M. Sc. Chemistry Examination, 2019

(4th Semester)

Analytical Chemistry Special

Paper - XV-A

Time : Two hours Full Marks : 50

(25 Marks for each Unit)

Use a separate answer script for each unit.

UNIT – A- 4151

1. Answer the following questions ***(any five)*** : 2× 5=10

   a) "7-Hydroxy-4-methylcoumarin and Fluorescein are pH sensitive." Are they following same mechanistic approach ? Explain.

   b) Why do two monochromators are used in the Fluorescence Spectrophotometer and aligned perpendicular to each other ?

   c) What happens when a solution of $K_2C_2O_4$ is added to coulometrically oxidized $[Ru(bpy)_3]^{2+}$ solution at 1.26V in acetonitrile ? Write plausible mechanism of the reaction.

   d) "4-N, N-Dimethylbenzonitrile in hexane and in tetrahydrofuran is irradiated with UV light." Draw the emission spectrum and explain the difference, if any.

e) Upon addition of 4-N, N-diethylaniline to anthracene solution a new broad emission band at longer wavelength (585 nm) region to free anthracene (λ_{em}, 420 nm) is observed. The band intensity increases with increasing concentration of 4-N, N-diethylaniline but decreases on adding acid. Explain.

f) What happens when aqueous solution of $K_3[Cr(CN)_6]$ and $[Ru(bpy)_3]Cl_3$ is irradiated with light of 450 nm. Explain your observation.

g) "Upon light irradiation *trans*-rich isomer $[Cr(NH_3)_4(H_2O)Cl]^{2+}$ (where H_2O and Cl are in *trans* configuration) is ormed from aqueous solution of $[Cr(NH_3)_5Cl]^{2+}$ while thermal reaction shows scrambling of isomers." Explain.

2. a) Account on the quenching mechanism at different concentration of Quencher [Q] added to the solution of fluorophore. Also determine $\varphi F^0/\varphi F^Q$ (where φF^0 refers to in absence of Quencher and φF^Q refers to in presence of Quencher).

b) "A molecule 'M' is irradiated and mixed with a second molecule 'X' to synthesise $[M^+X^-]$ while no such reaction is observed upon warming the mixture, in this case." Draw the state diagram of the process and explain.

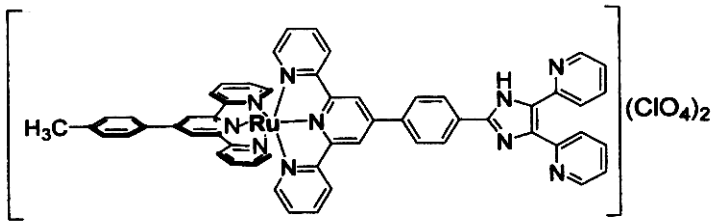
b) What are the different ion sources used for molecular mass spectrometry ? Discuss the relative merits and demerits of using "soft sources" and "hard sources". 3

c) The mass spectrum of $HSCH_2CH_2NH_2$ exhibits two peaks at m/e = 30 and m/e = 47. Which peak would you expect to be more intense ? State an appropriate reason in favor of your answer. 2

d) Describe with proper reasoning the different processes that occur when a hypothetical molecule B-C-D-E is bombarded with a highly energetic electron beam. 2

e) Assign the experimentally observed peaks at *m/z* = 318.38 and *m/z* = 477.06 in the ESI mass spectrum of the following complex in acetonitrile. Is it possible to predict the charge of the fractions by looking into its isotopic distribution pattern ?

(Given : atomic weight of Ru is 101.07) 3



c) How does life time (τ) is related with intensity of emission ? Is there any effect of M^{n+} (3d) on the value of τ of an organic fluorogenic ligand coordinated to the metal ion ?

Or

d) Write a short note on (any one) 'X-ray fluorescence (XRF) spectrometer' or 'Application of fluorescence technique in food quality control.' 4+3+3

3. a) "Emission life time of Pyrene is $1{\cdot}8 \times 10^{-3}$ s which is much longer than Fluorescence lifetime (ns) but λ_{em} is the fluorescence wavelength." Explain with plausible mechanism.

b) "Benzoic acid is less acidic while phenol is more acidic at excited state." Explain.

Or

c) What happens when DNA is irradiated with UV light ?

3+2

UNIT – A- 4152

4. Explain the significance of "Dosimetry" in a study involving ionizing radiation. Briefly explain the principle and the method of evaluating dose rate of an ionizing radiation using either 'Fricke dosimetry" or "Ceric Sulphatedosimetry". What are the common units used to measure dose ? $1+3+1\frac{1}{2}$

5. Answer ***any two*** questions :

a) What is a scintillation counter ? Discuss its operation. $1+2\frac{1}{2}$

b) With the help of suitable reactions discuss "radiolysis of water" showing formation of primary products of radiolysis with probable G values of their formation. $3\frac{1}{2}$

c) With a suitable example explain "rediometric titration" where the indicator has a radiolabelled isotope on it. $3\frac{1}{2}$

6. Answer ***all*** questions :

a) Deduce a relation between m/e of a positively charged particle of mass m, charge e with strength of the electric field V and magnetic field H which can be used to make all positively charged particles traverse the same semicircular path of radius r. $2\frac{1}{2}$