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UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

End Semester Examination-Online Bb mode, July 2020 (date of exam: 12th July 20)

Course: Reactions, Kinetics, Mechanisms in Coordination Compounds and Boron Chemistry **Semester:** II
Program: M Sc (H) Chemistry **Time 03 hrs.**
Course Code: CHEM7011 **Max. Marks:** 100

PART- A(Answer ALL questions) 30 x 2 = 60 Marks

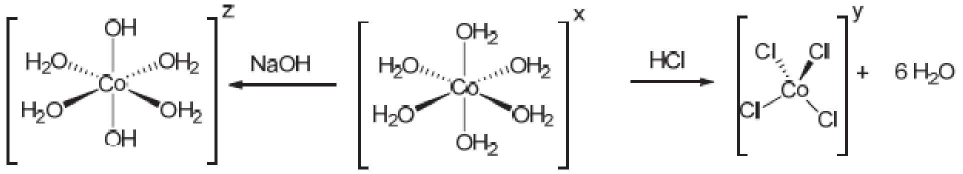
PART A contains 30 questions for a total of 60 marks.

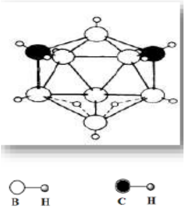
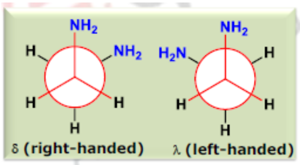
Part-A contains multiple (MCQs) choice and multiple answer questions(MAQs)(Negative marks for MAQs incorrect answers)

Q 1	In the base-catalysed substitution of Cl^- by $[OH]^-$ in $[Co(NH_3)_5Cl]^{2+}$ under strongly basic conditions, the first step in the mechanism is: A. conversion of an ammine to amido ligand B. substitution of Cl^- by $[OH]^-$ C. dissociation of Cl^- to give a 5-coordinate intermediate D. association of $[OH]^-$ to give a 7-coordinate intermediate
Q 2	Reactivity of borazole is greater than that of benzene because. A. Borazole is non-polar compound B. Borazole is polar compound C. Borazole is electron deficient compound D. Of localized electron in it
Q 3	BCl_3 does not exist as dimer but BH_3 exist as dimer (B_2H_6) because : A. Chlorine is more electronegative than hydrogen B. There is pπ-Pπ back bonding in BCl_3 but BH_3 does not contain such multiple bonding C. Large size chlorine atom do not fit in between the small born atom whereas small sized hydrogen atom get fitted in between boron atom. D. None of the above
Q 4	Which statement is incorrect about the mechanisms of electron transfer? A. Electron transfer may occur by an inner or outer-sphere mechanism depending on the system B. Long range electron-transfers such as in cytochromes are most likely to occur by outer-sphere mechanisms C. Marcus-Hush theory applies to inner-sphere mechanisms D. In an inner-sphere mechanism, electron transfer between two metal centres involves a bridging ligand
Q 5	In diborane? A. 4 bridged hydrogen and two terminal hydrogen are present. B. 2 bridged hydrogen and four terminal hydrogen are present. C. 3 bridged hydrogen and three terminal hydrogen are present. D. None of the above.
Q6	Which of the following is false statement ? A. BH_3 is not a stable compound B. Boron hydride are formed when dil. HCl reacts with Mg_3B_2

	C. All the B – H bond distance in B_2H_6 are equal D. The boron hydride are readily hydrolyzed
Q7	The order of CO bond strengths in the following metal hexacarbonyls is likely to be: A. $V(CO)_6^- < Mn(CO)_6^+ < Cr(CO)_6$ B. $V(CO)_6^- < Cr(CO)_6 < Mn(CO)_6^+$ C. $Mn(CO)_6^+ < Cr(CO)_6 < V(CO)_6^-$ D. $Cr(CO)_6 < Mn(CO)_6^+ < V(CO)_6^-$
Q8	Which statement is incorrect about CO ligands? A. A CO ligand can accept electrons into its π* MO; this weakens the C–O bond B. In the IR spectrum of $Fe(CO)_5$, absorptions assigned to the CO stretching modes are at higher wavenumber than that of free CO C. CO ligands can adopt terminal, μ and μ3 bonding modes; the amount of back donation depends on the bonding mode D. Fluxional behaviour is common in metal carbonyl compounds, and can be investigated by 13C NMR spectroscopy
Q9	The reaction: ***$Mn(CO)_5Me + CO \rightarrow Mn(CO)_5(COMe)$*** is an example of: A. a ligand addition B. a β-elimination C. an oxidative addition D. an alkyl migration
Q10	The conversion of ***$Mn_2(CO)_9(PPh_2H)$ to $Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}H)$*** is best described in terms of loss of ***CO*** in association with: A. an oxidative addition B. a substitution reaction C. α-hydrogen abstraction D. β-hydrogen elimination
Q11	Which compound is most likely to undergo oxidative addition of H_2? A. $RhCl(PPh_3)_3$ B. $Fe(CO)_5$ C. $[RhI_4(CO)_2]^-$ D. $[HFe(CO)_4]^-$
Q12	Highly Trans directing ligand is? A. H_2O B. NH_3 C. $C_6H_5^-$ D. NO
Q13	Which statements are not correct?

	A. A dissociative mechanism is a 2-step mechanism with the leaving group departing in the second step B. An associative mechanism is a 2-step mechanism; the intermediate has a lower coordination number than the starting complex C. In a dissociative interchange mechanism, bond breaking dominates over bond formation D. In an associative interchange mechanism, the entering group associates with the substrate after the leaving group has departed
Q14	Anation is: A. the substitution of an uncharged ligand by an anionic ligand B. the substitution of an uncharged ligand by another uncharged ligand C. the substitution of an anionic ligand by another anionic ligand D. the substitution of an anionic ligand by an uncharged ligand
Q15	Form the following ions identify two kinetically inert ions A. Gd^{3+} B. Cd^{2+} C. Ru^{3+} D. Cr^{3+}
Q16	Which of the following will have the largest crystal field splitting? A. $[Co(H_20)_6]^{3+}$ B. $[Fe(H_20)_6]^{3+}$ C. $[V(H_20)_6]^{3+}$ D. $[Mn(H_20)_6]^{3+}$
Q17	Which metal centres does not obey the 18-electron rule? A. Fe in $Fe(\eta^5\text{-}C_5H_4COMe)_2$ B. Co in $Co_2(CO)_8$ C. Ru in $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$ D. V in $V(CO)_6$
Q18	How many metal – metal bonds are present in the structure of $Fe_2(CO)_9$ A. One B. Two C. Three D. Four
Q19	According to FTIR Spectroscopic Features of Carbonyl Complexes, identify all correct statements A. Uncoordinated CO: 2143 cm^{-1} B. Terminal M-CO: 2125 to 1850 cm^{-1} C. Terminal M-CO: 1850 to 1750 cm^{-1} D. Uncoordinated CO: 1675 to 1600 cm^{-1}

Q20	In normal ORD, spectra there are ___ maxima and __ minima. A. 1,2 B. 1,1 C. 0,0 D. 0,1
Q21	At the absorption peak an anomalous ORD, curve ______________. A. reaches minimum B. crosses the base line C. reaches maximum D. none of the above
Q22	As a part of application of Wade's rule in determining the structure of higher boranes. Consider borane molecule $B_7H_7^{2-}$, Heptahydroheptaborate(2-) and identify correct statemments belongs to this molecule based on Wade's rule. A. there are 2 B-H bonds in the molecule B. anionic charge on the cluster is -3 C. number of electron pairs are 8 D. there are 3 C-H bonds in the molecule
Q23	STYX code for the nido borane B_6H_{10} is A. 4120 B. 4220 C. 4320 D. 4420
Q24	For Co in oxidation state II, predict the overall charges of the coordination complexes shown in the reactions below:  A. z = +2; x = -2; y = +2 B. z = 0; x = +2; y = -2 C. z = 0; x = +2; y = +2 D. **z = -2; x = +2; y = -2**
Q25	Example for Cr(III) complex reaction: $[Cr(en)_2(ox)]^+ + 4\ H_2O$ -----> $[Cr(ox)(H_2O)_4]_+ + 2$ en **slow reaction** where en = ethylendiamine, ox = oxalate metal complex that undergo ligand substitution reactions with $t_{1/2} < 1$ min. at 25 ^oC are called kinetically A. Labile B. Inert C. both labile and intert D. neither labile nor intert

Q26	$[Co(NH_3)_5X]^{2+} + [Ru(NH_3)_6]^{2+} \rightarrow [Ru(NH_3)_6]^{3+} + Co^{2+} + 5NH_3 + X^-$ A. outer-sphere ET reaction B. inner-sphere ET reaction C. both outer and inner-sphere ET reactions D. only inner-sphere ET reaction without outer-sphere ET reaction
Q27	 In the above structure *ARACHNO CARBORANES* the following statements are correct A. Two corners of triangulated polyhedra is removed B. Total number of electron in bonding framework is(2n+6)e$^-$ C. Total number of electron in bonding frameworkis (2n+4)e$^-$ D. General formula: $C_2B_nH_{n+6}$
Q28	 From the above figure assignment of ligand conformation using Circular Dichroixm (CD): which are correct statements A. this is tris(chelate) octahedral complexes B. dissymmetric ligand present in the complexes C. both are enantiomers D. No chirality in this complexes
Q29	correct statements of **Circular dichroism** (**CD**) are A. CD involving circularly polarized light B. Left-hand circular (LHC) and right-hand circular (RHC) polarized light represent two possible spin states for an a photon C. CD and circular birefringence are manifestations of optically inactive D. circularly polarized light passes through an absorbing optically active medium
Q30	Jemmis' mno rule states that A. m + n + o skeletal electron pairs are necessary for a closed macropolyhedral system to be stable B. For borane and carborane clusters, the structures are based on deltahedra, which are polyhedra in which every face is triangular C. a cage molecule with a geometry based on a closed polyhedron D. e structures are based on deltahedra, which are polyhedra in which every face is a cuboid

Part- B (Answer ALL questions) 5 x 8 = 40 Marks

1. There are total of five questions attempt all carry equal marks
2. **PART B** consist of long answer based questions and has the total weightage of 40%. (Whereas **PART A** it is 60%)

3. **The PART B** responses(Answers) should be attempted in blank white sheets (hand written) with all the details like programme, semester, course name, course code, name of the student, SAP ID at the top (as in the format) and signature at the bottom (right hand side bottom corner)

Q 1 Explain migratory insertion mechanism when $(OC)_5Mn-CH_3$ reacts with CO

Q 2 Draw the ligand field activation energy profile diagrams for octahedral substitution what it happens through dissociation path

Q 3 How can we differentiate between terminal and different kinds of bridging carbonyl groups in metal carbonyls?

Q 4 The circular dichroism (CD) spectral data for dextrorotary enantiomer of tris(*R*,*R*-trans -1,2-diaminocylohexane)cobalt(III) cation, $(+)_{589}$-[Co(*R*, *R*-chxn)$_3$]$^{3+}$, if listed in the below Table1, would appear as follows:

Table1

	υ (cm^{-1})	$\varepsilon_1 - \varepsilon_r$
$(+)_{589}$-[Co(*R*, *R*-chxn)$_3$]$^{3+}$	20,000	-2.28
	22,500	+0.69

Assign the correct (Δ or ʌ) configuration to the metal. Discuss in detail.

Q 5 **a)** Draw the structures for diborane, borazole and anions, $B_2H_7^-$ and $B_6H_6^{2-}$.

b) Assuming that the external H-B-H angle in B_2H_6 accurately reflects the interorbital angle:

i) Calculate the *s* and *p* character in these bonds.

ii) Calculate the s and p character remaining for the bridging orbitals

iii) Compare the value from ii) with the experimental internal angles. **(4+4)**