

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

THIRD YEAR

B.A./B.SC. SIXTH SEMESTER (January – June) 2013

Mid-Semester Examination, March 2013

Date : 19/03/2013

Time : 11 am – 1 pm

CHEMISTRY (Honours)

Paper - VIII

Full Marks : 50

[Use Separate Answer Books for each unit]

[Answer any one question from each unit]

Unit – I (K.R.)

1. a) The spectral bands in lanthanide complexes are usually larger in number and sharper than that of d-block elements. Explain.
b) On going from Nd(III) to Pm(III) the number of unpaired electrons increases from f^3 to f^4 but magnetic moment decreases. Explain. [3+3]
2. a) Calculate the ground state magnetic moment in BM of Pr(III) with outer electronic configuration $4f^2$.
b) Ce(III) ions (f^1 in aqueous solution is colourless. Justify. (Given, $\lambda = 643\text{ cm}^{-1}$) [3+3]

Unit – II (D.M)

3. a) Applying 18e rule Calculate the value of x in $\text{HFe}_5\text{N}(\text{CO})_x$. [1]
b) $[\text{Cr}_2\text{Cl}_9]^{-3}$ is paramagnetic while $(\text{W}_2\text{Cl}_9)^{-3}$ is diamagnetic. Explain [2]
c) What are the conditions for Metal-Metal bonding? [2]
d) What is the structure of $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$? [1]
4. a) Explain Beer Lambert law. What are the limitations? [2+1]
b) 0.45 gm steel sample containing Mn was dissolved in acid and treated with KIO_4 . Volume of oxidised MnO_4^- solution was marked to 100 ml and OD of diluted solution was found to 0.40 in 1 cm cell. Find the % of Mn in the sample (given, molar extinction co-efficient 2.2×10^3) [3]

Unit – III (S.G.)

5. a) What are systematic and random errors? [2]
b) Analysis of a sample of iron ore give the following percentage value of iron content : 7.08, 7.12, 7.21, 7.09, 7.16 and 7.14. Calculate the mean, standard deviation and co-efficient of variation for the values. [3]
6. a) What do you mean by 'accuracy' and 'precision' in quantitative analysis? For titrating 10 ml of a 0.1(N) solution with a 0.1(N) titrant the following volumes of titrant were obtained by two analyst.
Analyst A : 9.80 9.91 9.85 10.08 10.25 ml
Analyst B : 10.09 10.12 10.10 10.12 10.08 ml
Calculate the mean and standard deviation for the above two sets of the results and hence comment on the accuracy and precision of the results. [1+4]

Unit – IV (S.R.)

7. a) What do you mean by argentometry? [1]
b) Describe the titration of a 100ml 0.1(M) NaCl solution by a same molarity of AgNO_3 solution using 10^{-2} (M) solution of K_2CrO_4 (indicator). K_{SP} of Ag_2CrO_4 and AgCl are 1.1×10^{-2} and 1.0×10^{-10} . [3]

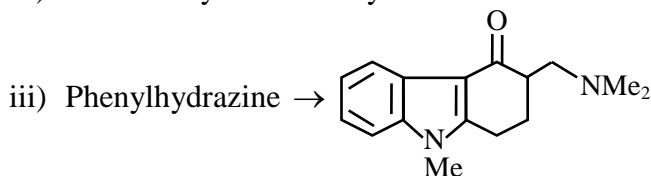
8. Explain the term iodo and iodimetry with examples and the characteristic points of iodometric determination. [2+2]

Unit – V (A.B.)

9. Answer **any two** from the following : [2×2]
- Write down the advantage of gravimetric analysis over that of volumetric analysis.
 - Write down the requirements of gravimetric analysis.
 - Give an example of a masking agent and demasking agent. Why EDTA is a very suitable reagent in complexometric titration.
10. Answer **any two** from the following : [2×2]
- Explain the term : Simultaneous precipitation, Co-precipitation and post precipitation. Why in gravimetric analysis precipitation is always done in hot condition?
 - State the conditions necessary for a metal ion indicator to be used in EDTA titration. Name (with structure) any two metal ion indicator.
 - Write down the feasible conditions for complexometric estimation.

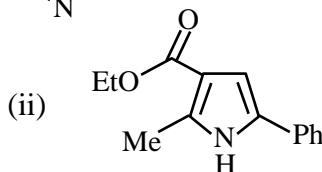
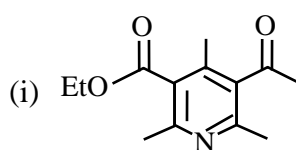
Unit – VI (A.B.H)

11. a) Carryout the following conversions : [3×3]
- D-glucose \rightarrow 2,4-di-O-methyl-D-glucose
 - Benzaldehyde \rightarrow Phenylalanine

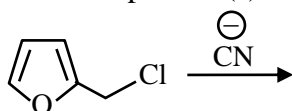


- b) Predict the product of the following reaction : [1]
- Methyl α -D-glucopyranoside $\xrightarrow[\text{H}^+]{\text{PhCHO}}$
- c) Draw the structure of dAMP and ADP. [2]
12. a) Outline the mechanism of mutarotation in chair perspective formula in aqueous acid medium. [3]

- b) Taking ethyl β -aminocrotonate as moiety outline the synthesis of the following compounds : [5]



- c) Predict the product(s) of the following reaction : [2]



- d) In acidic solution nucleosides are hydrolysed. Propose a mechanism for this reaction. [2]

Unit – VII (D.J.)

13. a) Explain the followings : [2×2]
- In electronic spectroscopy, the absorption spectra and the emission spectra are mirror image to each other.
 - Studying absorption spectrum of S_2 , it is observed that certain spectral bands are diffuse.

- b) Using collision theory, estimate the collision number for 1 mol of HI present in a vol. of 1m^3 at 300K. Take $d_{\text{AA}} = 0.35\text{ nm}$. If the activation energy for the decomposition of HI is 184 KJ mol^{-1} , what rate constant does kinetic theory predict at 300°C ? Find out the pre-exponential factor? [2+1]
14. a) Give the mechanism of Lindemann-Christiansen unimolecular reaction and therefrom show that $[A]_{1/2} = \frac{k'_\infty}{k_1}$; where k'_∞ is $k_1 k_2 / k_{-1}$ and $[A]_{1/2}$ is the 50% of reactant, A. [3]
- b) Point out the 1st order transitions using Jablonskii diagram using S_0 , S_1 and T_1 . [2]
- c) What is Frank-Condon principle? Explain with PEC of different electronic states. [2]

Unit – VIII (S.S.R.)

15. a) Starting with the expression for transition moment integral in case of a spectroscopic transition, show that the essential conditions for rotational and vibrational transitions respectively are
- Rotational transition – the molecule must have a non-zero dipole moment.
 - Vibrational transition – the dipole moment of the molecule must change with the vibration. [2.5×2]
- b) The C-C vibrational line in ethane comes at a lower frequency (2954 cm^{-1}) than the same in acetylene (3374 cm^{-1}). Explain [1]
16. a) Comment and explain whether light induced transition may take place between two states described by the following wave functions.
- $$\psi_i = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{y^2}{2}} ; \psi_f = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}} (2y^2 - 1) e^{-\frac{y^2}{2}} \quad (\alpha \rightarrow \text{constant}) \quad [3]$$
- b) i) Show that the intensity of spectral lines for rotational transition between the states J to J+1 passes through a maxima as J changes.
- ii) Calculate this J_{max} in terms of T and other molecular constants. [2+1]

