehydrated zeolites? Comment on the usefulness of zeolites in heterogeneous catalysis.

1+1+3=5

3. State what is meant by "styx" in the statement '2002 is the styx number of B_2H_6 '.

2

Or

Give the reaction using which triethylaluminium is commercially prepared.

2

4. What are silicones? Comment on their properties and common applications.

1+2=3

Or

Comment on the role of organotin compounds as marine antifouling agents.

3

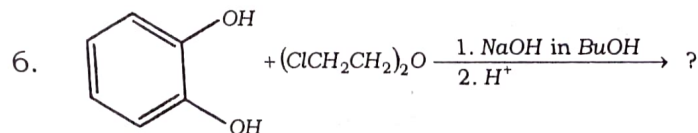
5. Lapis lazuli is the name of a semiprecious aluminosilicate gemstone of deep-blue colour. What is the origin of its colour?

2

Or

PF_5 is commonly seen as a molecule having C_{3v} symmetry. However, it shows only one ^{19}F NMR signal at room temperature. Explain this observation.

2



Predict and name the main product formed in the above reaction reported in 1967 by a Nobel Prize winning chemist.

1+1=2

Or

Draw the structure of or the polycyclic polydentate ligand called either as 2.2.2-crypt or cryptand-222 that can form complexes with alkali metal cations.

2

7. What are Zintl phases?

2

Or

What is the origin of colour of the well-known gemstone known as ruby?

2

8. Draw the unit cells of face-centred cubic (fcc) and body-centred cubic (bcc) lattices. What are the fractional coordinates of the lattice points present in these two unit cells? Confirm by counting lattice points and their contributions to the unit cells that the fcc and bcc unit cells contain four and two lattice points respectively.

$$1+1+2=4$$

Or

Metallic sodium adopts a bcc structure with density 970 kg m^{-3} . What is the length of the edge of the unit cell of the crystal structure of sodium metal?

4

9. What is spinel? Discuss structural characteristics of the spinel structure type. When is a structure said to have the inverse spinel structure? State briefly about the utility of these mixed-metal oxides.

$$1+2+1=4$$

Or

Describe the coordination around the oxide ions in the perovskite structure, ABO_3 , in terms of coordination to the A- and B-type cations.

4

10. Describe the steps in a sol-gel method of synthesizing solid state compounds with a suitable example.

4

Or

Describe the powder X-ray diffraction method as a useful technique for the characterization of solid state compounds.

4

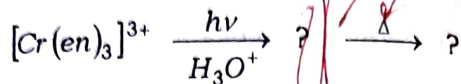
11. Answer **any three** from the following **four** questions :

$$3 \times 4 = 12$$

- A. (i) What happens when $[\text{Cr}(\text{CN})_6]^{3-}$ is irradiated in degassed DMF?

1

- (ii) Complete the following sequence:



1

- (iii) Draw the different steps of Vanquickenborne-Ceulemans model for photosubstitution taking $[CrCl(NH_3)_5]^{2+}$ as an example.

2

- B. (i) Fill the following : $\frac{1}{2} \times 4 = 2$

Quantum yield for a particular process is a number below _____. Total quantum yield for all processes in case of a particular absorption event is _____. For each photon of ordinary light absorbed by a chemical system a maximum of _____ molecule will be excited. A photochemical effect is directly proportional to _____.

- (ii) " Cr^{III} complexes are inert under normal condition but becomes labile when excited with photons" — Explain.

2

- C. (i) Write a brief note on solar energy conversion by ruthenium complexes.

2

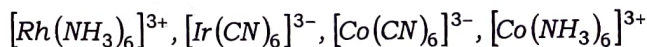
- (ii) What happens when $[Cr(bipy)_3]^{3+}$ is irradiated under basic aqueous condition in absence and presence of 0.1M KI? What is the conclusion to be drawn from the two different observations to be made?

$$1\frac{1}{2} + \frac{1}{2} = 2$$

- D. (i) Draw the different steps involved in the photosubstitution of NH_3 in $[CrCl(NH_3)_5]^{2+}$ by H_2O to form $[CrCl(H_2O)(NH_3)_4]^{2+}$.

2

- (ii) Define phosphorescence. Which two of the following species show phosphorescence?



$$1 + 1 = 2$$

12. Draw the metal-ligand bonding in Fischer and Schrock carbene complexes and write the differences between the complexes.

$$2 + 2 + 2 = 6$$

Or

Discuss the bonding in ferrocene. 6

13. Discuss the situations that lead a metal alkene complex to approach metallacyclopentane. Give one example of such type. 3+1=4

Or

Identify the Oxidative Addition and Insertion Reactions in Tolman catalytic loop of hydrogenation of alkene. What do you mean by β -hydride elimination? Predict the molecule that will eliminate from the following complex. 1+1+1+1=4

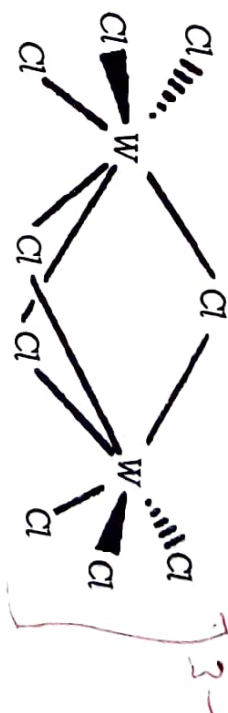


14. How many electron(s) is contributed to the skeletal electron count by $Ru(CO)_3$ and $CoCp$ fragments? 1½+1½=3

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Or

Give one example of edge sharing bioctahedra complex. Find out the number of $M-M$ bond in the following face Sharing Bioctahedra complex. 1+2=3



15. Draw the catalytic cycle of Wacker process. What is the role of Cu^{2+} salt in this cycle? 3+1=4

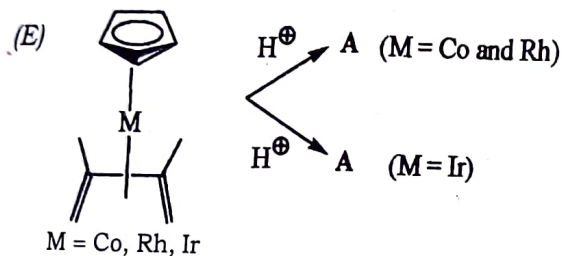
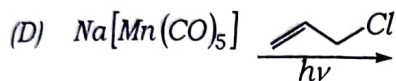
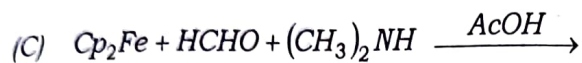
Or

Draw the catalytic cycle of hydrogenation reaction by Wilkinson's catalyst. What happens to the reactivity of the catalyst when Ph_3P is replaced by Et_3P and Rh is replaced by Ir ? 2+2=4

16. Write the products : (any three) 1+1+1=3



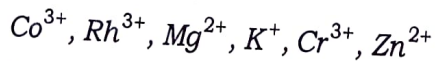
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17. Answer **any two** of the following four questions : 2×1=2

(i) How do the spectator ligands of a complex play role in making the complex labile or inert? 1

(ii) Arrange the following metal ions on the basis of increased lability of their aqua complexes. 1



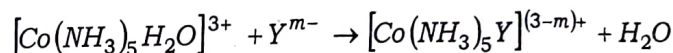
(iii) In some cases, how can you tell whether inner sphere or outer sphere electron transfer is taking place in a particular reaction by observing the products? 1

(iv) Co^{3+} octahedral complexes are generally inert. Give reason. 1

18. Answer **any four** of the following seven questions : 4×3=12

(i) Deduce the rate equation for the Dissociative mechanism (D) of substitution reaction in octahedral complex. 3

(ii) What is Interchange Dissociative mechanism? Rate constants for the reaction of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{m+}$ with Y^{m-} are given in the following table.



Y^{m-}	$k (10^{-6} \text{s}^{-1})$
H_2O	100
N_3^-	100
SO_4^{2-}	24
Cl^-	21
NCS^-	16

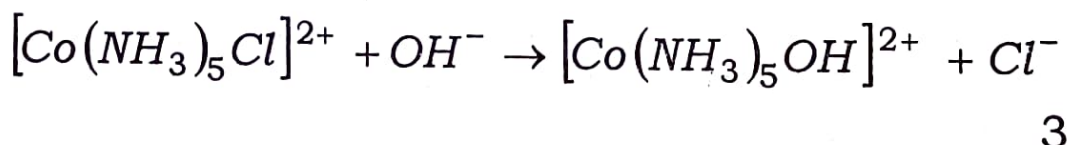
From the above data, write whether the reaction mechanism is Associative or Dissociative. 1+2=3

(iii) How does a strong π -acceptor ligand show strong trans effect? Give examples of *two* strong π -acceptor ligands. 2+1=3

(iv) Show the *Bailer twist* mechanism of intramolecular racemization of trisoxalatoferrate(III). 3

(v) Find the different possible products produced during the substitution of X with Y in *trans*- $[M(LL)_2BX]$, which proceeds through trigonal bipyramidal intermediate where B is in the equatorial position (LL is a bidentate ligand). 3

(vi) Write the steps involved in the following substitution reaction which follow conjugate base mechanism. Does $[Co(pyridine)_4Cl_2]^+$ follow Conjugate base mechanism?



(vii) In the self-exchange electron transfer reaction for $1\frac{1}{2} + 1\frac{1}{2} = 3$

$[Ru(NH_3)_6]^{2+} / [Ru(NH_3)_6]^{3+}$, k_{11} is $6.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and for

$[Co(NH_3)_6]^{2+} / [Co(NH_3)_6]^{3+}$, k_{11}

is, $2 \times 10^{-8} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Explain.

$1\frac{1}{2} \times 1\frac{1}{2} = 3$