

2018

M.Sc.

Part-I Examination

CHEMISTRY

PAPER—III

Full Marks : 100

Time : 4 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Inorganic)

Answer any *five* questions,

taking at least *two* from Group-A and B

and *five* from Group-C.

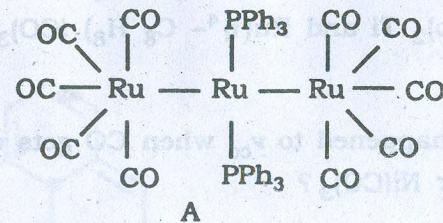
Group-A

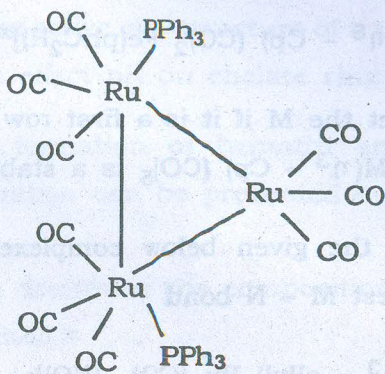
1. (a) Write down the name of three essential and three beneficial metals? Discuss the biological function of them. 3+6

(Turn Over)

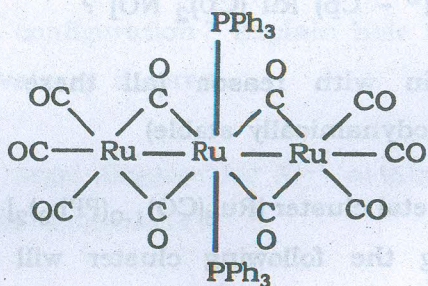
- (b) Write down the active site structure of transferrin and describe the effect pH on chelate ring of it.
- (c) Discuss the formation of hematin and cite how hematin formation can be prevented?
2. (a) How will you determine the composition of complex by Job's method? 5
- (b) Derive ground state term symbols for d^3 , d^6 and d^9 electronic configuration? Explain hole formalism or hole equivalency theorem. 3+2
- (c) Draw the Orgel diagram for Ni^{2+} octahedral system showing all transitions? 5
3. (a) Following the 18e rule as a guide, determine the 'x' in the following complexes.
- (i) $[(CO)_3 Ni - Co(CO)_3]^x$
- (ii) $IrBr_2 (CO)_n (PPh_3)_2 (CH_3)_3$
- (iii) $[(Cp)_3 Ni_3(\mu^3 - CO)_3]^x$ (has 3 Ni - Ni bond)

- (iv) $[(\eta^5 - Cp) (CO)_2 Fe(PhC_2H)]^x$
- (b) Predict the M if it is a first row transition element and $[M(\eta^3 - Cp) (CO)_5]$ is a stable compound. 2
- (c) From the given below complexes which one have shortest M - N bond
- (i) $[(\eta^3 - allyl) Ru (CO)_2 (NO)]$.
- (ii) $[(\eta^5 - Cp) Ru (CO)_2 NO]$?
- Explain with reason (all these complexes are thermodynamically stable) 5
- (d) The metal cluster $[Ru_3(CO)_{10}(PPh_3)_2]$ is stable. Which among the following cluster will be the actual structure of molecule? Justify your answer. 4





B



C

4. (a) How could you measure the fluxionality of $(\eta^1 - \text{Cp})_2(\eta^5 \text{Cp})_2 \text{Ti}$ and $\text{Ru}(\eta^4 - \text{C}_8\text{H}_8)(\text{CO})_3$ molecules?

- (b) What happened to ν_{CO} when CO gets coordinated to BH_3 or $\text{Ni}(\text{CO})_3$? 2

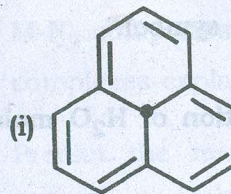
- (c) Arrange the following in the decreasing order of back donation $[\text{Cr}(\text{CO})_6]$, $[\text{Ti}(\text{CO})_6]^{2-}$, $[\text{Mn}(\text{CO})_6]^+$, $[\text{Ir}(\text{CO})_6]^{3+}$. If cis-cyclooctene and trans-cyclooctene olefin is bind to Cr then which of them will form the stronger complex and why? 2

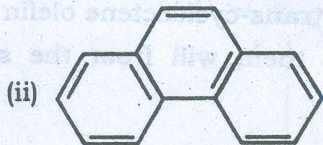
- (d) The C - C bond distance (1.37Å) in $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ is slightly longer than in the free ethylene (1.34Å) - Explain. 3

5. (a) What do you mean by improper axis of rotation? Prove that C_3 axis is collinear and coexist with C_9 axis? Write down the all symmetry elements present in CH_4 molecule indicating where they are passing from. 2+2+6

- (b) If in a molecule has $\text{C}_4(x)$ axis and the $\text{C}_2(y)$ axis then what will be the single step symmetry operation? 2

- (c) Find out the point group for the following molecules. 3





(iii) Ferrocene (staggered)

(iv) B_2H_6

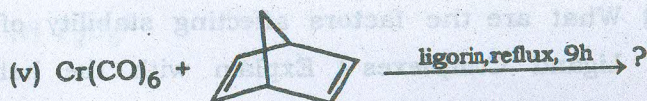
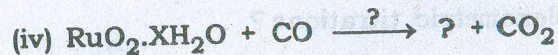
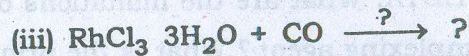
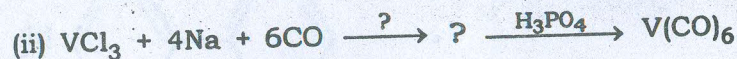
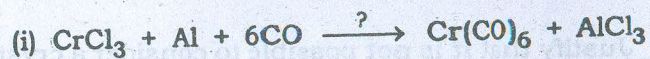
(v) $P_2O_6^{4-}$

(vi) NO_2^+

Group-B

6. (a) State 'rearrangement theorem'. 2
- (b) Find all the irreducible representations of C_{3v} point group giving the Mullikans symbol. 4
- (c) Find the matrix representation of H_2O molecule. 5
- (d) Write Hermann-Mauguin notation for D_{3h} , C_{3v} , D_2 and Td point group. 2

- (e) Justify that it is not possible to consider a crystal with C_5 axis of rotation. 2
7. (a) Derive an expression for conditional stability constant in terms of EDTA. What are the limitations of using EDTA as complexing agent? What is the principle of spectro-photometric determination of end point in complexometric titrations? 3+3+2
- (b) What are the factors affecting stability of Metal-Ligand Complexes? Explain with the help of a suitable example, the masking-demasking method of estimating different ions in a mixture by titrating against EDTA. 3+4
8. (a) What do you mean by homoleptic complex? Why $V(CO)_6$ readily reacts with Na? 2+2
- (b) Although N_2 and CO are isoelectronic molecules but M- N_2 complexes are much weaker compare to M-CO complexes-explain. 3
- (c) Predict the missing reagents or products for the following reaction. 8



9. (a) Define the common terms used in chromatography :

(i) Stationary phase

(ii) Mobile phase

(iii) Analyte

(iv) Elute.

4

(b) A solute has a K_D between water and chloroform of 5.00. Suppose we extract a 50.00-mL sample of a 0.050 M aqueous solution of the solute with 15.00 mL of chloroform. What is the separation's extraction efficiency? 4

(c) Write down the advantages of chromatography over other separation techniques. 3

(d) What is role of precision in analysis?

Define the all term listed bellow

(i) Standard deviation

(ii) Coefficient of variation

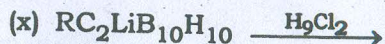
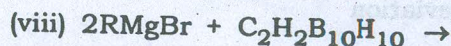
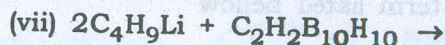
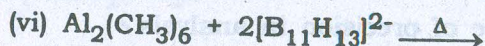
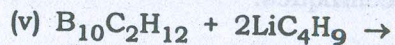
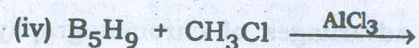
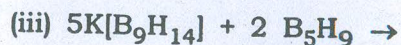
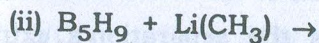
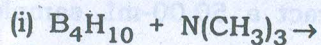
(iii) Variance. 1+3

10. (a) Calculate the all possible STYX number and comment on plausible structure for B_3H_7 and B_3H_6^+ molecule? 4+4

(b) Classify the following borons as closo, nido and arachno :



(c) Complete the following reactions :



5

Group-C

11. Answer any five questions :

5×5

- (a) Write down the active site structure of haemoglobin ?
What are the important functions of heme protein ?
Why color of blood is red ?

- (b) 'All vibration modes present in water molecule are IR and Raman active' justify this statement. What is abelian group ?
- (c) A metal forms two complexes in the same oxidation state. In one complex the magnetic moment is 4.9 BM another is 0.0 BM. Which of the following metal fit this description ? Cr(III), Mn(II), Mn(III), Fe(II), Fe(III) and Co(II). What do you mean by picket fence models ?
- (d) Write down the active site structure of carbonic anhydrase. Suggest a reaction mechanism of its enzymatic conversion of CO_2 .
- (e) Write down the structural feature of cytochrome C ? Explains the biological importance of this enzyme ?
- (f) Given Δ_0 for H_2O is 13900 cm^{-1} what would be the CFSE of $[Cr(H_2O)_6]^{2+}$ in high spin and low spin configuration ? In terms of CFT explain why all six Cu-OH₂ distance in $[Cu(H_2O)_6]^{2+}$ are not equal ?

3+2

- (g) What do you mean by crystal field stabilization energy (CFSE)? Explain the following facts that $10 Dq$ increases in the order $[\text{CrCl}_6]^{3-} < [\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{CN})_6]^{3-}$.