M. Sc. Chemistry Examination, 2019

(3rd Semester)

Advanced General Chemistry - II

Paper - X

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - 3101

Answer ***any five*** questions .

1. Write down the polarographic reduction wave equation. What do you mean by "log-plot analysis" in polarography ? Mention the significant aspects of this 'log-plot analysis'. 1+1+3

2. a) Distinguish between Cathodic Stripping Voltammetry (CSV) and Anodic Stripping Voltammetry (ASV). 2

   b) Mention the limitation(s) of conventional DC polarography. 1

   c) Describe the construction of an "OTTLE". 2

3. Write a concise note on "Chronoamperometry". 5

4. a) Compare and contrast between LSV and CV. 3

   b) How do you test for the quasi-reversibility of a redox reaction in CV ? 2

5. Write down the working principle of a solid-state fluoride ion selective electrode. 'This electrode is limited to use over the

pH range of 0-8.5'–explain why. 3+2

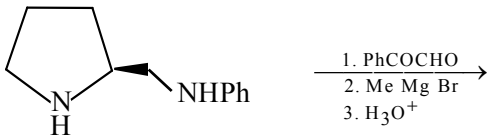
6. a) Mention the principle of an ethanol sensing electrode. 3

b) How does a urea sensing electrode function ? 2

UNIT - 3102

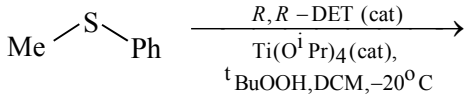
Answer any ***five*** questions .

7. a) Write the structure of the major enantiomer obtained after the following sequence of reactions, and account for your answer for the step involving enantioselectivity. $2\frac{1}{2}$



b) Why is Ti special for carrying out Sharpless asymmetric epoxidation reaction ?

Write the structure of the major enantiomer obtained from the following reaction.



Write the structure of the loaded catalyst for the above sulfoxidation reaction. $1+1+\frac{1}{2}$

b) Deduce the structure of the organic compound with the following analytical and spectral data. 3

Analysis : C = 74.98%, H = 6.86%

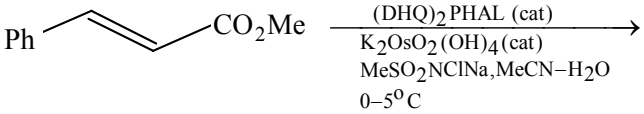
Mass : 176, 131 (base peak),

IR_{max} : 1714, 1639 cm^{-1}.

^{1}H-NMR : δ 1·31 (t, 3H, J = 7·1 Hz),
4.2 (q, 2H, J = 7·1 Hz),
6·43 (d, 1H, J = 15·8 Hz),
7.24–7·57 (m, 5H),
7·67 (d, 1H, J = 15·8 Hz),

^{13}C-NMR : δ 14·3, 60·4, 118·4, 128·1, 128·9, 130·2, 134·5, 144·5, 166·8.

8. Depict the catalytic cycle for asymmetric aminohydroxylation reaction. Write the structure of a typical chiral ligand used for such reaction. With the help of a 'Mnemonic device' draw the structure of the major enantiomer of the major regioisomeric product. $1\frac{1}{2}+1+2\frac{1}{2}$



9. Discuss briefly about the underlying principle involved in the "Electro spray Ionisation" with a schematic diagram. What are the advantages and disadvantages of ESI over the other ion sources ? $3\frac{1}{2}+1\frac{1}{2}$

10. a) How is multiple charge states deconvolved into neutral mass ? Positive ion ESI spectra of hen egg white lysozyme shows multiple charge ions at m/z 1023, 1001, 1193, 1302, and 1432. Calculate the neutral mass of the sample. $1\frac{1}{2}+1\frac{1}{2}$

    b) ^{15}N-NMR spectroscopy exhibits negative NOE. Justify the above statement with proper reason. 2

11. a) An organic compound with molecular formula $C_{11}H_{14}O$, shows the following spectral data : ^{1}H–NMR : δ (in ppm) 7.25 - 7.82 (m), 2.82 (t), 1.84 (quin), 1.54 (sextet); 0.82 (t). ^{13}C-NMR and DEPT experimental results are tabulated below. Deduce the structure of the compound with justification of data. 3

[Turn over

^{13}C (δ in ppm)	DEPT-135	DEPT-90
14	+	NP
22	–	NP
26	–	NP
38	–	NP
128	+	+
129	+	+
133	+	+
137	NP	NP
200	NP	NP

[NP = No Peak]

    b) Explain in brief 'Gated decoupling' and 'Off-resonance decoupling' techniques and their utilities. 2

12. a) How will you estimate the amount of epoxide present in nanomaterials or in carbon nanotubes using ^{31}P–NMR spectroscopic technique ? 2