West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013

PART – III

CHEMISTRY — HONOURS

Paper –VI (Gr. A + B)

Duration : 4 Hours]   [Full Marks : 100

Answers to different Groups must be made in separate answer scripts.
The figures in the margin indicate full marks.
Use separate answer scripts for each Group.

GROUP – A

Answer any *three* questions taking *one* from each Unit.

UNIT – I

1. a) Name the principal ore of uranium and give its stoichiometry. How is uranium extracted from its ore ? Give a flow-chart.   1 + 1 + 4

    b) Aqueous Mn^{2+} ion is stable while Cr^{2+} ion is readily oxidised. Explain.   2

    c) Discuss the preparation and uses of any *two* of the following compounds :
        i) $Na_2[Fe(CN)_5NO]$ ii) $(NH_4)_2PtCl_6$ iii) $KMnO_4$.   3 + 3

    d) What happens when NH_4VO_3 is ignited ?   2

2. a) Absorption spectra of actinides are more intense as well as broad than those of the lanthanides. Explain.   4

    b) Give the extraction of uranium from U_3O_8. Give the balanced equations of the reactions involved.   4

    c) The most stable oxidation state of copper is +2 whereas Au^{2+} is unstable towards disproportionation to Au^{3+} and Au^+. Explain.   4

    d) How would you prepare $Na_3[Co(NO_2)_6]$? Give one example of its application in qualitative analysis.   4

UNIT – II

3. a) Give the *d*-orbital splitting of the central metal atom in the following complexes :   4
        i) $Fe(CO)_5$ ii) $K_2[Ni(CN)_4]$.

    b) Of the two isomers of $[Pt(NH_3)_2Cl_2]$, one (A) reacts with thiourea (tu) to produce $[Pt(tu)_4]^{2+}$ whereas the other isomer (B) produces $[Pt(NH_3)_2(tu)_2]^{2+}$ when treated with the same reagent. Which isomer of $[Pt(NH_3)_2Cl_2]$ is cis- and which one is trans- ? Justify your answer.   1 + 1 + 2

c)   The magnetic moment values of two Co(II) complex are 4·5 BM and 5·2 BM. One of the complexes is octahedral and other is tetrahedral. Which is which and why ?   2 + 2

d)   Find out the μ_s values in the following complexes :   1 + 1
   i) $K_4[Mn(CN)_6]$ ii) $K_3[COF_4]$.

e)   Which one of the following pairs of complexes has larger crystal field stabilization energy and why?   2 + 2
   i) $[CoCl_4]^{2-}$ and $[Co(H_2O)_6]^{2+}$ ii) $[CO(NH_3)_6]^{2+}$ and $[CO(NH_3)_6]^{3+}$.

4.   a)   "Octahedral Cu(II) complexes are distorted." Explain it in the light of CFT using approximate energy diagram. What will be the energy difference between $d_{x^2-y^2}$ and d_{xy} in the distorted state ?   4 + 2

b)   Of $K_4[Fe(CN)_3]$ and $K_3[Fe(CN)_6]$, one is paramagnetic while other is diamagnetic. Which is which and why ?   2 + 2

c)   Between cis- $[Co(en)_2 Cl_2]^+$ and trans- $[Co(en)_2Cl_2]$, which one will give more intense d-d transition and why ?   1 + 3

d)   Find out μ_s in $[Fe(H_2O)_5NO]SO_4$.   2

e)   Explain why $KFe^{II}[Fe^{III}(CN)_6]$ and $KFe^{III}[Fe^{II}(CN)_6]$ have the same colour.   2

UNIT – III

5.   a)   How is Zeise's salt prepared ? Discuss its structure and bonding. What happens when the salt is warmed with water ?   1 + 3 + 1

b)   Complete the following reactions :   2
   i) $CO_2(CO)_8 + NO \rightarrow$ ii) $Cr(CO)_6 + C_6H_6 \rightarrow$

c)   What metals are present in the following metallo-enzymes ?   4
   i)   Carboxypepdisase   ii)   Nitrogenase
   iii)   Hydrogenase   iv)   Phosphatase.

d)   What metal ion causes Wilson's disease ? How would you remove the ion from the body ? What are ultratrace elements in the biological systems ?   1 + 3 + 1

6.   a)   What do you mean by hapticity of organometallic ligands ? Give one example of each mono- , tri- and pentahapto modes of bonding of cyclopentadiene.   1 + 3

b)   Write short note on any one of the following :   4
   i)   Hydroformylation of alkenes
   ii)   Hydrogenation of olefins.

c)   What do you mean by chelation therapy ? Give an application of chelation therapy in the treatment of metal toxicity.   2 + 2

d)   Between deoxy-haemoglobin and haemoglobin which one is paramagnetic ? How does carbon monoxide destroy the normal activity of haemoglobin ? Give the chemical formula of British-Anti-Lewsite.   1 + 2 + 1

GROUP – B

Answer any *three* questions taking *one* from each Unit.

UNIT – I

7. a)   What do you mean by determinate and indeterminate errors in chemical analysis ? Find the product of the two binary numbers 1011 and 1001. Transform the product into decimal number.   2 + 2

    b)   State Lambert-Beer's law and the conditions for its applicability in quantitative estimation. Does a change of pH influence the colour of a solution ? State with an example.   2 + 2 + 1

    c)   Discuss the principle of radiocarbon dating.   3

    d)   State the principle of potentiometric redox titration with an example. Briefly discuss the method of end point detection for such titration.   4 + 2

8. a)   The result of a quantitative analysis is 21·39 g compared to the accepted value of 22·05 g. What is the relative error in % and parts per thousand ?   2

    b)   Distinguish between atomic absorption spectroscopy and atomic emission spectroscopy.   3

    c)   Briefly discuss the principle of isotope dilution analysis. Give an example.   4

    d)   Sketch the pH titration curve of a weak acid against a strong base in aqueous solution.   3

    e)   Describe the principle of the spectrophotometric estimation of manganese.   4

    f)   What safety measures are taken to eliminate the hazards of radiations ?   2

UNIT – II

9. a)   State the principle of gravimetric estimation of aluminium.   4

    b)   Give examples of masking and demasking agents indicating their role in complexometric titrations.   4

    c)   Describe the estimation of the following :   2 + 2

         i)   Pb in water samples

         ii) NO_3^- in soil.

    d)   Oxidation of oxalate ion by permanganate in 2(N) H_2SO_4 medium is slow at the early stages, but takes place rapidly thereafter. Explain.   2

    e)   Why is starch added near the end point in an iodometric titration ?   2

10. a)   Describe the principle of gravimetric estimation of phosphate explaining gravimetric factor.   4

    b)   Briefly discuss the principle of estimation of Ca^{2+} and Mg^{2+} in a mixture by EDTA.   4

c) How does the dye fluorescein act as indicator in the titration of chlorides wi AgNO$_3$ solution ?

d) Which one is a better oxidising agent — KMnO$_4$ in acidic medium or KMnO$_4$ alkaline medium ? Explain.

e) Outline a principle for the estimation of Cr and Mn present together in sample of steel.

UNIT – III

11. a) R$_f$ values of L-lysine, DL-α alanine and L-leucine are 0·14, 0·36 an 0·65 respectively. Which one of these amino acids in the TLC separation wi occur at the top and which one at the bottom ? Justify your answer.

b) How is the strength of a formalin solution determined ? Why is formali solution always acidic ?

c) State the principle for estimation of glucose.

d) Define the following terms :
   i) SPM in air sample
   ii) DO and TOC in water sample. 1 +

e) What is extraction coefficient in solvent extraction ? What is its importance ?

f) Calculate the distribution ratio of iodine when 25 ml of aqueous iodine wa extracted with 25 ml of chloroform and the % of extraction was found be 98·5%.

12. a) State the principle for the estimation of the following : 4 ×
   i) Phenol ii) Glycine
   iii) SO$_2$ in air iv) NO$_x$ in air.

b) Give the principle and one application of column chromatographic technique.

c) Define exchange capacity of an ion-exchanger. How is the exchange capacity a cation-exchange resin determined ?