

M. SC. CHEMISTRY EXAMINATION, 2022

(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 *any five* questions : 5×2
- a) Phenol shows higher acidity at excited state while 2-hydroxybenzaldehyde does not with reference to its ground state. Explain.
- b) What happens upon irradiation of light to a mixture of methylene blue and Mohr's salt in dilute sulfuric acid? Explain your response.
- c) $T_1 + \Delta \rightarrow S_1$; $S_1 \rightarrow S_0 + h\nu$
Account on the feasibility of such reaction and explain giving an example.
- d) Irradiation of a hexane solution of 4-N, N'-Dimethylbenzotrile (DMBN) shows emission at < 400 nm while tetrahydrofuran solution of DMBN shows broad high intense longer wavelength (> 550 nm) emission band. Explain this observation.

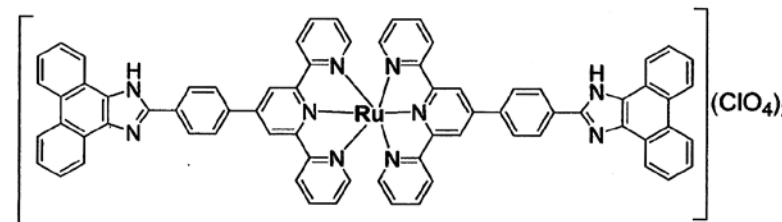
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[2]

- e) Account for the quenching mechanism at different concentration of Quencher [Q] added to a solution of fluorophore. Also determine Φ_F^0 / Φ_F^Q (where Φ_F^0 refers to absence of Quencher and Φ_F^Q refers to presence of Quencher).
- f) Discuss the effect of the concentration of pyrene on the nature and energy of fluorescence spectrum in methanol.
- g) Account on the effect of metal ions (M^{n+}) on the fluorescence process of a fluorogenic ligand. Consider M^{n+} to be a transition metal ion.
- h) "Photodecomposition is sometimes observed at a lower energy than that of the chemical dissociation energy." Explain with quantum mechanical reasons.
2. Write notes on any *two* of the following : 3×2
- a) Use of fluorescence technique for quality control of food products.
- b) Draw a schematic line diagram of a spectrofluorometer and explain every part. Why are two monochromators placed perpendicularly?
- c) Design a molecule for FRET and mention its advantages.
3. a) How is X-ray fluorescence useful for element detection? 2

[5]

- $m/e = 30$ is about ten times more intense than the peak at $m/e = 31$ peak. Predict the appropriate mode of fragmentation with chemical reasoning. 2
- e) Assign the experimentally observed peaks at $m/z = 575.78$ 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). $3\frac{1}{2}$



[4]

- c) Discuss the importance of “dosimetry” in a study involving ionizing radiation. With a suitable graphical representation discuss “Fricke dosimetry”.
4
- d) Explain radiometric titrations *either* when the substance to be titrated is radiolabelled *or*, when the indicator used is radiolabelled.
4
8. a) Deduce a relation between m/e of a positively charged particle of mass m and charge e with the strength of the electric field V and magnetic field H , which can be used to make all the positively charged particles traverse the same semicircular path of radius r .
3
- b) What do you mean by “gas phase sources” and “desorption sources” with regard to molecular mass spectrometry? Discuss with examples the relative merits and demerits of the said ion sources.
2
- c) Describe the different processes with proper reasoning that occur when a hypothetical molecule B-C-D-E is bombarded with a highly energetic electron beam.
2
- d) Fragmentation of $\text{OHCH}_2\text{CH}_2\text{NH}_2^+$ can occur to produce CH_2OH and CH_2NH_2^+ or CH_2NH_2 and CH_2OH^+ . Experimental results show that the peak at

[3]

- c) “Although Cr(III) is paramagnetic, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is eligible for photo-assisted aquation reaction.” Explain.
2

Or

4. The fluorescence lifetime of a molecule in a solution is 5×10^{-9} s. The sum of all non-radiative rate constants (Σk_{nr}) for the decay of excited state is $1.2 \times 10^5 \text{ s}^{-1}$.
What is the value of the fluorescence Quantum Yield of the molecule.
4
5. a) What happens when a solution of $\text{K}_2\text{C}_2\text{O}_4$ is added to a solution of $[\text{Ru}(\text{bpy})_3]^{3+}$ obtained by the electrochemical oxidation route in acetonitrile? Write chemical reaction and explain.
 $2 \frac{1}{2}$
- b) Explain the role of Chlorophyll in the water oxidation process.
 $2 \frac{1}{2}$

UNIT: A-4152

6. Describe the constitution of a gas ionization detector and briefly explain how it works.
 $4 \frac{1}{2}$
7. Answer any two questions:
- a) Discuss the working of a typical inorganic scintillator $[\text{NaI}(\text{Tl})]$.
4
- b) Describe the principle behind “Neutron Activation Analysis”. How is the amount of an unknown element determined by this technique?
4

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