

M. Sc. CHEMISTRY EXAMINATION, 2018

(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

Attempt *any five* questions.

1. Explain the following : 1× 5
 - i) Pyridine is weakly emissive and become nonfluorescent on acidification.
 - ii) Very dilute solution of Phenol is emissive while concentrated solution of phenol is nonemissive.
 - iii) Phenolphthalein is a nonfluorophore but Fluorescein in Fluorescence active although the functional groups are the same.
 - iv) $\text{Eu}(\text{acac})_3$ (acac = acetylacetonato) is emissive although $\text{Eu}(\text{III})$ is $4f^6$ and paramagnetic.
 - v) Emmissivity of Coumarin > Napthalene > Vitamin A although all have five conjugated doubles bonds.

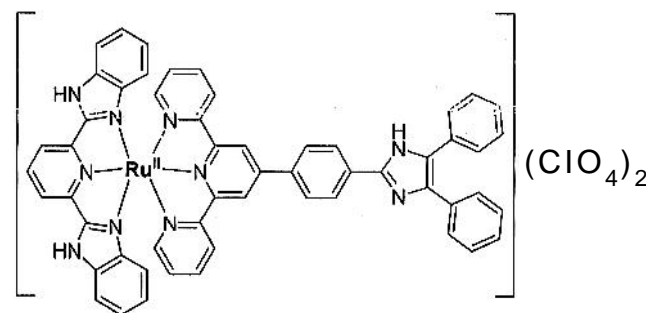
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2. a) What are the possible ways of non radiative decay of an optically excited molecule? Briefly describe the mechanism of radiative and nonradiative processes. 5
3. a) Why does pyrene solution show longer wavelength emission at higher concentration? Design some pyrene appended molecules to accomplish this property for analytical applications.
- b) Write a short note on delayed Fluorescence. 3+2
4. a) In a metal complex, the metal dominated excited state (M_1) lies in between S_1 and T_1 energy levels and also a metal dominated orbital (M_0) appears closer to S_0 state. Draw the state diagram and comment on the emission spectral feature.
- b) Describe the mechanism of quenching. 3+2
5. What happens when (give chemical reaction) 1×5
- a) Aqueous solution of $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is irradiated with UV light.
- b) Acidified (0.1N H_2SO_4) solution of $[\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]]$ is exposed in day light,
- c) Mixture of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and 2,2'-bipyridine in aqueous medium is exposed to UV light;

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- $m/e = 31$ peak. Predict the appropriate mode of fragmentation with chemical reasoning. 2
- c) How do gaseous and desorption sources differ in the mass spectrometric measurement? What are the advantages of each? 2
- d) How many peaks would you expect in the mass spectrum of CH_3Cl ? Predict their m/e values. 2
- e) The electrospray ionization mass spectrum (ESI-MS) of the following complex exhibits two peaks, at $m/z = 470.06$ and $m/z = 938.08$ in acetonitrile. Identify the ions responsible for the peaks. (Given atomic mass of Ru : 101.07 and Cl = 35.5) 4



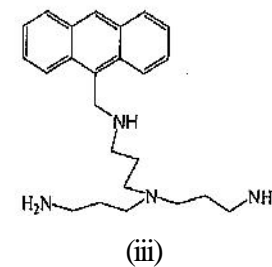
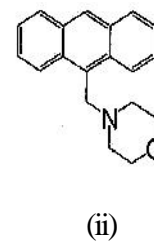
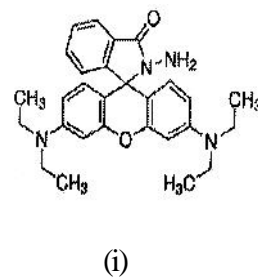
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UNIT – A- 4152

8. Discuss the working of an organic scintillator explaining the principle involved. 4 $\frac{1}{2}$
9. Answer *any two* questions :
- a) Describe the principle behind the functioning of “Gas ionization detectors”. 4
- b) Discuss radiolysis of water following interaction of an ionizing radiation with it. What are the major products formed as a consequence ? 4
- c) With suitable graphical representation discuss “Ceric Sulphate dosimetry”. 4
- d) With a suitable example of your choice explain radiometric titrations. 4
10. a) Write an equation for the appearance potential of the fragment (R^+) derived from the molecule, R-X, in terms of ionization potential and dissociation energy. How the appearance potential can be obtained from ionization efficiency curve ? 2 $\frac{1}{2}$
- b) Fragmentation of $\text{OHCH}_2\text{CH}_2\text{NH}_2^+$ can occur to produce $\dot{\text{C}}\text{H}_2\text{OH}$ and $\dot{\text{C}}\text{H}_2\text{NH}_2^+$ or $\overset{+}{\text{C}}\text{H}_2\text{NH}_2$ and CH_2OH^+ . Experimental results show that the peak at $m/e = 30$ is about ten times more intense than the peak at

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- d) $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in dry MeCN solution is electrochemically reduced (at -1.5V) and ammonium perdisulfate is added. A strong emission is observed.
- e) Why do phosphorescence emission appears at longer wavelength and life time is higher than fluorescence ?
6. a) “Ethidium bromide is nonfluorescent while in DNA environment emission is enhanced.” Explain
- b) Upon irradiation of light to acidified (0.1N H_2SO_4) solution of Mohr’s salt and Methylene blue (MB), colour bleaches while colour reappears when it is placed in dark. Explain with MO approach. 3+2
7. Explain the followings properties (a) the molecule (i) is a chemosensor to H_2O_2 catalysed by Fe (III); (b) the molecule (ii) is a H^+ sensor; (c) the molecule (iii) is a sensor for HPO_4^{2-} . 2+1+2



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