Second Semester M Sc Chemistry

AN2C05/AP2C05/ CH2C05/ PH2C05/ PO2C05
COORDINATION CHEMISTRY

(common to all branches of Chemistry)

Model Question Paper

Time: 3 Hrs Max. Weight: 30

Section A

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

01. What is nephlauxetic effect?
02. Give one evidence for metal ligand orbital overlap.
03. Explain Irwing William order of stability of complexes.
04. Account for the difference in intensities of colours of aqueous solutions of Na_2CrO_4 and $Cr(NO_3)_3$. Give the origin of those colours.
05. How CD spectra is useful in determining the absolute configuration of metal complexes?
06. Derive the ground term symbol for octahedral Cr^{3+} ion.
07. Explain the d orbital splitting diagrams of for triagonal-bipyramidal and square pyramidal complexes of formula ML_5. What would be the expected magnetic properties of such complexes of Ni(II)?
08. Characterize the following complexes as high spin or low spin:

    $[Co(NH_3)_6]^{2+}$ (μ: 5 BM), $[Co(NO_2)_6]^{4-}$ (μ: 1.9 BM), $[CoF_6]^{3-}$(μ: 5.3 BM), $[Fe(CN)_6]^{3-}$ (μ: 2.3 BM).
09. What is *trans* effect? What would be the sequence of substitutions required to get $[PtClBrNH_3Py]$ (with Br *trans* to Cl) from $[Pt\ Cl_4]^{2-}$?
10. Explain Curies law? What is its significance?
11. How many *d-d* bands would be expected in the electronic spectrum of an octahedral Cr(III) complex?
12. Explain the difference between *4f* and *5f* orbitals.
13. Electronic absorption spectra of lanthanide ions are very sharp. Explain.

(10 x 1 =10 weights)

Section B

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

14. How can Ni(II) complexes with various geometries be distinguished using their electronic spectra?
15. What is Jahn-Teller effect? How electronic spectra could be used to detect Jahn-Teller distortion in transition metal complexes?
16. What are the merits and demerits of crystal field theory of complexes?
17. Distinguish between Orgel diagrams and Tanabe-Sugano diagrams.
18. Explain Temperature Independent Paramagnetism with suitable examples.

19. What is meant by circular dichroism and ORD? Discuss the important applications of Cotton effect in coordination chemistry.
20. What is meant by stability of a complex? Explain the factors determining the stability of a complexes.
21. Explain the use of lanthanide complexes as shift reagents.

(5 x 2 =10 weights)

Section C

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

22. (a) What is Chelate effect? Why it is considered as an entropy effect? Predict which of the following pairs would have higher order of stability. Give reasons.
    (i) $[Cu(en)_2]^{2+}$ and $[Cu(NH_3)_4]^{2+}$
    (ii) $[Cu(acac)_2]^{2+}$ a$[Cu(en)_2]^{2+}$

    (b) Predict and explain the possible electronic transitions in $[Co(NH_3)_6]^{2+}$.

23. (a) How will you distinguish the terms hydrolysis, acid hydrolysis and base hydrolysis of coordination compounds? Using examples, explain the mechanism of base hydrolysis of an octahedral complex.
    (b) Explain the Taube mechanism of inner sphere electron transfer reactions in metal complexes.

24. (a) State and explain the selection rules for electronic spectra of transition metal complex.
    (b) Discuss the use of electronic spectral data for the structure elucidation of transition metal complexes.

25. Explain the geometrical and optical isomerism exhibited by inorganic complexes with suitable examples.

(2 x 5 =10 weights)

AN2C06/AP2C06/ CH2C06/ PH2C06/ PO2C06
ORGANIC REACTION MECHANISM

(common to all branches of Chemistry)

Model Question Paper

Time: 3 Hrs Max. Weight: 30

Section A

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

01. Explain regioselectivity in addition reactions, with special reference to Markovnikov's addition. What are the mechanistic reasons for the selectivity?
02. Comment on the role of reagents and leaving groups in SN^1 and SN^2 reactions.
03. What are the important factors affecting the stability of carbanions? Discuss the structure of carbanions.
04. Give examples of sulphur and phosphorous ylides. Explain Peterson olefination.
05. Write the mechanism of Benzil-Benzilic acid rearrangement.
06. Write briefly on classical and non-classical carbocations.
07. How will you distinguish between singlet and triplet carbenes based on their stability and stereochemical bahaviour in addition reactions?
08. Amination of haloarenes show high preferences in orientation. Explain with examples.
09. Explain the structure and stability of carbon free radicals.
10. What is auto-oxidation? Illustrate with examples.
11. Explain the mechanism of Robinson annelations.
12. Give an example of an electrocyclic reaction. Explain the mechanism.
13. Write briefly on sigmatropic rearrangements. Illustrate with examples.

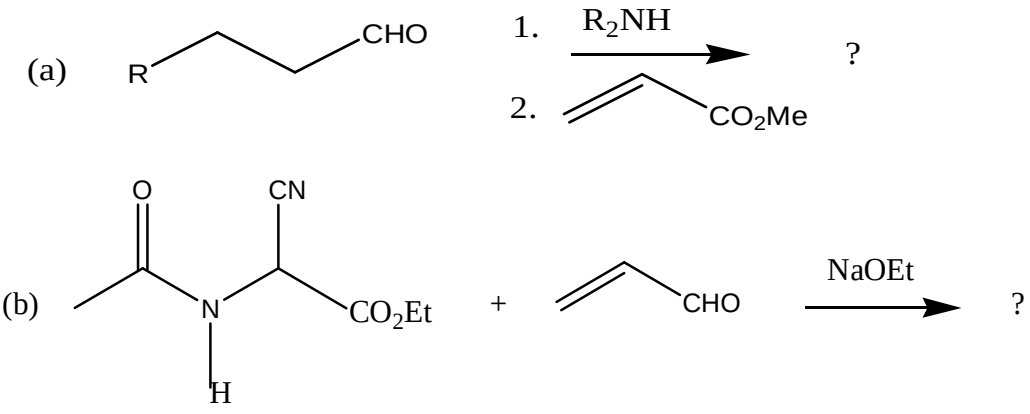
(10×1=10 weights)

Section B

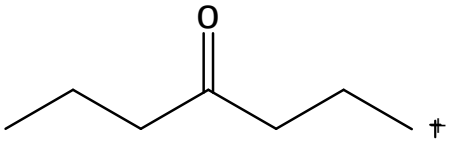
(Answer 5 questions by attempting not more than 3 questions from each bunch. Each question carries a weight of 2)

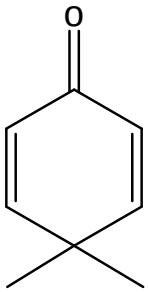
Bunch 1(Problem Type)

14. Predict the products that would be formed in these conjugate additions.

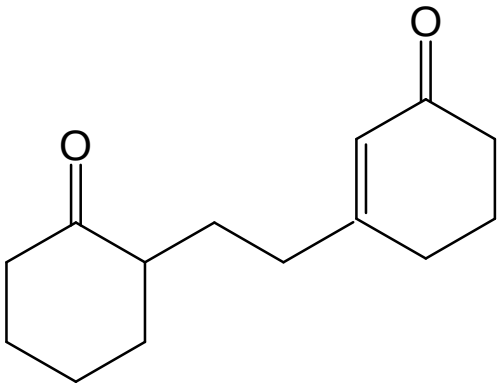


15. Predict the product(s) and explain the mechanism of the following reactions:

(a)  + $ArSO_2NHNH_2$ ⟶ ? $\xrightarrow[2.\ Me_3SiCl]{1.\ 2BuLi}$?

(b)  $\xrightarrow{H^+}$? $\xrightarrow{\text{rearranges}}$? (a 3^o Carbocation) $\xrightarrow{\text{loss of proton}}$?

16. Predict which enone product would be formed in this intramolecular aldol condensation. Explain the mechanism of the reaction.

 $\xrightarrow[AsOH]{TsOH}$? (MF:$C_{14}H_{18}O$)

17. In Cannizzaro reaction, what are the evidences obtained in support of:
(a) ionic mechanism
(b) mechanism involving the formation of an intermediate dimeric adduct, and
(c) mechanism involving the formation of an ester intermediate.

Bunch 2(Short Essay Type)

18. What are cycloaddition reactions? Explain (4+2) cycloaddition by FMO method.
19. Explain the mechanisms of Aldol condensation and Michael reaction.
20. Distinguish between Saytzef and Hofmann elimination.
21. Comment on the chemistry of enolates and enamines. What is meant by kinetic and thermodynamic enolates?

(5×2=10 weights)

Section C

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

22. Explain the mechanism of nucleophilic addition to carbonyl compounds. Write notes on:
    (a) Favorski rearrangements
    (b) Shapiro reaction
    (c) Julia elimination, and
    (d) Darzen and acyloin condensations.

23. Give a detailed account of the C-C bond forming reactions involving carbocations.

24. Write briefly on the molecular rearrangements involving nitrene intermediates, with special reference to Hofmann, Curtius, Lossen and Beckmann rearrangenets. Discuss the stereochemical preferences in Beckmann rearrangement.

25. Discuss and illustrate the applications of pericyclic reactions in organic synthesis taking examples such as Claisen, Cope, Mislow-Evans and Wittig reactions.

(2×5=10 weights)

AN2C07/AP2C07/ CH2C07/ PH2C07/ PO2C07
CHEMICAL BONDING AND COMPUTATIONAL CHEMISTRY
(common to all branches of Chemistry)

Model Question Paper

Time: 3 Hrs Max. Weight: 30

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

01. Explain the independent particle model.
02. What is Hellmann-Feynman theorem?
03. What are Slater determinants?
04. Compare GTO and STO.
05. Explain free valence with an example.
06. Illustrate non-crossing rule with an example.
07. Derive the term symbols for N_2.
08. Which of the following has higher bond order and bond energy: O_2, O_2^+, O_2^- ?
09. Distinguish between global minimum and local minimum.
10. State Hohenberg–Kohn theorems.
11. Calculate the number of basis functions on each atom for a 6-31G(d,p) basis set calculation of H_2O.
12. Explain the notation MP2/6-31G(d,p)//HF/6-31G.
13. Write the z-matrix of ethane.

(10 x 1 =10 weights)

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

14. Apply perturbation method to He atom.
15. Use HMO theory to determine the energies and wave functions of the pi electron system in allyl group.
16. Write a note on HFSCF Theory.
17. Draw a correlation diagram for the orbitals of a homonuclear diatomic molecule. How does it differ from that of a heteronuclear diatomic molecule?
18. Calculate the SALCs corresponding to the stretching vibrations of NO_3^- (D_{3h}).
19. Describe any two computational methods that include electron correlation.
20. Write an input file for geometry optimization of ammonia at HF/6-31G(d,p) level of theory followed by frequency calculation in GAMESS.
21. Write a note on basis set.

(5 x 2 =10 weights)

Section C

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

22. Taking H_2 as an example compare and contrast VB and MO theory.
23. Describe the hybridization in BF_3 using the concepts of group theory.
24. State and prove the variation theorem. Apply it to particle in a 1-D box using the trial function x(a-x).
25. Write a note on molecular mechanics method.

(2 x 5 =10 weights)

AN2C08/AP2C08/ CH2C08/ PH2C08/ PO2C08
MOLECULAR SPECTROSCOPY

(common to all branches of Chemistry)

Model Question Paper

Time: 3 Hrs Max. Weight: 30

Section A

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

01. Explain the principle of Lamb-dip spectrum.
02. Derive an expression for J_{max} for the rigid rotor.
03. What is the effect of substituting a hydrogen atom by a deuterium atom in hydrogen molecule on rotational constant B?
04. Discuss the factors influencing band width.
05. Explain Fermi resonance.
06. Explain the Raman activity of the various modes of vibrations of pyramidal AB_3 molecules.
07. Discuss the applications of microwave spectroscopy in chemical analysis.
08. Explain predissociation.
09. Write Mc Connel equation and explain the terms.
10. Explain Kramer's degeneracy.
11. Calculate the resonance frequency of hydrogen nucleus in an applied field of 2.4 T if $\beta_N = 5.05 \times 10^{-27}$ JT^{-1} and g = 5.585.
12. Draw the EPR spectrum of methyl free radical.
13. Explain the principle of NQR spectroscopy.

(10 x 1 =10 weights)

Section B

(Answer 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. Explain the various factors influencing the intensity of spectral lines.
15. What are selection rules? Discuss the selection rules in microwave, IR, Raman and EPR spectroscopy.
16. Discuss FT techniques in spectroscopy and explain its advantages.
17. Explain Karplus relationship.

Bunch 2 (Problem Type)

18. The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines separated by 0.71433 cm^{-1}. Calculate the rotational constant, moment of inertia and Br-F bond length.
19. The fundamental and first overtone transition of $^{14}N^{16}O$ are centred at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Calculate the force constant, zero point energy, anharmonicity constant and equilibrium vibration frequency of the molecule.
20. Predict the EPR spectrum of the following radicals (a) CF_2H, (b) $^{13}CF_2H$ and (c) $(C_{10}H_8)^-$
21. Calculate the relative population N_{upper}/N_{lower} if $\Delta E = 7 \times 10^{-26}$ J in a 2.3487 T field and 6×10^{-24} J in a 0.33 T field for nuclei and electrons respectively.

(5 x 2 =10 weights)

Section C

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

22. Discuss any three methods used for simplification of second order NMR spectra.
23. Outline the principle of Mossbauer spectroscopy. Explain the application of this technique in the study of Fe(II) and Fe(III) cyanides.
24. Discuss
    a) Relaxation methods in NMR spectroscopy
    b) Nuclear Overhauser Effect.
25. Discuss
    a) Classical and quantum theory of Raman effect.
    b) Resonance Raman scattering and resonance fluorescence.

(2 x 5 =10 weights)