Third Semester M.Sc. ANALYTICAL CHEMISTRY

AN3C09/CH3C09/PO3C09 STRUCTURAL INORGANIC CHEMISTRY

(Common to M.Sc. Analytical Chemistry, Chemistry and Polymer Chemistry)

MODEL QUESTION PAPER

Time : 3 Hrs Max. Weights: 30

Section A

(*Answer any **10** questions. Each question carries a weight of **1***)

01. Briefly explain 'Perovskite' structure.
02. Explain Martensitic transformation with an example.
03. What is meant by sintering?
04. Define Piezoelectricity. Describe one application of Piezoelectric crystal.
05. Comment on the magnetic properties of 'Garnets'.
06. What are 'phosphors'? Explain its application in the working of fluorescent lamps.
07. Define 'Meissner effect'. Where does it find its applications?
08. Borazine is called inorganic benzene. Why?
09. Illustrate the role of Zeolites as supported metal catalysts.
10. The styx number of B_4H_{10} is (4012). Draw its topological structure.
11. Distinguish between closo, nido and arachno carboranes.
12. Discuss the preparation of Zintl anions and cations of Sn and Bi.
13. What are ceramic materials? Differentiate between traditional and advanced ceramics.

(10 x 1 =10 weights)

Section B

(*Answer any **5** questions. Each question carries a weight of **2***)

14. How will you distinguish between Fluorite and Antifluorite structures? Explain.
15. What are the factors influencing solid state reactions?
16. Explain the BCS theory of superconductivity.
17. What is photoconductivity? Give examples of photo conducting materials. How are photoconductors used for detection and measurement of radiation?
18. Explain the concept of heteropoly acids with special reference to Molybdenum.
19. Give a brief note on silicones and their applications.
20. Write a brief account of cage like structures of phosphorous.
21. What are safety glass and fibre glass? How are they made? What are their important uses?

(5 x 2 =10 weights)

Section C

(*Answer any **2** questions. Each question carries a weight of **5***)

22. (a) Discuss the structure of A_mX_2 and ABX_3 type crystals.
    (b) Discuss the kinetics of phase transitions in solids.

23. Discuss the salient features of classical free electron theory of metals. What are the drawbacks of free electron theory? How are these drawbacks rectified by the introduction of quantum Mechanical Treatment?

24. (a) Give an account of the structure of silicates.
    (b) Explain the structure and bonding in poly phosphazenes.

25. (a) How is $[Re_2Cl_8]^{2-}$ synthesized? Point out the characteristic features in bonding. Mention the evidence of M-M bond in it.
    (b) What is ceramic processing? Using a specific example, illustrate the use of sol-gel method in ceramic processing.

(2 x 5 =10 weights)

AN3C10/CH3C10 ORGANIC SYNTHESES

(Common to M.Sc. Analytical Chemistry and Chemistry)

MODEL QUESTION PAPER

Time: Three hours Total Weights: 30

Section A

(*Answer any **10**questions. Each question carries a weight of **1***)

01. Give examples of chromium and manganese based oxidation of alcohols to carbonyl compounds.
02. Discuss any two methods for the synthesis of diols from alkenes using Osmium.
03. What is DIBAL-H? Give any two applications of DIBAL-H.
04. What is Nef reaction? Explain its mechanism.
05. Give the structures of NBS and DCC.
06. Give one method each for the synthesis of (a) Pyrrole (b) Imidazole (c) Oxazole.
07. What are the important amino protecting groups? What is the importance of amino protection in peptide synthesis?
08. What is Umpolung equivalence? Give one example.
09. What is meant by chemo and regio selective protection and deprotection?
10. Discuss the contraction and expansion of ring systems. Give an example of Demjenov reaction.
11. How can you synthesis Corey lactone by enantioselective method?
12. Give an example of Preterson olefination.
13. Explain the relative reactivity of pyrrole, furan, thiophene and imidazole.

(10×1=10 weights)

Section B

*(Answer any **5** questions. Each question carries a weight of **2**)*

14. Discuss the method of synthesis of epoxide from alkenes. Explain the mechanism of (a) Sharpless asssymmetric epoxidation and (b) Shi epoxidation.
15. Write a note on Click reaction.
16. Explain the method of construction of macrocyclic rings by ring closing metathesis.
17. Discuss the mechanism and applications of inter and intra molecular ketene cycloaddition
18. How will you synthesize esters and lactones from ketones? Explain Baeyer-Villigar oxidation.
19. Write note on biomimetic synthesis of progesterone.
20. Briefly explain the basic principles for the biosynthesis of terpenes.
21. Explain the enantioselective synthesis of luciferin and longifolene.

(5×2=10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. Write an essay on the applications of the metal and non-metal based oxidations of (a)alcohols and (b)alkenes in organic synthesis. Illustrate with examples.

23. Write an essay on metal mediated C-C and C-X coupling reactions with special reference to (a) Suzuki coupling (b) Heck reaction (c) Suzuki-Miyaura coupling (d) Glaser coupling and (e) Nozaki-Hiyama reaction.

24. Discuss the basic principles of retero synthesis. Explain one group C-C and two group C-C disconnections.

25. Write an essay on the role of protection, and deprotection in peptide synthesis. Illustrate with examples with special reference to SPPS method. Explain the mechanism.

(2×5=10 weights)

AN3C11 SELECTED TOPICS IN PHYSICAL CHEMISTRY

MODEL QUESTION PAPER

Time : 3 Hrs Max. Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. Define steric factor. Explain how it is related to entropy of activation.
02. Explain with an example how NMR can be used in the study of fast reactions.
03. Compare transition state theory with collision theory.
04. Discuss primary kinetic salt effect.
05. What is cage effect?
06. What is Tafel equation?
07. Discuss the effects of pH and temperature on catalysis.
08. Distinguish between excimers and exciplexes.
09. What is meant by photostationary state? Discuss with reference to formation of ozone in the atmosphere.
10. What is Debye-Falkenhagen effect.
11. What are liquid crystals?
12. Define zeta potential.
13. Explain the principle of photoelectron spectroscopy.

(10 x 1 =10 weights)

Section B

*(Answer any **5** questions by attempting not more than **3** questions from each bunch. Each question carries a weight of **2**)*

Bunch 1 (Short Essay Type)

14. What are explosive reactions? Explain the mechanism with a suitable example.
15. Write a note on the Debye-Huckel theory.
16. Illustrate Rice-Herzfeld mechanism with thermal decomposition of acetaldehyde.
17. Discuss the single crystal X-ray diffraction technique.

Bunch 2 (Problem Type)

18. A second order reaction has a rate constant k = 2.5 x 10^{-3} L mol^{-1} S^{-1} at 25°C. Its energy of activation is 48 kJ mol^{-1}. Calculate $\Delta S^{\neq}$ for the reaction, assuming that the reaction takes place in solution.
19. For a homogeneous gaseous reaction the rate constants are 3.0 x 10^{-5} L mol^{-1} S^{-1} and 1.2 x 10^{-3} L mol^{-1} S^{-1} at 629 and 700K respectively. Calculate the energy of activation and frequency parameter.
20. In a photochemical reaction A → 2B + C the quantum efficiency with 500 nm light is 2.1 x 10^{2} mol $Einstein^{-1}$. After exposure of 300 m mol of A to the light 2.28 m mol of B was formed. How many photons were absorbed by A?
21. In an experiment to measure quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100W source for 45 minutes. The intensity of transmitted light was 40% of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the quantum efficiency.

(5 x 2 =10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. a) Explain the BET theory of adsorption.
    b) Discuss the use of Langmuir and BET isotherms for surface area determination.
23. a) Explain the principles of ESCA and Auger electron spectroscopy.
    b) Discuss the applications of SEM and TEM in the study of surfaces.
24. a) Distinguish between E-type and P-type delayed fluorescence.
    b) Discuss the working of solar cells.
    c) Discuss the applications of LASER in the study of photochemical kinetics.
25. a) Derive the Butler-Volmer equation.
    b) Discuss the different theories of overvoltage.

(2 x 5 =10 weights)

AN3C12/AP3C12/ CH3C12/ PH3C12/ PO3C12

SPECTROSCOPIC METHODS IN CHEMISTRY

(common to all branches of Chemistry)

MODEL QUESTION PAPER

Time: Three hours Total Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. How would the fluorine NMR spectrum for F-CH_2-CO-CH_2-CH_3 appear?
02. How will you distinguish between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions? Apply the effect of solvation to illustrate this.
03. Predict the signal pattern in DEPT-90 and DEPT- 135 spectra of phenyl acetic acid.
04. A trisubstituted benzene possessing one bromine and two methoxy substituents exhibits three aromatic resonance bands at 6.40, 6.46 and 7.41 ppm in its proton NMR spectrum. What is the substitution pattern?
05. Explain ORD with example.
06. What is meant by finger printing in IR spectroscopy?
07. How will you confirm the conversion of benzene to cyclohexane with ^{1}H NMR and ^{13}C NMR spectroscopy?
08. What is MALDI? Explain with example.
09. Comment on the differences between the scales in ^{1}H and ^{13}C NMR spectroscopy.
10. How will you estimate ring strain using IR and UV-Visible spectra.
11. Predict the proton and deuterium NMR spectra of D-CH_2-O-CH_3 (for D, I=1).
12. What are the applications of 2D- COSY spectra?
13. Sketch Karplus curve. Explain its characteristic features.

(10×1=10 weights)

Section B

*(Answer **5** questions. Each question carries a weight of **2**)*

14. Explain how IR spectroscopy can be applied to predict the product formation at each step in the following reaction series.

Benzaldehyde → Benzoin → Benzil → Benzilic acid.

15. Apply ^{1}H NMR and ^{13}C NMR spectroscopic techniques and explain how will you confirm the following conversions. Explain all characteristic features of the ^{1}H NMR and ^{13}C NMR of the substrates and the products.

a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{[O]} CH_3\text{-}CH_2\text{-}CHO$

b) $CH_3\text{-}CH(OH)\text{-}CH_3 \xrightarrow{[O]} CH_3\text{-}CO\text{-}CH_3$

16. Sketch the H-H HOMOCOSY of (a) 2- chloro propane and (b) ethanol.
17. Write a note on (a) axial halo ketone rule and (b) Cotton effect.
18. Discuss the applications of HRMS and MS-MS techniques in structure analysis.
19. Define NOE. Explain Nuclear Overhauser Enhancement based on cross polarization theory.
20. Predict the structure of the compound with the following spectral characteristics:
    UV: 290 nm
    IR : 2980, 1718, 1440 cm^{-1}
    ^{1}H NMR : 2.3ppm (q), 2.15ppm(s), 1.1ppm(t)
    Mass (m/z) : 72(M^{+}), 43 (base peak), 29
21. Sketch the approximate ^{1}H NMR and ^{13}C NMR and mass spectra of 2-butenone. Explain the spectral features.

(5×2=10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. Define and explain spin-spin coupling. Using tree diagram method explain AX, AX_2, AX_3, A_2X_3, AB and ABC type coupling.
23. Write an essay on the application of DEPT, INEPT, and RINEPT in the structural elucidation of organic compounds. Illustrate the application of DEPT with examples.
24. (a). Predict the structure of the compound (commercial sample) with the following spectral characteristics and justify your answer.

    MF: $C_4H_{10}O$; IR: 3450 (broad), 2980, 1450, 1200, 1050cm^{-1}.

    ^{1}HNMR: 1.5 (3H, t), 2.8 (2H, dq), 3.4 (1H, m), 4.5 (1H, s), 2.1 (3H, d).

    ^{13}C NMR: 22.6, 68.7, 32.0, 9.9 ppm.

    DEPT 45: 4 signals, DEPT 90 : 1 signal, DEPT 135: 3 +ve and 1 –ve signals.

    (b). Discuss the theory and applications of MRI.

25. (a) An ester $C_5H_8O_2$ shows the following ^{13}C spectral results (off-resonance decoupled).

20 ppm (q), 50 ppm (q), 126 ppm (t), 130 ppm (s) and 160 ppm (s).

Predict the structure.

(b) Determine the structure of the compound with the following spectral characteristics.

MF: $C_5H_9NO_4$; IR: 1750, 1562, 1320$cm^{-1.}$

^{1}HNMR: 5.2 (q), 4.2 (q), 1.8 (d), 1.3 (t).

^{13}C (ppm)	PT 135	PT 90
		peak
		peak
		peak
	peak	peak

(2×5=10 weights)