

(2½ Hours)

B. : (1) All questions are compulsory.

(2) Figures to the right indicate full marks.

(3) Use of logarithmic table/non programmable calculator is allowed.

1. a) Attempt any two of the following:-

i) Draw a labeled schematic diagram of Michelson's interferometer. Explain its working in FTIR 4

ii) With respect to UV absorption spectroscopy, explain the following terms with examples 4

a) bathochromic shift (b) hyperchromic effect

iii) Differentiate between Laser sources and other sources of electromagnetic radiation. 4

iv) With the help of a labeled diagram, explain the principle and working of prism monochromator in spectrophotometer. 4

b) Attempt any one of the following:-

i) Explain the KBr pellet method and Nujol mull method for handling solid samples in IR spectroscopy. 4

ii) A solution containing two absorbing species A and B was analyzed spectrophotometrically at two wavelengths in a 1.0cm cell. The absorbance of mixture was 0.899 and 0.185 at 530nm and 390nm respectively. Calculate the molar concentration of two species A and B, if the molar absorptivity of the two species at two wavelengths is as follows:- 4

Species	Molar absorptivity, $\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	
	530nm	390nm
A	8879	560
B	545	8755

2. a) Attempt any two of the following:-

i) With the help of a labeled schematic diagram, describe gas filled transducer in X-ray spectroscopy. 4

ii) Explain the principle of mass spectrometry. Draw a neat labeled diagram of mass spectrometer. 4

iii) Describe the construction and working of Quadrupole mass analyzer. 4

iv) Describe the following techniques used to compensate for absorption and enhancement effect in X-ray fluorescence analysis:- 4

a) External standard calibration

b) Use of internal standard

b) Attempt any one of the following:-

i) Give an account of fast atom bombardment source used in mass spectrometry. 4

ii) With the help of a suitable diagram, explain energy dispersive instrument used in X-ray fluorescence. What are its advantages? 4

3. a) Attempt any two of the following:- 4

i) Explain the principles of electrogravimetry.

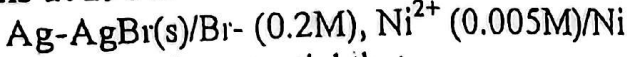
ii) What are ion selective electrodes? Give the characteristic properties of membrane used in these electrodes. 4

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- iii) Give an account of 'Ion Selective Field Effect Transistors' 4
- iv) Give comparative account of Coulometric and Volumetric titrations. 4

b) Attempt any one of the following:-

i) The following cell was set up in the determination of Ni²⁺ ions in presence of bromide ions at 298 K 4



Calculate the potential that: -

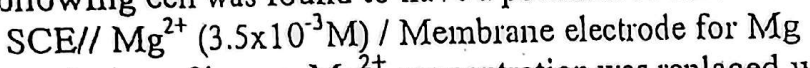
- (1) must be applied to prevent current from developing in the cell when the two electrodes are connected and
- (2) must be applied to cause an electrolytic current of 1.0 mA to develop.

Assume that the internal resistance of the cell is 10.0 Ohms.

Given:- $E^0_{Ag/AgBr(s), Br^-} = 0.071 V$

$E^0_{Ni^{2+}/Ni} = -0.24 V$. and $\frac{2.303RT}{F} = 0.0592$ at 298 K.

ii) The following cell was found to have a potential of 0.275 V at 298K. 4



When the solution of known Mg²⁺ concentration was replaced with an unknown concentration of Mg²⁺ solution, the potential was found to be 0.185V. Calculate the concentration of Mg²⁺ in the sample solution as pMg.

4. a) Attempt any two of the following:-

i) Using Cottrell equation, derive the Ilkovic equation for diffusion current i_d 4

ii) Describe cyclic voltammetry with respect to :- 4

- (1) Potential-time curve
- (2) Current-voltage curve

iii) Explain the nature of titration curves obtained in amperometric titrations using two micropolarisable electrodes. Why such titration method is called 'dead stop end point' method? 4

iv) What is pulse polarography? Draw the excitation signals used for differential pulse polarography. What are the advantages of this technique over conventional polarography? 4

b) Attempt any one of the following:-

i) A certain metal ion undergoes reduction by taking up two electrons. The average diffusion current of 0.0025 M solution of the metal ion is found to be 15.0 μA . The value of the capillary characteristic is 1.6. Calculate the diffusion coefficient of the metal ion.

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ii) Calculate the concentration of nickel ion in the sample solution on the basis of the following information for current measured at -1.1 V versus SCE in a polarographic analysis.

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	Solution	Current in μA
(1)	25.0 cm^3 of 0.2 M K_2SO_4 soln., diluted to 50.0 cm^3 with distilled water.	12.6
(2)	25.0 cm^3 of 0.2M K_2SO_4 soln. + 10.0 cm^3 of nickel sample soln., diluted to 50.0 cm^3 with distilled water.	50.9
(3)	25.0 cm^3 of 0.2M K_2SO_4 soln. + 10.0 cm^3 of nickel sample soln. + 5.0 cm^3 of 0.02 M nickel soln., diluted to 50.0 cm^3 with distilled water.	74.0

Attempt any four of the following:

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- Discuss the limitations of quantitative IR methods.
- Explain the effect of solvents on λ_{max} values in UV-visible spectroscopy.
- Discuss the advantages and disadvantages of X-ray fluorescence methods.
- What are the advantages of gaseous and desorption sources used in mass spectrometry?
- Describe with a suitable example liquid membrane electrode.
- Explain the application of Coulometric titrations to study the neutralization and complex formation reactions.
- Why is it necessary to place a reference electrode very close to the working electrode in voltammetric analysis? What is the role of counter electrode in three electrode system?
- Describe the principle of Karl Fischer method.

