# 2020

# CHEMISTRY

**[HONOURS]**

**Paper : IV**

**[SUPPLEMENTARY]**

Full Marks : 75 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 : 37 $\frac{1}{2}$)**

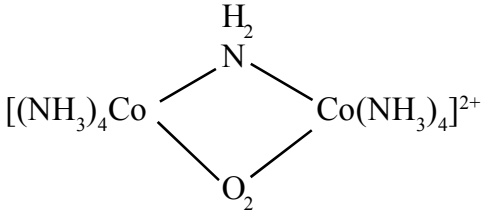
1. Answer any **three** questions: 1×3=3

   a) Show the lewis acidity order of the compound $SiX_4$ (X=F, Cl, Br).

   b) Give the name and structure of a redox indicator.

   c) What is ambidentate ligand?

   d) Give IUPAC name of the followings:






2. Answer any **three** questions: 2×3=6

   a) Establish Nernst equation for the following red-ox couples:

      i) $Cr_2O_7^{2-}/Cr^{+3}$ in acid medium

      ii) $BrO_3^-/Br^-$ in alkaline medium.

   b) Give all geometrical isomers of the complexes given below:

      i) $\left[Ru(Py)_3Cl_3\right]$

      ii) $\left[Co(en)_2(NO_2)Cl\right]^+$

   c) Using VSEPR theory predict the shape of $BrF_4^-$. Indicate the state of hybridisation of the central atom.

   d) Indicate the effects of the following ionisation processes on bond order and bond lengths:

      i) $O_2 + e \rightarrow O_2^-$

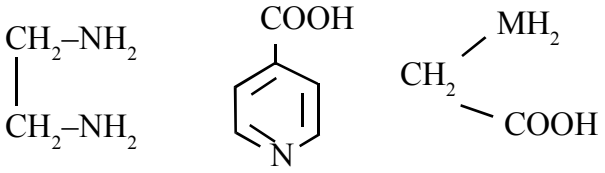
      ii) $N_2 - e \rightarrow N_2^+$

3. Answer any **three** questions: 6×3=18

   a) i) Explain why: N–O bond in $NO^+$ is stronger than that in NO molecule.

      ii) What indicator will you use during the titration of Mohr's salt solution with $K_2Cr_2O_7$ in acid medium? Explain its indicator action. 3+3

b) i) Which among the following ligands A, B and C will be able to form innermetallic complex of the first order with an $M^{2+ion}$? Justify your answer:



(A) (B) (C)

ii) Chloride ion is oxidised to chlorine by permanganate solution only at low pH____Give reasons:

$$MnO_4^-/Mn^{+2} = +1.51 \text{ and } \tfrac{1}{2}Cl_2/Cl^- = +1.36V$$

3+3

c) i) The compound $[Co(en)_2(NO_2)_2]Cl$ (en=Ethylene diamine) has been prepared in a number of isomeric forms. One form undergoes no reaction with either $AgNO_3$ or Ethylene diamine. A second form reacts with $AgNO_3$ but not with Ethylene diamine. A third form reacts with both $AgNO_3$ and Ethylene diamine. Identify each of the three forms by their IUPAC names:

ii) Give the synthetic schemes for the preparation of all three isomers of $\{Pt(Py)(NH_3)(Br)(Cl)\}$



[Given:

i) The order of trans directing ability:

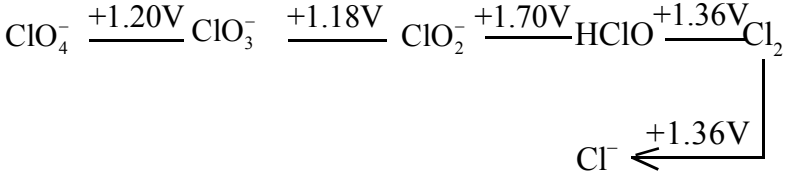
$$NH_3 < Py < Cl^- < Br^-$$

ii) Pt-N bond strength is greater than Pt-cl bond strength] 3+3

d) i) Are the bond angles LHCH and LFCF in $CH_2F$ molecule equal? Give reasons in support of your answer.

ii) On the basis of VSEPR theory write the possible structures of $ClF_3$ and predict the most favoured structure showing your arguments. 3+3

e) i) From the following latimer diagram, calculate the reduction potential of $ClO_4^-$–HClO




ii) Find out the equivalence point potential during the titration of a $0.1(M)Fe^{+2}$ solution with $0.1(M)Ce^{+4}$ solution.

Given: $E^0_{Fe^{+3}/Fe^{+2}} = +0.77\,V$ and

$E^0_{Ce^{+4}/Ce^{+3}} = +1.57\,V$ 3+3

4. Answer any **one** question: 10×1=10

a) i) Draw the possible isomers of $\left[Co(NH_3)_2(H_2O)_2(CN)_2\right]^+$ ion.

ii) Mention the conditions for linear combination of atomic orbitals (LCAO), relating to the formation of molecular orbitals.

iii) Explain the significance of solubility product principle and common ion effect in the precipitation of iron, aluminium and chromium ions as hydroxides in conventional qualitative analysis.

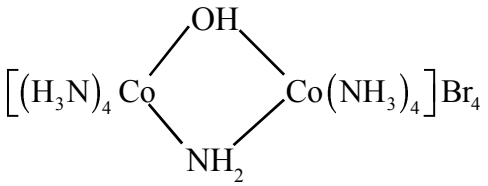
3+3+4=10

b) i) Predict the shapes and indicate the state of hybridisation of the central atom for the following:

$XeF_5^-$, $SO_2Cl_2$, $ClO_3^-$, $IO_2F_2^+$

ii) "The efficiency of complex formation by EDTA increases at higher pH"— Explain.

iii) Give the IUPAC name of the following complex:




iv) The C–Cl bond distance in $CH_3Cl$ and $CF_3Cl$ are 1.78 Å and 1.75 Å, respectively. Comment on this difference with the help of Bent's rule.

(1×4)+2+1+3=10

**(General Proficiency - $\frac{1}{2}$)**

## GROUP-B

**(Marks : 37$\frac{1}{2}$)**

5. Answer any **three** questions: 1×3=3

a) Give name and chemical composition of an anion exchange resine.

b) Write down the structural formula of oxine and its aluminium complex.

c) Define the term “extraction co-efficiency”.

d) Name one important ore of uranium.

e) Give the general electronic configuration of lanthanids.

6. a) Calculate the $\mu_{eff.}$ of $E_u^{2+}$. Give two facts that effect the selectivity of ion exchange resins.

2

b) In solvent extraction of uranium with 8 hydronyquinolui in chloroform the volume of aqueons and organic phase was both 25 mg when percentage extraction was 99.8% calculate the distribution ratio. 2

c) Give the principle of separation by column chromatography. 2

7. Answer any **three** questions: 6×3=18

a) i) Write down the structural formula of oxine and its aluminium complex. Discuss the principle of estimation of aluminium in presence of magnesium using oxine as precipitant.

ii) Find the $\mu_{eff}$ value of $Gd^{3+}$. 4+2=6

b) i) Give the general electronic configuration of lanthanides and explain the trends in ionic radii of $M^{3+}$ ions of this class.

ii) Mention why the most accessible 4+ ion among the lanthanides is $Tb^{4+}$. (1+3)+2=6

c) i) How $Fe(CO)_5$ is prepared? Discuss the metal-carbonyl bonding in $Fe(CO)_5$.

ii) What properties made 1, 10-phenanthrolene a suitable reagent in inorganic analysis? 2+2+2=6

d) i) In the complexometric estimation of $Ca^{2+}$ by disodium EDTA using EBT indicator,



some $Na_2MgEDTA$ is added to the $Ca^{2+}$ solution before starting the titration. Explain its necessity showing all the reactions involved in the process.

ii) Write the principle of gravimetric estimation of Cu stating the gravimetric factor involved (Atomic weight of Cu = 63.5). 3+3=6

e) i) In solvent extraction process, the extracting solvent is used in a number of parts instead of using the whole liquid in one lot— Explain.

ii) What are "stationary phase' and 'mobile phase' in an ion-exchange chromatography?

iii) Give a scheme for spectrophotometric estimation of Iron. 2+2+2=6

8. Answer any **one** questions: 10×1=10

a) i) What happens when $Fe(CO)_5$ undergoes photolysis?

ii) How would you prepare sodium nitro-prusside? Give one use of sodium nitro prusside in qualitative analysis.

iii) How $Ni(CO)_4$ can be prepared?

iv) In a paper chromatographic separation of $Hg^{2+}$, $Pb^{2+}$ and $Ag^{+}$, the solvent front was 21 cm,while fronts due to these metals

were7,14 and 18.5 cm, respectively. Calculate the $R_f$ values of them.

2+(2+1)+2+3

b) i) Describe one method of determination of $Al^{3+}$ using an organic precipitant. State the limitations of this method.

ii) Explain why: $La^{3+}$, $Lu^{3+}$ are diamagnetic, while $Sm^{3+}$ has low paramagnetism.

iii) How can $Cu^{2+}$ and $Zn^{2+}$ in a mixture be estimated complexometrically using EDTA? State the principle involved.

5+2+3

**(General proficiency : $\frac{1}{2}$)**

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