Ramakrishna Mission Residential College (Autonomous)

Narendrapur, Kolkata-700103

B.A./B.Sc. Examinations 2019

Subject: Chemistry (Inorganic)

Semester-III

Course Code: HCHEIIICC05LTH

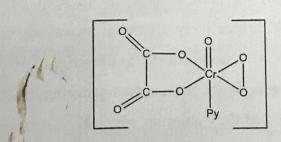
Time: 2 hrs

Full Marks:50

1. Answer any four questions:

[3X4 = 12]

- (a) Give examples of complexes with coordination number 7, 8 and 9.
- (b) Give an example of a carbon free optically active complex isolated by Werner. Predict the number of stereo-isomers of a $[M(a-a)_2X_2]$ type complex.
- (c) The stepwise stability constants of the mercury cyanide complex are log K₁, 18.0; log K₂, 16.7; log K₃, 3.8 and log K₄, 3.0. Explain the trend.
- (d) A chelate is more stable than the corresponding non-chelate. Explain with an example.
- (e) The binding modes of L in [Pd (NH₃)₂L₂] and [Pd (PPh₃)₂L₂] when $L = SCN^-$ are different. Explain.
- (f) Write the IUPAC names of the ligands, the complex and coordination number of the given complex.



2. Answer the following questions:

[3]

(a) Explain magic numbers of nuclei and produce evidences in support of extrastability of such nuclei.

OR

A piece of wood recovered in an excavation is found to have the activity 15% compared to that of a fresh sample. Find the dead time of the wood. Given, Half life of 14 C = 5578 year.

(b) Define Spallation with an example.

[2]

How will you establish by Tracer method that oxidation of H₂O₂ does not involve cleavage of peroxo bond.

(c) Calculate the maximum K.E. of the β^- particle emitted in the radioactive decay of He⁶. Assume that the β^- has its maximum energy when no other emission accompanies the process. Given, the mass of He⁶ = 6.01889, Li⁶ = 6.01512 amu respectively.

OR

(i) In 189^{F} , $\frac{n}{p}$ ratio = 1 still it is radioactive. Explain.

3.

a) Answer any three:

[3x3]

- (i) Copper displaces zinc from a solution of zinc(ii) salt in presence of excess KCN. Explain.
- (ii) Find out the standard electrode potential for MnO₄⁻/MnO₂ redox couple in 1(M) acid medium, given E⁰ for MnO₄⁻/Mn²⁺ & MnO₂/Mn²⁺ are 1.51V &1.2V, respectively.
- (iii) Explain the role of phosphoric acid in the titration of Fe²⁺ by Cr₂O₇^{2—}in presence of BDS indicator.
- (iv) The E⁰ values of the redox couples Cu²⁺, I⁻/CuI, Fe³⁺/Fe²⁺ & ½ I₂/I⁻ are 0.85V, 0.77V &0.54V, respectively. Can you suggest any condition that will enable estimation of Cu²⁺ iodometrically in presence of Fe³⁺? Justify your answer.
- (v) Find out the equivalence point potential during the titration of 0.1M Fe²⁺ solution with 0.1M Ce⁴⁺ solution, given E⁰ values for Fe³⁺/Fe²⁺ & Ce⁴⁺/Ce³⁺ are 0.77V &1.57V. Name one suitable indicator for this titration.
- b) Answer any one:

[3×1]

- i) Calculate the solubility of AgCl in 0.1 KCl solution at 25° C (Given K_{sp} of AgCl= 1.0×10^{-10} at 25°). Compare this value with that in pure water at the same temperature.
- ii) Explain the role of NH₄Cl in qualitative analysis of Group-IIIA basic radicals in ammoniacal medium. Do you think that the same purpose will be served if NaOH is used instead of NH₄OH?

4.

A. Answer any two:

[3×2]

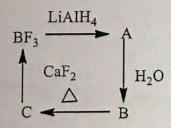
- a) Discuss the structure and bonding of diborane (B₂H₆) in the light of VB theory and MO theory.
- b) What are polythiazyl? How are they prepared? What is the special electrical property associated with polythiazyl? Draw the structure of polythiazyl.
- c) Draw the structures (according to VBT), mentioning the hybridisation of the central xenon atom;
- i) XeO₄²⁻ ii) XeF₅⁻ iii) XeO₂F₂
- d) Interhalogen compounds are always diamagnetic, covalent and generally more reactive the elemental halogens. Explain.

B. Answer any four

[4×2]

- a) NO2 but not CIO2 readily forms dimer. Explain.
- b) Elucidate "clathrate "compound citing at least one example.
- c) Give examples of two basic halogen compounds.
- d) Beryllium chloride exhibits different structures in solid and gaseous states.

 Explain.
- e) Identify A, B and C of the following transformations.



(f) Draw the structures of basic beryllium nitrate and basic beryllium acetate.

5. Answer any two:

 $[2.5 \times 2]$

- (i) "Borazine is called inorganic benzene, but this is a misnomer (wrong or inaccurate name)". Justify or criticize this comment citing at least two reaction.
- (ii) Write down the structure of the product formed in reaction of I mole of [NPCl2]3 with 3 mole Me2NH. Explain the course of the reaction.
- (iii) Comment on the structure of 'Zeolite' and explain its cation exchange property.
- (iv) Compare the common properties between organic and inorganic polymers.

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B.A./B.Sc. Semester-III Examination, 2018 Subject: Chemistry (Honours) Paper-V

Time: 2 Hrs

F.M.- 50

Write Group-A or Group-B on the top of the separate answer scripts.

Group-A Unit-I

1. Answer any three questions:

 $3 \times 3 = 9$

- a. Define primary and secondary valencies with examples.
- b. Predict the number of stereo-isomers of [Co(NH₂CH₂CO₂)₃].
- c. What is the role of ethylenediamine in the chemical distinction of isomers of [PtCl₂(NH₃)₂].
- d. Compare the overall stability constants of [Ni(en)₃]²⁺ and [Ni(NH₃)₆]²⁺ complex ions.
- e. Name the following compounds according to IUPAC system.
 - i. [(NH₃)₄Cr(OH)(NH₂)Cr(NH₃)₄](SO₄)₂
 - ii. [(CO)₃Fe(CO)₃Fe(CO)₃]

Unit--2

2. Answer question (a) and any three from the rest:

 $4\times2=8$

a. Write down the structures of the products (X) and (Y) in the following scheme of reaction and indicate the states of hybridization of B and N in them.

$$B_2H_6 + NH_3 \xrightarrow{heat} X+Y$$

- b. On burning in oxygen, lithium forms Li₂O while sodium forms Na₂O₂. Explain.
- c. As we go down group 2, the hydroxides become more soluble in water, while their carborators become gradually less soluble. Explain.
- d. Account for the magnetic property of KO2, and GaCl2.
- e. K₂Cr₂O₇ can be used as a primary standard for oxidometric titration, while Na₂Cr₂O₇ is not preferred. Explain.

f. When Til₃ which is isomorphous with alkali metal triiodides, is treated with aqueous sodium hydroxide, hydrated Ti₂O₃ is quantitatively precipitated. Comment on the above observation.

Unit-3

3. Answer any four questions:

 $4 \times 2 = 8$

- a. How will you identify nitrite in presence of nitrate in wet test in the laboratory? Give relevant chemical equation?
- b. What is Nessler's reagent? How it is prepared? Mention its analytical use with equations.
- c. 'Fluorine is a superhalogen'. Discuss
- d. In O₂F₂ the O-O bond is abnormally short while O-F bonds are larger than expected.
 Explain.
- e. What are thionic acids? How does dithionate differ from polythionates?
- f. Oxygen is O2 gas while sulphur is S8 solid. Explain.
- g. Interhalogen compounds have even number of halogen atoms while polyhalide ions have odd number of halogen atoms. Explain.

Group-B (Use separate Answer script) Unit-4

4. Answer the following questions:

III.

a. Predict the product/s in the following reactions with explanation: (any two). $2x2\frac{1}{2} = 5$

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B.Sc. Semester-V Examinations, 2019

Subject: Chemistry Honours

Paper: IX

Time: 2 hrs.



Full Marks: 50

Unit-1

1. Answer question (a) and any three from the rest:

 $1+(3 \times 3)=10$

- a) Give d- orbital splitting pattern in square pyramidal crystal field.
- b) Δ_0 Value for a given set of ligands in case of Fe^{III} complexes is more than that for Fe^{II} complexes. Explain.
- c) Calculate respective OSSE values and hence comment on Spinel type of NiCr₂O₄.
- d) An octahedral Au(II) complex is unstable and disproportionates to Au(0) and Au(III). Explain.
- e) Negatively charged OH is a weaker field ligand than neutral H₂O. Explain why?
- f) Aqueous Co(II) is neither oxidizing nor reducing. It becomes strongly reducing on addition of KCN. Explain the observation in terms of CFT.

Unit-2

2.

(i) Answer any two questions:

 $(2 \times 3) = 10$

- (a) How does electronic transition of a d³ metal ion differ from a d⁴ (high spin) metal ion? Explain.
- (b) An equimolar mixture of aqueous Ni²⁺ and Co²⁺ is colourless. Explain.
- (c) The experimental magnetic moment of CsCoCl₄ is higher than the spin only value. Explain.

(ii) Answer any two of the following questions:

 $(2\times 2)=4$

- (a) VO₄³- is white, while MnO₄- is purple. Explain.
- (b) What is spin isomerism? Explain with an example.
- (c) Lanthanide ions give sharp spectral band while those by d block metal ions broad. Discuss.

Unit-3

3. Answer any five

 $(2\times5)=10$

- a) Compare the O2 binding nature of hemocyanin and hemerythrin.
- b) What are the role of poximal and distal Histidine of Haemoglobin.
- c) What is Vaska's complex? Mention its importance in context of bio-inorganic chemistry.
- d) Write a note on 2Fe-2S ferredoxin.
- e) Write down the biological role of cytochrome C.
- f) Why does nature choose Zn²⁺ over Cu²⁺ in Carboxypeptidase A?
- g) Which metal involved in Wilson's disease? What is the antidote for this metal?
- h) Write a note on cis-platin.

4.

(i) Answer any three:

 $(3 \times 2) = 6$

- a) Why transition elements exhibit variable oxidation states?
- b) Would the f- block metal ions be expected to form strong field complex? Why or why not?
- c) Why most of the heavier transition metals form LS complexes? Why the paramagnetic species of such metals rarely conform to μ_s values.
- d) Give one example with formula & structure of entirely inorganic Rh complex that was resolved into optical isomer.

e) Compare the stability between Cu(III) and Au(III) ions.

(ii) Answer any one:

 $(1\times4)=4$

- a) Give a brief outline of the separation of lanthanide elements by the ion-exchange method.
- b) Outline the synthetic routes of the three isomers of [Pt (NH₃) (py) (Br)(Cl)] with the help of trans effect whose relative order being Br>Cl>py>NH₃.

Unit-5

1. Answer of the following questions (any five):

 $(2 \times 5) = 10$

- i. What is the difference between 'Precision' and 'Accuracy'
- ii. Distinguish between Random and Systematic errors with suitable examples.
- iii. What do you mean by retention time in Chromatography?
- iv. What are the most common sources of errors in the measurements in UV- visible spectrophotometric estimations?
- v. Explain two factors on which one cation is preferably adsorbed over another by ion exchange resin.
- vi. A spectrophotometer cell when filled with liquid X transmits 50% and when filled with another liquid Y transmits only 25 % of the incident light. What would be the optical density when the same cell is filled with a mixture of equal volumes of two liquids?
- vii. What are the crucial differences between DTA and DSC techniques?
- viii. When and how hydride generation method is used for AAS analysis of an element?

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B.A./B.Sc. Semester-V Examination, 2018 Subject: Chemistry (Honours) Paper-IX

Time: 2 Hrs

F.M.- 50

Unit-1

1. Question (a) is compulsory and attempt any three from the rest:

 $1 + 3 \times 3$

- a. Show the d-orbital splitting pattern in a square pyramidal crystal field.
- b. $[Fe(CN)_6]^{4-}$ is more stable than $[Fe(CN)_6]^{3-}$, while $[Fe(H_2O)_6]^{3+}$ is more stable than $[Fe(H_2O)_6]^{2+}$. Explain.
- c. Δ_0 values are larger than Δ_t values for a given metal ion with a given set of ligands. Justify or Contradict.
- d. What is the trend of the Δ_0 values of $Cr(CO)_6$, $MO(CO)_6$ and $W(CO)_6$? Explain with proper reason(s).
- e. The values of Δ_0 , for the high-spin cations $[(Ni(H_2O)_6]^{2+}]$ and $[Mn(H_2O)_6]^{3+}$ have been evaluated spectroscopically as 8400 and 21000 cm⁻¹ respectively. On the assumption that these values hold also for the corresponding oxide lattices, predict whether Ni^{II} Mn_2 III O₄ should have the normal or inverse spinel structure. What other factors might make your prediction unreliable?
- f. Aqueous Co(ll) is neither oxidizing nor reducing. it becomes strongly reducing on addition of KCN. Explain the observation in terms of VBT.

Unit-2

2.

a. Answer any two questions:

3×2

- i. All the lanthanide ions are colored. Explain.
- ii. Compare the electronic spectra of [Fe(H₂O)₆]³⁺ and [FeCl₄]⁻ ions.
- iii. The color intensities of [NiCl₄]²⁻ and [Ni(H₂O)₆]²⁺ ions are notably different. Explain.
- b. Answer any two questions from the followings:

2 × 2

- i. Give important differences between ferromagnetic and anti-ferromagnetic substances.
- ii. The ligand to metal charge transfer band increase in energy in the sequence: [CoI₄]²- < [CoCl₄]²-.. Explain.
- iii. Calculate the effective magnetic moment μ_{eff} of a f^2 ion.

Unit-3

- 3. Answer any four questions:
 - Answer (a) and any three from (b) (f)

 $1 + 3 \times 3$

- a. What is Wilson's disease?
- b. Draw the active sites of oxy-hemerythrin and oxy-hemocyanine.
- c. Write a short note on [4Fe-4S] ferredoxin.
- d. Describe the role of Zn-metal in carbonic anhydrase.
- e. Describe the mechanism of action of carboxy-peptidase A.
- f. Write the structures of two gold and platinum containing drugs.

Unit-4

4. Answer (a) and any three from (b) - (f):

 $1 + 3 \times 3$

- a. Give an example of an oxidizing agent containing a lanthanide element.
- Aqueous solution of Co (II) is pale pink, it turns intense blue on adding conc. HCI explain.
- c. Give outline of the synthetic routes of the isomers of [Pt (NH₃) (py) (B_r) (CI)] from [Pt Cl₄]²⁻ using trans effect phenomenon, given the order of trans effect as NH₃< py <CI <Br -.
- d. Cupric acetate monohydrate exhibits subnormal magnetic moment. Explain.
- e. Lanthanides exhibit +3 oxidation state in general, while actinides show variable oxidation states. Explain.
- f. In comparison to Mo(VI) and W(VI), Cr(VI) does not show polyanion chemistry. Explain.

Unit-5

5. Answer of the following questions (any five):

 $2 \times 5 = 10$

- a. Briefly discuss the method of determination of total cation concentration in water by ion exchange method.
- b. What do you mean by diffusional titration error electroconlometry?
- c. What do you mean by ion exchange capacity? How will you determine the exchange capacity of an anion exchanger?
- d. Write a note: Reverse phase chromatography.
- e. Write down the difference between thin layer chromatography and paper chromatography.
- f. At 460 nm a blue filter transmits 25% of the light and a yellow filter transmits 75% of the light. What is the transmittance at the same wave length of the two filters in combination?
- g. Draw a DSC curve for a typical organic polymer.
- h. When and how cold vapour technique is used for AAS analysis of an element?

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B.A./B.Sc. Semester-III Examination, 2017 Subject: Chemistry (Honours)

Paper-V

Time: 2 Hrs

F.M.- 50

Group-A Unit-I

1. Answer any three questions:

 $3 \times 3 = 10$

- a. Give examples of complexes having coordination number six, seven and eight.
- b. Draw the possible isomers of [CoCl₂(NH₃)₂(H₂O)₂].
- c. What is a chelation effect? Explain with an example.
- d. The stepwise stability constants of the reaction of Hg^{2+} and CN^{-} are $logK_1 = 18$, $logK_2 = 16$, $logK_3 = 3.8$ and $logK_4 = 3.0$. Explain the features.
- e. Give examples showing flexideatate behaviour of sulphate and ambidentate behaviour of thiocyanate ion as ligands.

Unit--2

2. Answer any two questions:

3×2=6

- a. (SiH₃)₃N is planar while (SiH₃)₃P is pyramidal. Explain.
- b. What happens when excess NaOH solution is gradually added to BeCl₂ and MgCl₂ solutions separately?
- Amongst noble gases xenon is the most suitable to form chemical compounds. Explain
 - i. Answer any one:

 2×1

- 1. Give an example (with structure) of a cationic silicon compound.
- 2. Cis dimerization of NO is favourable to trans dimerization. Explain.

Unit-3

3. Answer any four questions:

 $4 \times 2 = 8$

- a. Phosphonium iodide is the most stable among the phosphonium halides justify.
- b. Neither BrF5 nor AsF5 are good conductors of electricity. However, a mixture of these two is a better conductor than either of the pure substances explain.

- c. Nitrogen trichloride and phosphorus trichloride hydrolyze differently. Explain.
- d. Rationalize the behaviour of halogens of the following reactions:

$$I_2 + 2KClO_3 \rightarrow 2KIO_3 + Cl_2$$

- e. Compare the bond energies of "P-H" with "N-H" and "P-F" with "N-F" in binary compounds.
- f. Show how will you interconvert the following:

NH₃ ≠ HN₃

Group-B Unit-4

- 4. Answer the following questions:
 - a. Explain the following:

Benzoin gives OH when treated with p- methylbenjaldehyde in presence of KCN/ EtOH.

OR

Butanone on bromination in presence of sodium hydroxide produces CH₃CH₂COCBr₃ where as in case of bromination in acetic acid medium the major product is CH₃CHBrCOCH₃. Explain the observations with mechanistic details.

b. Predict the product/s in the following reactions with explanation: (any two). $2\times2\frac{1}{2}=5$

3