

M.Sc. 3rd Semester Examination, 2022

CHEMISTRY

*(Physical Special / Organic Special / Inorganic
Chemistry Special)*

PAPER – CEM-302

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

*Candidates are required to give their answers in their
own words as far as practicable*

(Physical Special)

GROUP—A

Answer any four questions of the following : 2 × 4

1. According to Huckel theory, the π -electron charge density on the central carbon atom of propyl anion is given by

- (a) 1
- (b) $\frac{1}{2}$
- (c) $\frac{1}{\sqrt{2}}$
- (d) $\frac{1}{3}$

2. A one dimensional Harmonic oscillator is subjected to a perturbation, $H' = cx^3$ (where 'C' is a const.). Find the 1st order correction to its n th state energy.
3. Write down the expression of second order correction to energy $E_n^{(2)}$ in first order non-degenerate perturbation theory.
4. The IR of C_{2h} are A_g , B_g , A_u and B_u . The Raman active modes of trans 1-3-butadiene belongs to the IR.
- (i) A_g & B_g
 - (ii) A_g & A_u
 - (iii) A_u & B_g
 - (iv) B_g & B_u

5. When a H-atom is subjected to a electrical perturbation along the z-direction. Which among the three p-orbitals ($2p_x, 2p_y, 2p_z$) are going to be affected due to perturbation.
6. Write down the reduction formula to be used to find out IR present in the reducible representation for a linear molecule.

GROUP-B

Answer any four questions of the following : 4×4

- 7 Use internal co-ordinate method to obtain the vibrational modes of CH_2Cl_2 . Explain your results.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	(x^2, y^2, z^2)
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	X, R_y	xz
B_2	1	-1	-1	1	Y, R_x	yz

8. Show that the set of ' n ' degenerate molecular orbital serve as a basis of the representation of an ' n ' dimensional IR of the point group.
9. Obtain the transformation matrix which transform the ' n ' dimensional base vectors $(e_1, e_2, e_3, \dots, e_n)$ into its prime set $(e_1', e_2', e_3', \dots, e_n')$.
10. Show that direct product matrix form a representation of the point group.
11. Deduce the expression of first order correction to wave function for time independ non-degenerate perturbation theory.
12. Find the matrix representation of J^2 operator for a state $j = \frac{3}{2}$.

GROUP-C

Answer any two questions of the following : 2×8

13. Deduce the expression of energy and wavefunctions for $n = 2$ state of state of H-atom, when it is placed in an electric field in the z-direction.

14. The Hamiltonian for a certain three level system is represented by the matrix,

$$H = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

and one of its observable, A is presented by the matrix,

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Find the eigen values and eigen vectors of H and A .

15. The Hamiltonian of a three level system is given by,

$$H_0 = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$$

After a small perturbation its Hamiltonian is given by,

$$H = \begin{pmatrix} E_1 & a & b \\ a^* & E_2 + d & 0 \\ b^* & 0 & E_3 \end{pmatrix}$$

Find its first order and second order correction to energy eigen values.

16. Obtain the symmetry of the splitting of d-orbital of a transition metal ion when it is placed in an octahedral ligand field.

Given,

0	E	6C ₄	3C ₂ '	8C ₃	6C ₂	
A ₁	1	1	1	1	1	x ² + y ² + z ²
A ₂	1	-1	1	1	-1	
E	2	0	2	-1	0	(2z ² - x ² - y ² , x ² - y ²)
T ₁	3	1	-1	0	-1	(x, y, z) (R _x , R _y , R _z)
T ₂	3	-1	-1	0	1	(xy, yz, zx)

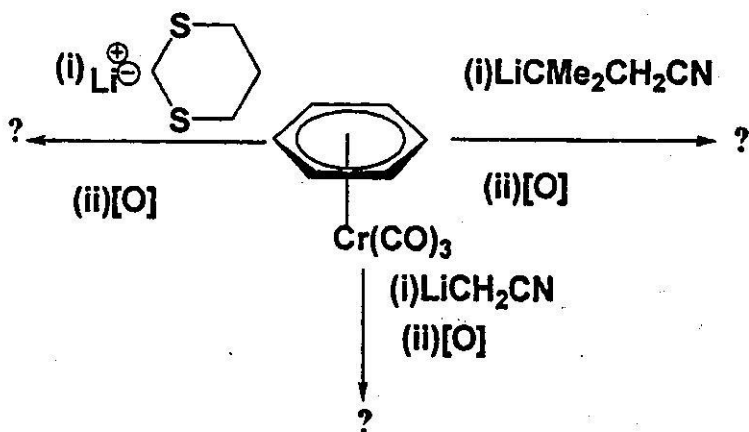
(Organic Special)

GROUP-A

Answer any four questions : 2 × 4

1. Examine using PMO method whether suprafacial-suprafacial [3, 3] sigmatropic rearrangements are thermally allowed or photochemically allowed.
2. Give an example each of [9, 9] and [5, 5] sigmatropic rearrangements.
3. What were the reasons for choosing the ionizations of meta- and para-substituted benzoic acids as reference reactions by Hammett?
4. What happens when chromium tricarbonyl complex of fluorobenzene is treated with *n*-butyl lithium followed by γ -butyrolactone?

5. Compare the reactivity of p-chlorobenzyl chloride with that of benzyl chloride in 50% acetone at 60° C toward hydrolysis reaction. Given : σ_p value for $-Cl = +0.23$ and the ρ value of the hydrolysis reaction of benzyl chlorides under the given condition is -1.70 .
6. Identify the products of the following reactions :

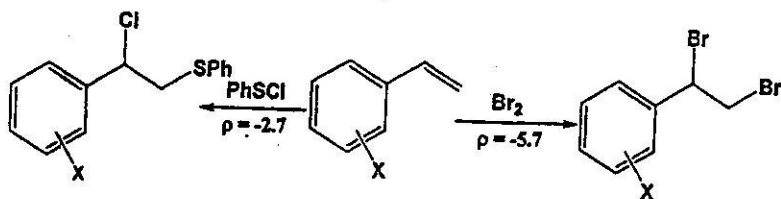


GROUP-B

Answer any four questions :

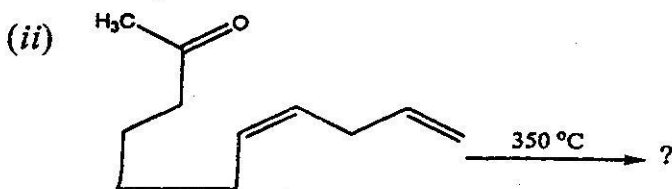
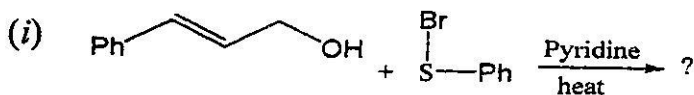
7. Discuss the nature of Hammett plots for the acetolysis of 3-aryl-2-butyl brosylates. 4

8. How will you account for the Hammett ρ values in the following reactions : 4



9. Draw the structure of Nysted reagent. How is it synthesized? Discuss the synthetic utility of this reagent. 1 + 1 + 2

10. Predict the products of the following reactions with plausible mechanism : 2 + 2



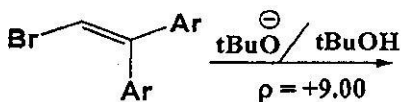
11. State and explain the Grunwald-Winstein equation. In this context discuss the significance of the compound parameter "m" ? 2 + 2
12. What happens when arylidene derivatives resulting from condensation of tricarbonyl complex of benzosuberone with aromatic aldehydes is treated with ethyl acetoacetate in presence of base ? Illustrate your answer with suitable reaction mechanism. 4

GROUP—C

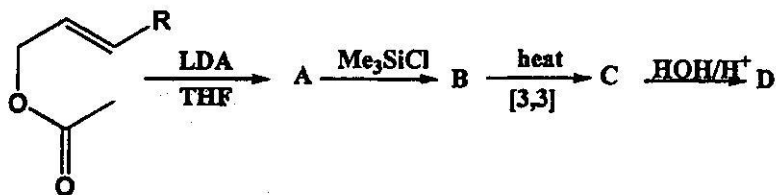
Answer any two questions : 8 × 2

13. (a) Discuss the effect of solvent on the Hammett reaction constant (ρ). 2
- (b) How will you account for the observation that alkaline hydrolysis of ethyl esters of benzoic acids (ArCOOEt) has a ρ value of +2.6 while the hydrolysis of the same esters in acid solution, has a ρ value of +0.1 ? 4

- (c) How will you ascertain the reaction mechanism of the following reaction from the Hammett ρ value? 2



14. (a) Discuss the stereochemistry of Cope rearrangement. 2
- (b) Identify the products A, B, C and D for the following reaction. 2



- (c) What do you mean by Modified and Degenerate Cope Rearrangements? Explain with suitable examples. What are the essential conditions for a 1,5-diene substructure to undergo Cope Rearrangement? 3 + 1

15. What is Sonogashira coupling? What are the drawbacks of using copper salts as cocatalysts in the typical Sonogashira protocol? Draw the proposed catalytic cycle for copper free Sonogashira coupling. In this context also suggest a suitable strategy for the synthesis of 2-substituted benzofurans from *ortho*-iodophenol? 2 + 2 + 2 + 2
16. (a) Write down Taft's equation and explain the terms involved in it. Discuss the practical applicability and drawbacks of this equation. 4
- (b) Draw the catalytic cycle for Suzuki reaction and discuss the role of base in this reaction. 4

(Inorganic Chemistry Special)

GROUP—A

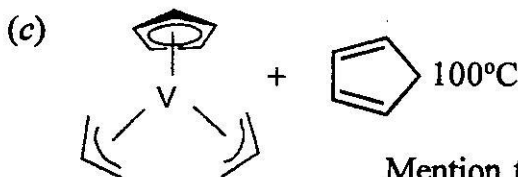
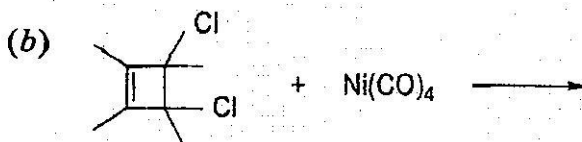
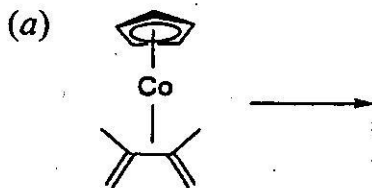
Answer any four questions :

2 × 4

GROUP-A(a)

1. Complete the following reactions (any two):

2 × 2



Mention the TVE count of this compound

GROUP-A(b)

Answer any two questions:

4 × 2

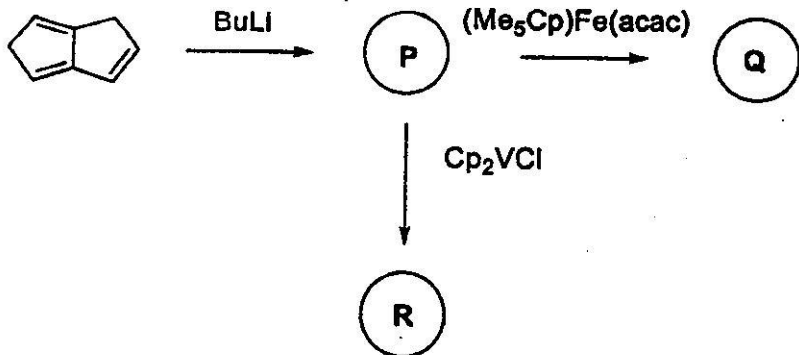
2. Complete the following reactions:



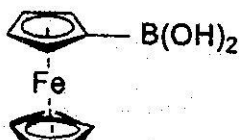
Draw the structure of this compound and mention the oxidation states of 'Re' centres.

3. Identify 'P', 'Q', and 'R' and draw the structures.

4



Mention the hapticity of the ligands in this compound

4. How  could be synthesized from ferrocene?

Which compound is formed when ferrocene is reacted with POCl_3 in DMF? What is Oxidative Coupling reaction? (1 + 1) + 2

GROUP—A(c)

Answer any one of the following questions : 8×1

5. (a) How oxidative addition reaction differs from a simple addition reaction?
- (b) Write down the reaction steps involved in the Wacker process. Mention the net reaction also.
- (c) Write down the catalytic cycle for hydrogenation using Mark's catalyst. 2 + 2 + 4
6. (a) Briefly discuss the kinetic aspects of the Monsanto process.
- (b) Mention the problems associated with the Monsanto process.

- (c) Write down the catalytic cycle for Monsanto acetic acid process. $2 + 2 + 4$

GROUP-B(a)

7. Answer any *two* of the following questions : 2×2

(a) Why do you configurations d^n and d^{10-n} give identical ligand field terms in any given field symmetry ?

(b) Using group theory how can you explain the intensity of colour of the following complex ions :

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$: light pink

$[\text{CoCl}_4]^{2-}$: deep blue

(c) Using group theory how can you explain the allowedness of d-d transitions in octahedral complexes ?

GROUP-B(b)

Answer any two of the following questions : 4×2

8. Use group theoretical principle to obtain the splitting of d -orbitals of Ni(II) ion in $[\text{Ni}(\text{CN})_4]^{2-}$ anion. (Given below the character table for rotational subgroup D_4).

4

D_4	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1	z, R_z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1		$x^2 - y^2$
B_1	1	-1	1	1	-1		xy
B_2	1	-1	1	-1	1		(xz, yz)
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	

9. What do you mean by "exclusion rule"? Show that this rule is applicable for $trans\text{-N}_2\text{F}_2$ molecule. (Given below the character table for C_{2h} point group).

1 + 3

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

10. Using group theoretical principle construct a qualitative σ -bonding molecular orbital energy level diagram for H_2O molecule. (Given below the character table for C_{2v} point group). 4

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

GROUP-B(c)

Answer any one of the following questions : 8×1

11. For $[\text{Co}(\text{NH}_3)_6]^{3+}$, the ground electronic state belongs to ${}^1A_{1g}$ representation and two excited states belong to ${}^1T_{1g}$ and ${}^1T_{2g}$ representations. Show that pure electronic transitions from the ground state to these excited states are not

allowed, but the transitions are vibronically allowed. (Given below the character table for O_h point group).

3 + 5

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		$(2z^2 - x^2 - y^2, x^2 - y^2)$
E_g	2	-1	0	0	2	2	0	-1	2	0		
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

12. With the help of group theory determine the symmetries of the group of orbitals of F atoms which are effective for σ -bond formation in BF_3 molecule. Write appropriate SALCs for these symmetries. Construct a qualitative σ -bonding molecular orbitals energy level diagram for BF_3 and from this energy level diagram comment about the Lewis acid character of BF_3 molecule.

(Given below the character table for D_{3h} point group).

$$3 + 2 + 2 + 1$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)