

Reg. No. :

Code No. : 8852

Sub. Code : KCHM 32

M.Sc. (CBCS) DEGREE EXAMINATION,
NOVEMBER 2017.

Third Semester

Chemistry

INORGANIC CHEMISTRY — III

(For those who joined in July 2016 – 2017)

Time : Three hours

Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Hexacarbonylvanadium, $(V(CO)_6)$, which is a paramagnetic and 17-electron stable molecule, does not dimerize to form $V_2(CO)_{12}$, an 18-electron species. What is the reason?
- (a) The coordination number increases to 7
 - (b) Too much steric hindrance to allow stability
 - (c) Ligand repulsion may provide a kinetic baffler to dimerization
 - (d) All of the above

20. (a) Discuss the applications of semiconductor based photo electrochemical cells in the storage of solar energy.

Or

- (b) (i) State Adamson's rules. How will you apply these rules to the photoaquation of $[Cr(NH_3)_4Cl_2]^+$ and of $[Cr(NH_3)_5Cl]^+$.
- (ii) Compare the photophysical and photochemical properties of $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$.

Page 10

Code No. : 8852



2. Which among the following metallocenes is ionic?
- (a) $(C_5H_5)_2Cr$ (b) $(C_5H_5)_2Fe$
 (c) $(C_5H_5)_2Mg$ (d) $(C_5H_5)_2Mn$
3. The term 'agostic' in organometallic chemistry refers to
- (a) oxidative addition
 (b) reductive elimination
 (c) covalent interaction between C-H groups and transition metal centers
 (d) coordinative unsaturation
4. $[RC(=O)Fe(CO)_3PPh_3]^- + Cl_2 \rightarrow \underline{X} + H_2O \rightarrow Y$.
 What is X and Y?
- (a) $RC(=O)R'$ and $RCOOH$
 (b) $RC(=O)Cl$ and $RCOOH$
 (c) $RCHO$ and $RCOCl$
 (d) None of the above
5. The 1H -NMR spectrum of the complex Hydrotetrakis-(triphenylphosphine) nickel(II) ion, $[HNi(PPh_3)_4]^+$, is a quintet in the intensity ratios 1:4:6:4:1. What would be the shape of the molecule?
- (a) Trigonal bipyramid (b) Square pyramid
 (c) Square planar (d) Tetrahedron

Page 2 Code No. : 8852

6. The characteristic feature of an electron spin resonance spectrum of frozen aqueous solution of $CuSO_4 \cdot 5H_2O$ at 77 K is
- (a) $g_{||} > g_{\perp}$ (b) $g_{||} < g_{\perp}$
 (c) $g_{||} = g_{\perp}$ (d) $g_{||} \neq g_y \neq g_z$
7. In atomic emission spectrometry, protective agents prevent interference by preferentially forming stable but volatile species with the analyte. The reagent(s) used for this purpose is (are)
- (a) EDTA
 (b) 8-hydroxyquinoline
 (c) Ammonium salt of I-pyrrolidine-carbodithioc acid
 (d) All of the above
8. Pick the correct statements about Atomic Absorption Spectrometry (AAS) from the following :
- (A) Hg lamp is not suitable source for AAS
 (B) Graphite furnace is the best atomizer for AAS
 (C) Non-metals cannot be determined with AAS
 (D) AAS is better than ICP-AES for simultaneous determination of metal ions.
- (a) A, B and C (b) B, C and D
 (c) C, D and A (d) D, A and B

Page 3 Code No. : 8852



9. A catalyst used in the photoreduction of CO_2 to H_2O is

- (a) $[\text{Os}(\text{bpy})_3]^{2+}$
- (b) $[(\text{C}_5\text{H}_5)_2\text{Cr}]$
- (c) $[\text{Fe}(\text{bpy})_3]^{2+}$
- (d) $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$

10. The essential condition(s) for a photochemical reaction to be used in the storage of solar energy is (are)

- (a) The reaction must be reversible and the back reaction must be slow at ambient temperature
- (b) The reaction must be endergonic
- (c) The back reaction should proceed rapidly by a catalyst or heat
- (d) All of the above

Page 4

Code No. : 8852

PART B — ($5 \times 5 = 25$ marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Beryllocene has slipped sandwich structure with ionic character. Substantiate this statement.

Or

- (b) Discuss the preparation, structure and bonding in Zeise's salt anion.

12. (a) What modification is to be made in the Wilkinson's catalyst to bring about enantioselective hydrogenation of prochiral alkenes?

Or

- (b) Explain the Wacker process of acetaldehyde production from ethylene and Oxygen.

13. (a) Predict and sketch the appearance of the ^{31}P -NMR spectrum of both fac - $\text{Rh}(\text{PPh}_3)_3\text{Cl}_3$ and mer- $\text{Rh}(\text{PPh}_3)_3\text{Cl}_3$. [^{31}P : $I = 1/2$ (100%); ^{103}Rh : $I = 1/2$ (100%)].

Or

Page 5

Code No. : 8852



- (b) What is meant by Kramer's degeneracy? Using this discuss the EPR spectrum of d^3 metal ion. For the complex $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $10Dq$ is 17400 cm^{-1} and $g = 1.977$. Calculate the spin-orbit coupling constant λ for the complex.

14. (a) Compare turbidimetry with nephelometry. Outline the use of these techniques with an example for each.

Or

- (b) (i) Explain inductively coupled Argon plasma source used in atomic absorption spectroscopy.
(ii) Discuss the principles and applications of atomic fluorescence spectroscopy.
15. (a) Write briefly on the photosubstitution reactions of Cr(III) complexes enumerating the role of different excited states involved in these reactions.

Or

- (b) Discuss the two principal mechanisms of energy transfer.

Page 6

Code No. : 8852

PART C — ($5 \times 8 = 40$ marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Discuss the preparation, structure and bonding in ferrocene using LCAO-MO approach.

Or

- (b) (i) How metal carbonyls are prepared?
(ii) Discuss the bonding mechanism in metal carbonyls.
(iii) How IR spectral data support this mechanism?
(iv) Explain the IR data for the following :

Complex	$\nu_{\text{Co}} \text{ cm}^{-1}$	$\nu_{\text{M-C}} \text{ cm}^{-1}$
$\text{Mn}(\text{CO})_6^+$	2090	416
$\text{Cr}(\text{CO})_6$	2000	441
$\text{V}(\text{CO})_6^-$	1860	460

17. (a) Discuss the carbonylation of methanol, when it is dry and when it has 5% water.

Or

Page 7

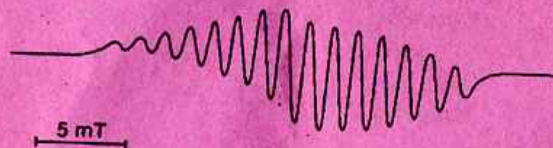
Code No. : 8852



- (b) What is Zeigler-Natta catalyst? How is it useful to prepare stereo regular polymer? Explain with mechanism.
18. (a) (i) How is NMR spectroscopy useful in elucidation of the structure of the following compounds :
- (1) $\text{PF}_3(\text{NH}_2)_2$
 - (2) $\text{P}_3\text{N}_3(\text{CH}_3)_2\text{Cl}_4$.
- (ii) How is NMR technique is useful in the study fluxional organometallic compounds?

Or

- (b) (i) The EPR spectrum shown below was recorded for a solution of $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{5+}$. What structural information can be deduced from this spectrum? How might the spectrum be modified if $^{17}\text{O}_2$ was used in the preparation of the peroxo-complex?



- (ii) Describe the applications of EPR spectroscopy in studying the Jahn-Teller distortion in $\text{Cu}(\text{II})$ complexes.

Page 8

Code No. : 8852

19. (a) (i) Bring out the relationship between fluorescence intensity and concentration. How will you estimate Al^{3+} and F^- ions by fluorimetric method?
- (ii) Sketch and explain the TGA curve of calcium oxalate monohydrate. 100 mg of calcium oxalate monohydrate was subjected to TGA. Calculate the weight loss in various temperature region $100^\circ\text{C} - 950^\circ\text{C}$.

Or

- (b) (i) Why a high concentration of potassium salt is added to standards and samples in flame absorption and emission methods?
- (ii) A solution in an organic solvent generally results in enhanced sensitivity in flame spectrometric methods. Explain.
- (iii) Why a sharp line source is desirable for AAS?
- (iv) Why high temperature nitrous oxide-acetylene flame sometimes required in atomic absorption spectrophotometry?
- (v) Why the technique of atomic absorption is only limited to metals?

Page 9

Code No. : 8852

