## 2016/ODD/08/22/CHM-301/346

PG Odd Semester (CBCS) Exam., December-2016

CHEMISTRY

(3rd Semester)

Course No. : CHMCC-301

#### (Inorganic Chemistry—III)

Full Marks: 70Pass Marks: 28

*Time* : 3 hours

The figures in the margin indicate full marks for the questions

Answer five questions, selecting one from each Unit

#### Unit—I

- **1.** (a) What is meant by organometallic compound? Write down different strategies to obtain kinetically stable organometallic compounds. 1+4=5
  - (b) Write down the products for the following (give structures) : 1×4=4
    - (i)  $WCl_6 + LiMe \longrightarrow ?$

(*ii*) 
$$[CpIrCl_2]_2 \xrightarrow{AlMe_3} ?$$

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( Turn Over )

(2)

(iii) Ni(PPh<sub>3</sub>)<sub>3</sub> + C<sub>2</sub>H<sub>5</sub>I  $\longrightarrow$  ?

(*iv*)  $K[Mn(CO)_5] + PhCH_2I \longrightarrow ?$ 

- (c) Illustrate the MO diagram showing d orbital overlap between metal atoms of  $[Os_2Cl_8]^2$ . Predict the bond order and draw the most stable structure. 3+1+1=5
- (a) Determine the total valence electrons (TVEs) of the following compounds and comment on their isolobal relationship : 1×4=4
  - (*i*)  $[(^{5} C_{5}H_{5})Fe(CO)_{2}]$
  - (*ii*) [CoH( <sup>8</sup> C<sub>8</sub>H<sub>8</sub>)]
  - (iii)  $[Pt(Ph)(CO)Cl_2]$
  - (*iv*)  $[Mn(CO)_6]$
  - (b) Taking suitable example, show how the change in ligands and metals influence the steric saturation in organometallic compounds.3
  - (c) Give products of the following reactions : 1×2=2

(*i*) 
$$\operatorname{Cp}_2\operatorname{Zr}(\operatorname{Ph})_2 \xrightarrow{h} [A] \xrightarrow{\operatorname{Ph}-C \equiv C - \operatorname{Ph}} [B]$$
  
(*ii*)  $(\operatorname{CO})_5 \operatorname{W}=C \xrightarrow{\operatorname{OMe}}_{R} + \operatorname{BBr}_3 \longrightarrow [C]$ 

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(Continued)

(d) Give a schematic route to obtain Schrock-alkylidene compound from Fischer-carbene compound. How does Fischer-type compounds differ from Schrock-type compounds? Discuss the bonding in Schrock-type organometallic compounds.  $1\frac{1}{2}+2+1\frac{1}{2}=5$ 

#### Unit—II

- **3.** (a) What is meant by 'coordinative unsaturation'? How is it related to catalytic properties of inorganic complexes? Furnish two examples. 1+2+2=5
  - (b) Write the products and comment on the following reactions : 2×3=6

$$(i) \quad \text{Fe}(\text{CO})_5 + \text{OH}^- \longrightarrow A \xrightarrow{\text{OH}^-} B + C$$

(*ii*) 
$$[Rh(CO)_2Cl_2] + CH_3I \longrightarrow A$$

(iii) 
$$H^+ \xrightarrow{H^+} A \xrightarrow{BH_4^-} B$$
  
Fe(CO)<sub>3</sub>  $H^+ \xrightarrow{H^+} A \xrightarrow{BH_4^-} B$ 

(c) Suggest a plausible mechanism for the oxidative addition of  $H_2$  to metal complexes.

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(Turn Over)

3

(4)

- 4. (a) The rate of reaction of O<sub>2</sub> with trans-IrX(CO)(PPh<sub>3</sub>)<sub>2</sub> in benzene decreases in the order X I Br Cl N<sub>3</sub> F. Explain the observation.
  - (b) Furnish the products of the following reactions and predict the probable structure :  $1\frac{1}{2}\times2=3$  (i) IrCl(CO)(PR<sub>3</sub>) H<sub>2</sub>S ?
    - (ii) CH<sub>3</sub>Rh(PPh<sub>3</sub>)<sub>2</sub> ?
  - (c) Briefly discuss Ziegler-Natta catalysis for polymerization of alkene.4
  - (d) Write a note on insertion reaction. 3

#### Unit—III

- **5.** (a) Deduce the symmetry point group notation for a planar *cis* and *trans*- $PtCl_2X_2$ .
  - (b) Develop the matrix for an inversion (i) operation performed on a vector having coordinates  $(x_1, y_1, z_1)$ .
  - (c) Work out the point group symmetry of the following :

$$PF_3Cl_2$$
,  $MnBr(CO)_5$ ,  $S_2O_3^2$ 

(Continued)

**6.** (*a*) Furnish the symmetry point groups of the following (explain with suitable illustrations) :

 $S_8$ ,  $CuCl_4^2$ 

- (b) What is meant by character of a symmetry element? Define dimension of representation. What is the dimension of  $C_2$  in a  $C_{2\nu}$  point group?
- (c) Show using figurative illustration for  $C_{3\nu}$  point group

$$_{\nu}C_{3}^{1} \ _{\nu} \ C_{3}^{2}$$
 3

4

3

(d) Show that

$$k^{2}_{i}(R) \quad h$$

where symbols have their usual significance in relation GOT. 4

### UNIT—IV

- 7. (a) Discuss the principle of ionization chamber for radiation measurements. Why is signal amplification needed in this technique?
  3+2=5
  - (b) Discuss the energetics of nuclear fission. 5

- (c) Explain the concept and utility of nuclear reaction cross section.
- **8.** *(a)* Explain the photochemical process in an inorganic scintillator. 4
  - (b) Discuss briefly the principle of Ge (Li) detector. Write down its advantages and disadvantages over NaI (Tl) detector. 4+3=7
  - (c) Write a short note on any one of the following: 3
    - (i) GM counter
    - (ii) Nuclear fusion

## Unit—V

**9.** (a) What is meant by molecular recognition? Write down the factors for high recognition. How can a spherical macrocyclic cryptand be useful for spherical, tetrahedral and anion recognition? Explain by taking suitable examples.

1+2+4=7

(b) ATP hydrolysis can be catalyzed by the protonated macrocyclic polyamines. Briefly discuss.3

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# (7)

(c) Discuss light driven (2e 2H) symport
 across a membrane via quinone carrier
 molecule, vitamin K<sub>3</sub>.

4

- 10. (a) Dithienylethene system bearing two phenol groups shows the dual mode of optical-electrical switching process. Explain.
   4
  - (b) Show schematically the processes involved in supramolecular photochemistry. Explain A-ET-E process by taking a suitable example. 2+2=4
  - (c) Hydrogen bonds have been used to drive the formation of rotaxanes and catenanes. Briefly discuss.

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