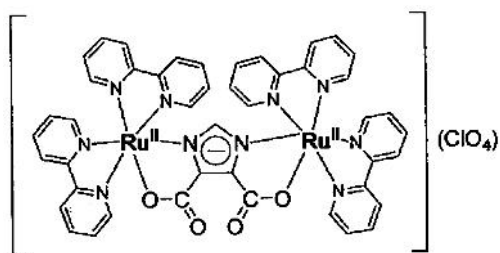


to make all the positively charged particles traverse the same semicircular path of radius r . 2

- c) The mass spectrum of $\text{HSCH}_2\text{CH}_2\text{NH}_2$ exhibits two peaks at $m/e = 30$ and $m/e = 47$. Which peak would you expect will be more intense? State appropriate reason in favor of your answer. 2
- d) How many peaks would you expect in the mass spectrum of CH_3Br ? Predict their m/e values. 2
- e) Assign the experimentally observed peaks at $m/z = 490.59$ (100%) and $m/z = 501.07$ (73%) in the ESI mass spectrum of the following complex in acetonitrile. Is it possible to predict the charge of a particular fraction by looking into its isotopic distribution pattern? $3\frac{1}{2}$



M. SC. CHEMISTRY EXAMINATION, 2017

(4th Semester)

ANALYTICAL CHEMISTRY SPECIAL

PAPER - XV-A

Time : Two hours

Full Marks : 50

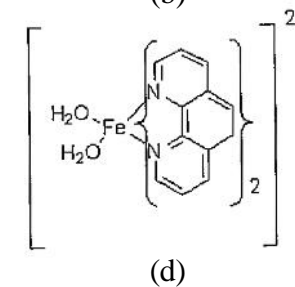
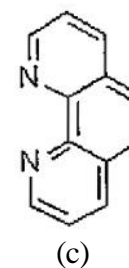
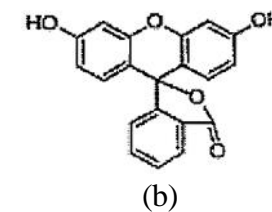
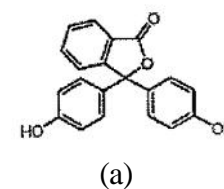
(25 Marks for each Unit)

Use a separate answerscript for each unit.

UNIT – A- 4151

Question 1 is compulsory and attempt *three* from the rest

1. Attempt the following questions (*any five*): 2×5
- a) What are the emission status of (a) and (b); (c) and (d) under identical condition in solution? Explain your answer.

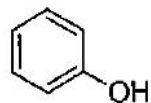


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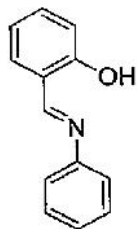
[2]

- b) "Photodecomposition sometimes observed at lower energy than that of chemical dissociation energy." Explain with quantum mechanical reasons.
- c) "Ethidium bromide is nonfluorescent while in DNA environment emission is enhanced." Explain
- d) Explain excited state acidity of (a) PhOH and

(b) Ph-N=CH-C₆H₄(OH)



(a)



(b)

- e) Pyrene and Eosin show abnormal excited state property. Explain.
- f) What happens when naphthalene solution is irradiated with increasing concentration of N, N-diethylaniline ?
- g) What happens when acidified (0.1 N H₂SO₄) solution of K₃[Fe(C₂O₄)₃] is exposed in day light ? Give chemical reaction.

[5]

UNIT – A- 4152

7. Describe briefly the constitution of a scintillation detector and its working. 4 $\frac{1}{2}$
8. Answer **any two** questions :
- a) Discuss the working of a typical inorganic scintillator, [NaI(Tl)]. 4
- b) Describe the importance of electron multiplication in obtaining a good signal in "Gas ionization detectors". What is the contribution of Townsend in this regard ? 4
- c) Discuss the importance of "dosimetry" in a study involving ionizing radiation. With suitable graphical representations 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
9. a) What do you mean by "gas phase sources" and "desorption sources" with regard to molecular mass spectrometry ? Discuss with example relative merits and demerits of the said ion sources. 3
- b) 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

[Turn over

[4]

- b) i) $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in dry MeCN solution is electrochemically oxidized and then sodium oxalate is added. Explain your observation. (Given : Ground state redox potential E^0 ($[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$) = 1.26 V ; E^0 ($\text{CO}_2/\text{Oxalate}$) = -0.49 V).
- ii) "Addition of acidified (dil H_2SO_4 sol.) Mohr's salt solution to Methylene Blue (MB) in aqueous medium followed by visible light irradiation causes decolorisation of blue solution and keeping at dark restores the blue colour." – Explain this observation.
6. a) Write a note on Chemosensor (give at least two examples)
- b) X-Ray fluorescence spectroscopy and its application.
- 2+3

[3]

2. Draw Jablonski diagram and define the meaning of the states. Why do $\lambda_{\text{Phosphorescence}} > \lambda_{\text{Fluorescence}} > \lambda_{\text{Absorption}}$? Explain pre-dissociation on the basis of quantum chemical principle.
- 2+1+2
3. a) Explain the emission characteristics of the molecules (i) with increasing conjugation (*viz.* benzene to naphthalene to anthracene), (ii) substituting electron donating and withdrawing group and (iii) generating paramagnetic centres.
- b) Write notes on application of Fluorescence technique in Food Quality Control.
- 3+2
4. $\text{M} + h\nu_i \rightarrow \text{M}^*$; $\text{M}^* \rightarrow \text{M} + h\nu_f$; $\text{M}^* + \text{Q} \rightarrow \text{M} + \text{Q} + \text{heat}$
- From the above scheme derive Stern-Volmer relation and explain K_{SV} . Give plausible mechanism of quenching. What are the factors that influence the quenching process ?
- $2+1\frac{1}{2}+1\frac{1}{2}$
5. What happens when (give reasons) 1×2+1 $\frac{1}{2}$ ×2
- a) i) Azobenzene is irradiated with UV light for few minutes followed by irradiation with visible light.
- ii) 4-N, N-Dimethylbenzointrile in hexane and in tetrahydrofuran is irradiated with UV light. Draw the corresponding emission spectra.

[Turn over