

2021
CHEMISTRY
[HONOURS]
Paper : IX

Full Marks : 100

Time : 4 Hours

*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.***GROUP-A****(Marks : 50)**

1. Answer any **five** questions: 2×5=10
- Explain the term trans-effect with specific example.
 - Which one of the following is diamagnetic and why?
 $K_2[NiF_6]$ and $K_3[CoF_6]$
 - Comment on magnetic moment of the $Re_2Cl_8^{2-}$ ion.
 - Draw the structure of $Fe_2(CO)_9$ and $Ir_4(CO)_{12}$ molecule.
 - What is CFAE? Why is it calculated?

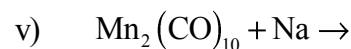
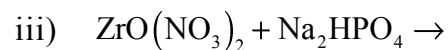
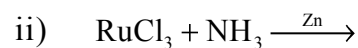
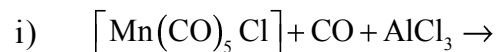
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- Write down 'd' orbital splitting pattern in square planar crystal field.
 - What happens when chlorine is passed into a suspension of hydrated ferric oxide in hot concentrated KOH solution?
 - "Cis-Platin" is used in cancer chemotherapy – Why?
2. Answer any **four** questions: 5×4=20
- With CN^- both Cu^{2+} and Ni^{2+} form square planar tetracyano complex but with NH_3 , Ni^{2+} forms $[Ni(NH_3)_6]^{2+}$ but Cu^{2+} forms $[Cu(NH_3)_4]^{2+}$ — explain.
 - Give an example of molecular nitrogen complex of Ruthenium. Write the method of its synthesis. 2+3
 - Arrange the following ligands in the order of increasing Π -acidity with reasoning: CN^- , CO , NO^+ .
 - "Predict the structures of Fe_3O_4 and Mn_3O_4 using O.S.S.E. 2+3
 - What are the different oxidation states of Ag? Write the preparations; draw the structures and mention the properties of the following: $K[AgF_4]$, $[Ag(pic)_2]$. 1+2+2

d) i) How will you prepare Zieses salt?
Discuss the structure and bonding in Zieses salt.

ii) Is the compound obey '18e' rule?
(1+3)+1

e) Complete the following reactions: 1×5



f) i) Substitution reaction of $[\text{Cr}(\text{CO})_6]$ are very slow, consistent with a low spin d^6 -complex. But the isoelectronic complex $[\text{V}(\text{CO})_5\text{NO}]$ is very reactive—
Comment.

ii) Discuss the structure and bonding in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ anion with special reference to Pt- C_2H_4 bond. 2+3

3. Answer any **two** questions: 10×2=20

a) Outline the preparatory method and draw the structure of the following:

i) Wilkinson catalyst

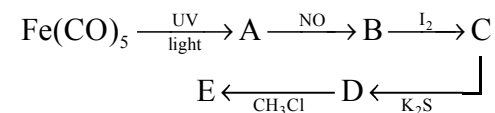
ii) Pottasium Ferricyanide

iii) Sodium nitropruside

iv) Copper acetate

v) Chrome Alum 2×5

b) i) Identify (A to E) in the following reaction scheme.



ii) Discuss the bonding in linear and bent nitrosyl.

iii) Find the value of 'x' and 'y' assuming validity of the 18e rule in case of the following compounds :



$$(1+1+1+1+1)+3+(1+1)$$

c) Explain—

i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic but $[\text{CoF}_6]^{3-}$ is strongly paramagnetic.

ii) Copper (II) acetate monohydrate shows usually low magnetic moment at room temperature.

iii) Electronic spectrum of $[\text{CoF}_6]^{3-}$ shows two maxima in the visible region.

- iv) Zn(II) shows a preference for a tetrahedral geometry.
- v) CO has negligible donor properties towards simple acceptors such as BF_3 , but can form strong bonds to transition metal atoms. $2+2+2+2+2$
- d) i) How do you extract Ti from its ore? How is it purified? Mention some uses of the metal. $3+1\frac{1}{2}+1\frac{1}{2}=6$
- ii) What is the number of moles of KMnO_4 that will be needed to react with one mole of SO_3^{2-} ion in acidic solution? 2
- iii) What is 'purple of cassius'? Give necessary equation of its preparation. 2

GROUP-B

(Marks : 50)

4. Answer any **five** questions: $2 \times 5 = 10$
- a) What is determinate error?
- b) What is the role of NH_4HF_2 in the estimation of Cu^{2+} in presence of Fe^{3+} ?
- c) Name a metal indicator and draw its structure.
- d) What is role of globin chain in hemoglobin oxygenation?

- e) Estimate the absolute standard deviation for the result of the following calculation:

$$Y = \frac{1.97(\pm 0.01)}{243(\pm 3)}$$

- f) Write down the names of redox enzymes in PS-I and PS-II of photosynthesis.
- g) High value of DO means pollution load is high— comment.
- h) What is iodimetry? Give an example.
5. Answer any **four** questions: $5 \times 4 = 20$
- a) i) Briefly explain the functioning and importance of Na^+ –ion pump.
- ii) Name one Zn-containing enzyme. $4+1$
- b) 50ml of 0.100(M) NaCl solution is titrated with 0.100(M) AgNO_3 solution. Calculate the chloride ion concentration during
- i) Start of the titration
- ii) After the addition of 10ml AgNO_3 solution
- iii) After addition of 49.9ml AgNO_3 solution.
- iv) Equivalence point.

- v) After addition of 60ml AgNO_3 solution.
1+1+1+1+1
- c) i) What is Zimmermann Reinhardt solution? Why is it used during estimation of Fe(II) with KMnO_4 ?
- ii) 25 ml of a solution containing Ca^{2+} is titrated with 0.05M EDTA using calcon indicator at pH12. 15ml EDTA is required when the indicator changes colour. Calculate the amount of Ca^{2+} in the solution in gm/L. 3+2
- d) State Beer's law. How do you test the validity of Beer's law? Explain why deviation occurs in some cases. $2+1\frac{1}{2}+1\frac{1}{2}=5$
- e) What is high frequency titration? How does it differ from common conductometric titration? 2.5×2
- f) What is thin layer chromatography? How can you identify some aminoacids in a mixture by TLC? 5
- g) i) The following results were obtained in the replicate determination of the lead content of a blood sample:

0.752, 0.756, 0.752, 0.751, and 0.760 ppm Pb. Calculate the mean and standard deviation of this set of data.

- ii) How is bromide estimated in solution by Volhard's method? 3+2

6. Answer any **two** questions: $10\times 2=20$

- a) i) What is the difference between the structures of hemoglobin and myoglobin? Which one carry oxygen more and why? 3
- ii) Explain why calibration curve is necessary for spectrophotometric determination. 2
- iii) What is the role of Mg(II) in chlorophyll? 2
- iv) What are the important properties which make Zn(II) biologically so important in nonredox metalloenzymes? 3
- b) i) Give an example of redox indicator and explain its function in a titration. Why should you add $\text{H}_2\text{SO}_4 - \text{H}_3\text{PO}_4$ mixture during estimation of Fe^{2+} with a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution? 1+2+2

- ii) 50ml 0.1M H_3PO_4 is titrated with 0.1N NaOH solution. Calculate the pH when 50ml, 75ml, 100ml and 150ml NaOH are added.

(K_1 for $\text{H}_3\text{PO}_4 = 7 \times 10^{-3}$, $K_2 = 6 \times 10^{-8}$, $K_3 = 5 \times 10^{-13}$)

1+1+1+2

- c) i) Discuss the structural features of hemoglobin and myoglobin.
- ii) What do you mean by cooperative interaction in O_2 affinity of hemoglobin?
- iii) Give an example of a naturally occurring M-C σ bonded species.
- iv) Write down the name of metal ions present in nature, in which the first one function as an electron transfer agent and the second one catalyses the hydrolysis reaction. 4+3+1+2
- d) i) The standard reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ is lower than that of I_2/I^- , yet copper is estimated iodometrically— How this becomes possible?
- ii) "Starch should be added towards the end point" – why?

- iii) H_3PO_4 can not be directly titrated as a tribasic acid but can be directly so titrated in presence of CaCl_2 – Why?
- iv) Mention the requisite characteristic of a redox indicator. 3+2+3+2
