PG Odd Semester (CBCS) Exam., December—2018

CHEMISTRY

(3rd Semester)

Course No. : CHMCC–301

(Inorganic Chemistry—III)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Why are transition metal alkyls kinetically unstable? Account the effect of steric factor (both ligand and metal) on the stability of organometallic compounds. 1+3=4

(b) Find out the first row transition metals (M) for the following compounds (all of them obey 18e rule) : ½×4=2

(i) $(\ ^4\text{-}C_8H_8)M(CO)_3$

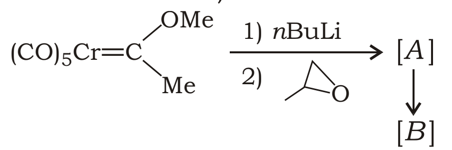
(ii) $M(CO)_4(PPh_3)(COCH_2R)$

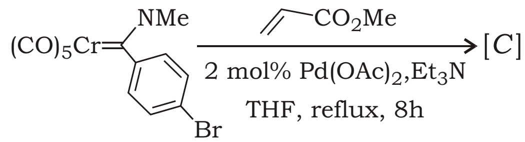
(iii) $(\ ^3\text{-}C_3H_5)M(CNMe)_5$

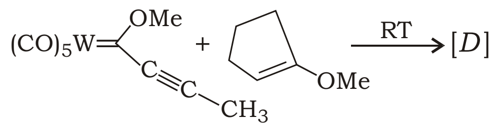
(iv) $[(\ ^5\text{-}C_5H_5)(CO)_3M]_2$

(one M—M bond)

(c) Complete the following reactions (provide structures) : 2+1+1=4

(i) 

(ii) 

(iii) 

(d) Explain the metal-metal bonding in $Re_2Cl_8]^2$ using *d* orbital overlap. Furnish its structure. Why is its geometry different from $Os_2Cl_8]^2$? 2+1+1=4

2. *(a)* Furnish two synthetic routes to obtain Fischer-carbene complexes. 1½×2=3

(b) Write brief accounts on the following : 1½×2=3

(i) Fluxional behaviour of indenyl complexes

(ii) Olefin metathesis

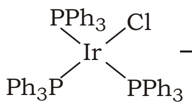
(c) Illustrate the structure of Pope's organometallic compound (Me_3PtI). Furnish TVE count. 1½+½=2

(d) Write down the products for the following reactions : 1×4=4

(i) $Cp_2Zr\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \xrightarrow{CO} [A]$

(ii) $Cp_2TiMe_2 \xrightarrow[2Me—C{\equiv}C—Me]{h} [B]$

(iii) $[CpIrCl_2]_2 \xrightarrow[[O]]{AlMe_3} [C]$

(iv)  $\xrightarrow{—HCl} [D]$

(e) Show the synthesis and catalytic applications of Tebbe's reagent. 2

UNIT—II

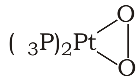
3. (a) What is coordinative unsaturation compound? Write two methods to generate coordinative unsaturation compound. Give reactions. 1+3=4

(b) On the basis of Lewis acid and base concept, explain oxidative addition reaction. "In a reaction

$$trans\text{-}\overset{I}{Ir}X(CO)L_2 \quad RCOOH \rightleftharpoons \overset{III}{Ir}HX(O_2CR)(CO)L_2,$$

the equilibria lie to the $\overset{III}{Ir}$ side in the order X Cl Br I and in the order L PPh_3 $PMePh_2$ PMe_2Ph PMe_3."
Explain. 2+2=4

(c) Write the products and comment on the natures of the following reactions : 1½×4=6

(i)  $+ CO_2 \longrightarrow$?

(ii) ${}^5\text{-}C_5H_5(CO)_3Mo—CH_2—CH{=}CH_2 \xrightarrow{H^+}$?

(iii) $Ru(PPh_3)_2(CO)_3 + H_2 \longrightarrow$?

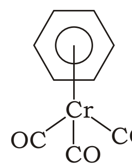
(iv) $CpMo(CO)_3Me + CN^- \longrightarrow$?

4. (a) What is hydrosilation reaction? Which catalyst is used for it? Discuss the stereochemical aspect of the reaction. 4

(b) Write the products and give explanations for the following reactions : 1½×2=3

(i) $(RO)_3Mo{\equiv}Mo(OR)_3 \xrightarrow{ROOR} [A]$

$(RO)_3Mo{\equiv}Mo(OR)_3 \xrightarrow{2Cl_2} [B]$

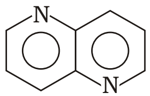
(ii)  $+ \bar{C}H_2CO_2Me \longrightarrow [C]$

(c) Show how $(CH_3)_2CHCH_2CHO$ can be prepared from $(CH_3)_2C{=}CH_2$ by the hydroformylation process. 4

(d) "Selectivity of Wilkinson's catalyst can be fine-tuned by using phosphine having different cone angles than PPh_3." Explain taking appropriate example. 3

UNIT—III

5. (a) Work out the point groups of the following : 2×2=4

(i) 

(ii) Allene

(b) Examine if CH_4 molecule possesses an S_4 or not. Show what are the associated symmetry operations generated by S_4. 2+3=5

(c) A partial character table for C_{3v} point group is given as

C_{3v}	E	$2C_3$	$3\ _{v}$
?	1	1	1
?	1	1	–1
?	2	–1	0

Assign the Mulliken labels for the representation and complete the table and hence deduce the number of irreducible representation. What are the order and class for this point group? 5

6. (a) Using figurative illustration for C_{3v} molecule, show the similarity transform of C_3 is

$$_{v}C_3 \quad C_3^2$$ 4

(b) Work out the character representation of hybrid orbitals of NF_3, deduce the irreducible representations. Show that the hybridization scheme is sp^3 for the molecule. 6

(c) Does CO_2 molecule have IR-active mode of vibrations? Briefly discuss the group theoretical criteria for IR-activity. 4

UNIT—IV

7. (a) What is spallation reaction? How does it differ from nuclear fission? 4

(b) Discuss the principle of ionization chamber of radiation measurements. Why is signal amplification needed in this process? 3+3=6

(c) Explain the concept and utility of nuclear cross section. 4

8. (a) Discuss the photochemical process in an inorganic scintillator, NaI(Tl). Write down the advantages and disadvantages of NaI (Tl) scintillator. 4+3=7 *(b)* Discuss briefly the energetics of nuclear reactions. What do you mean by the potential barrier of a nucleus? 4

(c) Write short note on any *one* of the following : 3

(i) Nuclear fusion

(ii) Proportional counter

UNIT—V

9. *(a)* What are the various types of non-covalent forces present in supramolecules? How are they different from covalent forces? 4

(b) What are recognition, transformation and translocation in connection with supramolecular species? Explain with examples. 6

(c) What is A-ET-E process in supramolecular photonic devices? Discuss the functioning of Eu(III)-cryptate complex. 4

10. *(a)* What is meant by coupled transport? Explain light coupled electron transport across a membrane via the quinone-carrier molecule vitamin K_3 and its hydroquinone form. 6

(b) Dithienylethene system bearing two phenol groups shows an EDRAW (Erase Direct Read After Write) process. Explain. 4

(c) ATP hydrolysis can be catalyzed by the protonated macrocyclic polyamines. Discuss briefly. 4

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