

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Second Semester M.Sc Chemistry Degree Examination, March /April 2019

MCHE2B08 – Electrochemistry , Solid State Chemistry & Statistical Thermodynamics  
(2018 Admission onwards)

Time: 3 hours

Max. Weightage : 36

**Section A**

**Answer all questions. Each carries 1 weightage**

Write down Debye-Huckel Limiting Law and explain the terms.

What is fuel cell? Give an example.

Explain overvoltage.

What is concentration polarization?

Name the seven crystal classes.

Explain Edge dislocation in solids.

What is piezoelectricity?

Describe Hall Effect.

Distinguish between microstate and macrostate.

0. Define thermodynamic probability

1. What is the physical significance of partition function?

2. What are the limitations of the Maxwell-Boltzmann Statistics?

**(12 x 1 = 12 weightage)**

**Section B**

**Answer any 8 questions. Each question carries 2 weightage**

13. Distinguish between ' Fermions' and 'Bosons'

14. Explain Bose-Einstein Condensation

15. Give the relationship between molar and molecular partition functions

16. Write the Fermi energy function and explain

17. What is 'Electrophoretic Effect'?

18. Explain the working of H<sub>2</sub>-O<sub>2</sub> fuel cell

19. Describe a method to determine overvoltage.
20. Write a note on Dropping Mercury Electrode used in polarography
21. Explain space groups in crystals and show how do they arise
22. What is Schottky defect?
23. How does LASER work? Explain.
24. Write down difference between ferrimagnetism and ferromagnetism.

(8 x 2 = 16 weightage)

### Section C

Answer any 2 questions. Each question carries 4 weightage

25. Derive Debye-Huckel -Onsager Equation in the case of strong electrolytes.
26. Write a brief note on superconductivity.
27. What is non-stoichiometry? Explain two non-stoichiometric defects.
28. Derive vibrational partition function of a diatomic molecule.

(2 x 4 = 8 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Second Semester M.Sc Chemistry Degree Examination, March /April 2019

MCHE2B07 – Organic Reaction Mechanism

(2018 Admission onwards)

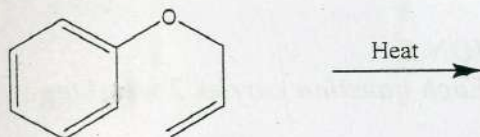
Time: 3 hours

Max. Weightage : 36

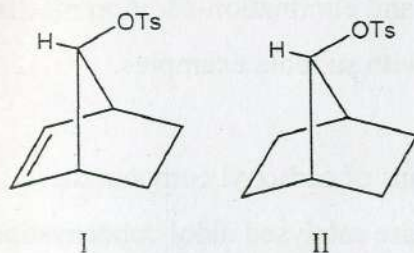
**SECTION A***Answer all questions. Each question carries 1 weightage*

1. Draw the structures of cephalosporin and quinine.

2. Complete and classify the reaction



3. Which of the following undergoes acetolysis at a faster rate? Explain why.



4. What are singlet and triplet carbenes? Give one method of preparation of them.

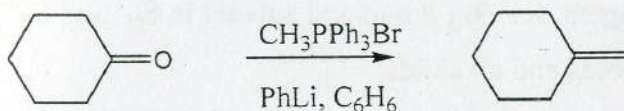
5. Explain  $E^1_{CB}$  mechanism with an example.

6. What are the products obtained when the cis and trans isomers of

1-bromo-2-methylcyclohexane is subjected to dehydrohalogenation.

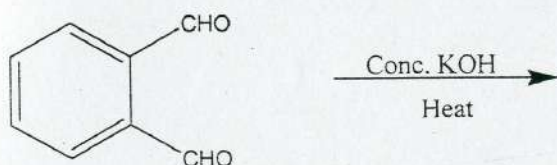
7. What is Ziesel's method? What is its use?

8. Explain the mechanism of the following conversion

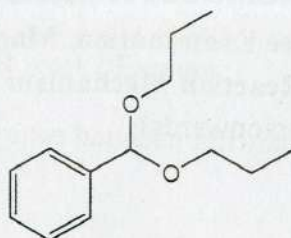


9. Illustrate the Norrish type II cleavage with an example

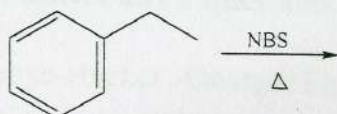
10. What is the product formed in the following reaction and explain the mechanism.



11. Name the compounds from which the following compound can be prepared and explain the mechanism of reaction.



12. Explain Wohl-Ziegler reaction? Complete the reaction



(12 x 1 = 12 Marks)

### SECTION B

Answer any 8 questions. Each question carries 2 weightage

13. Discuss the conversion of cholesterol into testosterone.
14. Explain the addition-elimination mechanism and elimination-addition mechanism of aromatic nucleophilic substitution reactions with suitable examples.
15. Explain the total synthesis of longifolene .
16. Give an account of the photochemical reactions of carbonyl compounds.
17. Write a note on mechanism of the acid and base catalysed aldol condensation.
18. Discuss the stereochemistry of Diels - Alder reaction with suitable examples.
19. Give an account of rearrangement of carbocations in the hydrohalogenation of alkenes and in the dehydration of alcohols with specific examples.
20. What are flavones and isoflavones? Outline any one method of synthesis of isoflavone.
21. Explain the stereochemistry of Hofmann's elimination? What are the products obtained when *erythro* and *threo* isomers of  $[\text{PhCHMeCHPhN}^+\text{Me}_3]\text{I}^-$  is treated with NaOEt?
22. Explain the effects of substrate, reagent, leaving group and solvent in  $\text{S}_\text{N}^1$  and  $\text{S}_\text{N}^2$  reactions.
23. Discuss the classification of terpenoids and alkaloids.
24. Discuss the mechanism of benzoin condensation and Perkin condensation.

(8 x 2 = 16 weightage)

**SECTION C**

*Answer any 2 questions. Each question carries 4 weightage*

Explain the total synthesis of reserpine.

Discuss the mechanism and applications of Mannich reaction, Prins reaction, Stobbe condensation and Darzen's glycidic ester condensation.

(i) Draw the Jabloski diagram and explain the radiative and nonradiative processes involved in it.

(ii) Draw the correlation diagram for  $(4n+2)$  cycloaddition reaction and explain why it is thermally allowed and photochemically symmetry forbidden.

(i) Give an account of the mechanism of ester hydrolysis in acidic and basic medium with supporting evidences.

(ii) Give an account of generation and application of carbenes.

**(2 x 4 = 8 weightage)**

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE  
 Second Semester M.Sc Chemistry Degree Examination, March /April 2019  
 MCHE2B06 – Coordination Chemistry  
 (2018 Admission onwards)

Time: 3 hours

Max. Weightage : 36

**Section A***Answer all questions. Each carries one Weightage*

1. Define Racah Parameters?
2. Based on Hund's rule arrange the following terms in the increasing order of energy:  $^4H$ ,  $^4G$ ,  $^2I$ ,  $^2M$ ?
3. Illustrate macrocyclic effect with an example?
4. When do we expect MLCT bands in metal complexes?
5. Write one example each of thermodynamically stable/kinetically labile and thermodynamically unstable/kinetically inert complexes?
6. Explain why do square planar complexes do not exhibit optical isomerism?
7. Mention quadrupole effect in Mossbauer spectroscopy?
8. Explain why the reduction of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  is approximately  $10^{10}$  time faster than  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ?
9. The B value for  $\text{Cr}^{3+}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  are  $957$  and  $618 \text{ cm}^{-1}$  respectively. Calculate the nephelauxetic parameter for the same?
10. Write short note on photoaquation?
11. Among the  $\text{Cr}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  transition metal ions which one is kinetically inert and why?
12. In which of the following complexes orbital contribution to magnetic moment is quenched. Justify your answer? (i)  $[\text{Mn}(\text{CN})_6]^{4-}$  (ii)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

(12 x 1 = 12 weightage)

**Section B***Answer any eight questions. Each carries two weightage*

13. What is chelate effect? Discuss its thermodynamic origin?
14. Discuss the mechanism of electron transfer reactions with reference to inner-sphere reactions.
15. What are the merits and demerits of crystal field theory of complexes ?
16. IR spectroscopy has proved to be the most effective technique in the study of metal carbonyls chemistry. Explain?
17. How the solvent plays an important role in the substitution reactions of square planar complexes?

18. Discuss antiferromagnetism and its various exchange pathways?
19. Briefly mention the photolysis of water using metal complex sensitizers?
20. Predict and explain the possible electronic transitions in  $[\text{Co}(\text{NH}_3)_6]^{2+}$
21. Discuss  $\pi$  bonding in octahedral complexes on the basis of MOT.
22. Illustrate the reducing and oxidising character of  $[\text{Ru}(\text{bipy})_3]^{2+}$ ?
23. How NMR spectroscopy can be used for the structural studies of diamagnetic metal complexes?
24. What is Jahn-Teller effect? How electronic spectra could be used to detect Jahn-Teller distortion in transition metal complexes?

(8 x 2 = 16 weightage)

### Section C

*Answer any 2 questions. Each carries 4 weightage*

25. (i) What are stepwise and overall stability constants of metal complexes? How are they related?  
(ii) What are the factors that affect the stability constant?
26. (i) Explain Gouy's method for the determination of magnetic susceptibility of a solid metal complex.  
(ii) The magnetic moments of  $[\text{NiCl}_4]^{2-}$  and  $[\text{CoF}_6]^{3-}$  were observed 2.82 and 4.87 respectively. With the help of these results, find out the correct hybridization and the number of unpaired electrons in both the complexes?
27. (i) Describe the principle, instrumentation and applications of Mossbauer Spectroscopy?  
(ii) Draw the Mossbauer spectra of the following iron complexes.  
(a)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$     (b)  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$     (c)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .
28. Give an account of A, D & I mechanisms of substitution reactions in Octahedral transition metal complexes.

(2 x 4 = 8 weightage)

## FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Second Semester M.Sc Chemistry Degree Examination, March /April 2019

MCHE2B05 – Applications of Quantum Mechanics &amp; Group Theory

(2018 Admission onwards)

Time: 3 hours

Max. Weightage : 36

**Section A***(Answer all questions; each question carries 1 weight)*

1. What are the types of trial functions in variation method?
2. The ground state energy of He atom according to independent particle model is 108 eV. Calculate the first ionisation potential of He atom. ( $E_H = -13.6\text{eV}$ )
3. Explain the terms quantum defect and screening constant in connection with STO?
4. What is the Roothans concept of basis functions?
5. Explain the magnetic nature of  $O_2$  molecule with the help of electron arrangement in MO's.
6. Write the term symbol of  $O_2$  and  $Cl_2$  molecules for the ground state.
7. Write the bonding orbital of  $H_2$  according to VB method and predict the covalent/ionic nature of the bond
8. In butadiene molecule, the  $\pi$  bond orders:  $p_{12} = 0.448$  and  $p_{23} = 0.896$ . Calculate the free valence at  $C_2$  of butadiene.
9. What are normal modes? Represent normal modes of  $NH_3$  molecule.
10. Show that the system of integers forms a mathematical group.
11. What are vanishing and non vanishing integrals?
12. Write the symmetry elements and determine the point groups of  $H_2O_2$  and allene

**(12x1=12 weightage)****Section B***(Answer any eight questions; each question carries 2 weights)*

13. Briefly explain the time independent perturbation method applicable to multi electron atoms.
14. Find the ground state energy for particle in 1D box ( $\hat{H} = \frac{-h^2}{8\pi^2m} \frac{d^2}{dx^2}$ ) using the trial function  $(x-a)$ ;  $x$  varies from 0 to  $a$
15. Write the STO for  $Cu^{29}$  atom
16. Write the Slater determinants for Li atom and prove that an AO can accommodate only two electrons with opposite spin.
17. Write the Huckel determinant of butadiene molecule. Obtain HMO coefficients and calculate  $\pi$  bond order.



18. What are self consist field orbitals?
19. Obtain the normalised functions of  $sp^2$  hybridisation.
20. Write a short note on Frost - Huckel circle mnemonic device for cyclic polyenes
21. Derive the reduction formula.

22. 
$$\begin{array}{c|cccc} C_{2v} & E & C_2 & \sigma_v & \sigma'_v \\ \hline \Gamma & 4 & 0 & 0 & 0 \end{array}$$

Split the above irreducible representation in to reducible representations of  $C_{2v}$  point group.

23. Using GOT obtain the reducible representations of  $C_{3v}$  point group.
24. Find MO's of  $H_2O$  molecule by group orbital method.

(8x2=16 weightage)

### Section C

(Answer any two questions; each question carries 4 weights)

25. Explain the variation treatment of many electron problem
26. Give the MO treatment of  $H_2^+$  molecule ion.
27. Find the normalised  $sp^3$  hybrid orbitals of C in  $CH_4$  molecule SALC method. Use  $T_d$  character table.
28. Predict allowed electronic transitions in  $H_2O$  molecule. Use  $C_{2v}$  character table.

$C_{2v}$	E					
	$C_2$	$\sigma_v$	$\sigma'_v$			
$A_1$	1	1	1		Z	$X^2, Y^2,$
$A_2$	1				$R_Z$	$Z^2$
$B_1$	1	1	-1	-1	X, $R_Y$	XY
$B_2$	1	-1	1	-1	Y,	X, $R_Y$
	1	-1	-1	1	$R_X$	Y, $R_X$

$T_d$	E						
	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$			
$A_1$	1	1	1	1	1		$X^2+Y^2+Z^2$
$A_2$	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2Z^2-X^2-Y^2, X^2-$
$T_1$	3	0	-1	1	-1	$R_X, R_Y,$	$Y^2)$
$T_2$	3	0	-1	-1	1	$R_Z$	
						(X, Y, Z)	(XY, XZ, YZ)

(2 x 4 = 8 weightage)