RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, MAY 2019

THIRD YEAR [BATCH 2016-19]

Date : 03/05/2019 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** VIII [Gr. A & D] Full Marks : 50

[Use a separate Answer Book for <u>each group</u>]

Group – A

UNIT-I **[12 marks]**

[Attempt **<u>one</u>** only]

1. a) What are the two important conditions to be satisfied for a molecular motion to be activated by a proper electromagnetic radiation? Explain involving the transition moment integral. [3]
   b) The rotation of HI molecules may be considered as an orbiting of H atom at a radius of 160 pm with I atom virtually stationary at the centre. What would be the wavelength of the radiation emitted for the transition from 1st excited to ground state ? $\left[\mu_{HI} = 1.64\times10^{-24}\text{gm}\right]$ [3]
   c) The fundamental and the first overtone transitions of $^{14}N^{16}O$ are centred at 876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Calculate the exact zero point energy. [3]
   d) How would you determine the atomic mass of C^{13} accurately using rotational absorption spectroscopy? [3]

2. a) State the experimental observations supporting the anharmonic vibration of a diatomic molecule A-B. Explain the observations. [3]
   b) The symmetric stretching of CO_2 is IR inactive but Raman active. Explain. [3]
   c) Pure rotational spectroscopy is incapable to determine the equilibrium bond length of a homonuclear diatomic molecule. Justify or criticize it. [2]
   d) The fundamental vibration frequency of $H^{35}Cl$ is 8.667×10^{13} sec^{-1}. What would be the separation between the IR absorption lines for $H^{35}Cl$ and $H^{37}Cl$? What is the assumption made here? [3+1]

UNIT-II **[13 marks]**

[Attempt **<u>one</u>** only]

3. a) What are the different radiative and non-radiative paths via which the excited state of a molecule can decay? Explain with the help of Jablonski diagram. [4]
   b) Why fluorescence is more intense than phosphorescence and always appears earlier than the latter? [3]
   c) What is photo stationary state? Explain with example. [3]
   d) In the photochemical decomposition of acetaldehyde by light of wavelength 3100 Å, carbon monoxide is produced with a quantum yield of 0.50. Calculate the rate of formation of CO for an incident light intensity of 10^5 erg sec^{-1}. [3]

4. a) A molecule on proper excitation undergoes photochemical dissociation. Draw the potential energy curves for the ground state and excited state of the molecule. [3]
   b) For the photochemical reaction, $A_2 \xrightarrow{h\nu} 2A$, the following mechanism has been proposed

$$A_2 \xrightarrow{h\nu} A_2^*; \qquad A_2^* \xrightarrow{k_2} 2A; \qquad A_2^* + A_2 \xrightarrow{k_3} 2A_2$$

Show that, $\frac{d[A]}{dt} = \frac{2k_2 I_{abs}}{k_2 + k_3[A_2]}$. [4]

c) Explain what is meant by [2+2]
   i) Photosensitized reaction
   ii) Chemiluminescence

d) Quantum yield is always one. Justify or criticize. [2]

Group – D

[Attempt **one** question from each unit]

UNIT-I [8 marks]

15. a) Write down the principle of argentometric estimation of chloride ion. [2]
    b) Calculate the ratio of the equivalent weight for $KH(IO_3)_2$ when it participates in both acid-base and redox reactions. [2]
    c) Explain the role of metal ion indicator in complexometirc titration. [2]
    d) Explain the role of Zimmermann-Reinhardt reagent during the permanganometric estimation of Fe^{+3}. [2]

16. a) A 0.7120 gm specimen of iron ore is brought into solution and is reduced to Fe(II). The reduced solution in 2(N) acid, requires 20 ml of 0.02(M) $KMnO_4$ solution for titration of Fe(II). Calculate the percentage of iron in the ore. [3]
    b) What do you mean by masking and de-masking agent in connection with complexometric tiration? Outline the procedure for estimation of Cu and Zn in a mixture compexometically. [3]
    c) A solution of 0.05 (M) $KMnO_4$ has been used for titration at pH = 10. What is the normality of the $KMnO_4$ solution ? Justify your answer. [2]

UNIT-II [8 marks]

17. a) 0.20 gm of an ore containing MnO_2 was treated with excess hydrochloric acid. The Cl_2 formed was distilled off and absorbed in KI solution. Titration of the liberated iodine consumed 42.5ml of 0.052 N sodium thiosulphate solution. Calculation the percentage of MnO_2 in the ore. [2]
    b) Discuss the difference between coprecipitation and postpreceipitation. [2]
    c) 0.452 gm of $AgNO_3$ gave a precipitate of 0.415 gm AgCl. Calculate the % Ag in the sample. At.wt. of Ag = 108 [2]
    d) What do you mean by co-precipitation and post precipitation? Give suitable examples. [2]

18. a) State any two advantages of organic precipitation agents over inorganic precipitation agents. [2]
    b) Out line the steps of gravimetric estimation of Ni^{+2} by dimethylglyoxime reagent. [2]
    c) Give outlines of the analytical procedure for estimation of Fe in Portland cement. [3]
    d) What do you mean by Gravimetric factor? [1]

UNIT-III [9 marks]

19. a) Write the process of detection of a trace amount of CO in air. [2]
    b) Estimate the standard deviation for the result of following calculation [3]

$$y = \frac{157(\pm 6) - 59(\pm 3)}{1220(\pm 1) + 77(\pm 8)}$$

c) How will you estimate 'Arsenic' in water sample. [2]

d) Define COD. Why is it always greater than BOD of a water sample. [2]

20. a) i) What do you mean by R_f value ? [1]

ii) R_f values of three amino acids A_1, A_2 and A_3 are 0.15, 0.5 and 0.65 respectively. Which one of the amino acids in their TLC separation will occur on the top and which one at the bottom. Give reason. [2]

b) How can you estimate 'DO' in water sample? [2]

c) The following results were obtained from a turbidimeter (an instrument that measure turbidity) in a calibration experiment when excess $BaCl_2$ was added to Na_2SO_4 solutions of different concentrations. Assuming a linear relationship between the concentration and instrument readings, calculate the least square slope for the best straight line among the points. [3]

Concentration (mg/L)	0.00	5.00	10.00	15.00	20.00
Instrument Readings	0.06	1.48	2.28	3.98	4.61

d) What is SPM2.5 ? [1]

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