

M.Sc. 3rd Semester Examination, 2023

CHEMISTRY

PAPER—CEM-302

Full Marks : 50

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

(Organic Special)

1. Answer any *four* questions : 2 × 4

(a) What do you mean by working and auxiliary ligands ? Explain with a suitable example.

(b) What is Glaser coupling ?

(Turn Over)

- (c) Give an example of [5, 5] sigmatropic rearrangement.
- (d) Examine using PMO method whether suprafacial and antarafacial [1, 5] sigmatropic rearrangements are thermally or photochemically allowed.
- (e) Why the ionizations of meta- and para-substituted benzoic acids were taken as reference reactions by Hammett ?
- (f) State the significance of Hammett reaction constant (ρ).

2. Answer any *four* questions : 4 × 4

- (a) State the Grunwald-Winstein equation and explain the terms involved in it. In this context also discuss the significance of the compound parameter 'm' ?

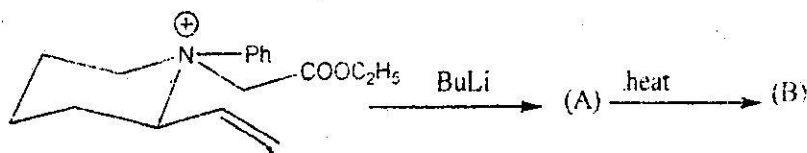
(b) Why Hammett equation is called a linear free energy relationship? Show quantitatively that *p*-nitrophenyl acetic acid is 2.4 times more acidic than phenyl acetic acid. Given: σ_p for $-\text{NO}_2$ group = +0.78; ρ for the ionization of $\text{H}-\text{C}_6\text{H}_4\text{CH}_2\text{COOH} = +0.49$.

(c) What is Tebbe's reagent? How is it prepared? What is it used for?

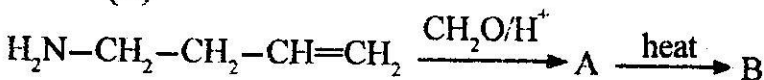
(d) What is Stille reaction? Draw the catalytic cycle for this coupling reaction.

(e) Predict the products with plausible mechanism:

(i)



(ii)



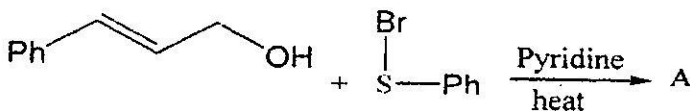
(f) Discuss the Woodward Hoffmann rules for [3, 3] sigmatropic rearrangement.

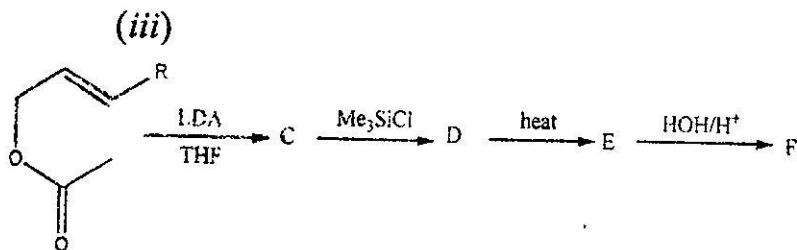
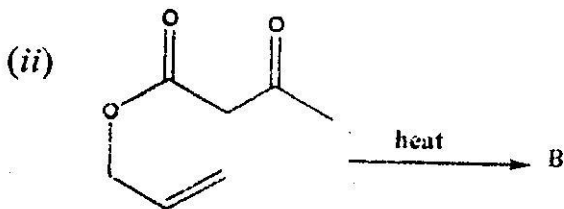
3. Answer any *two* questions : 8 × 2

(a) What is Sonogashira coupling ? What are the drawbacks of using copper co-catalyst in this reaction ? Draw the catalytic cycle for the so-called "copper free" Sonogashira coupling. How will you prepare 2-substituted benzofuran starting from o-iodo phenol ? 2+1+2+3

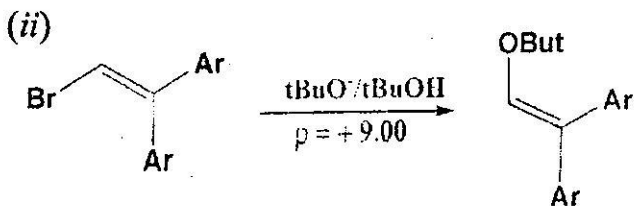
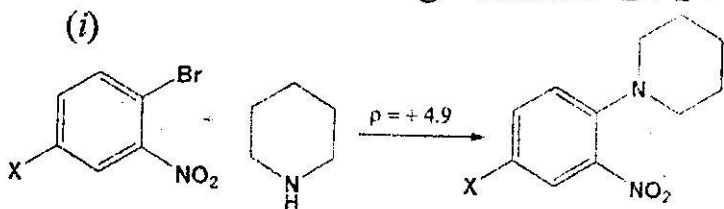
(b) Predict the products of the following reactions with plausible mechanism : 2+2+4

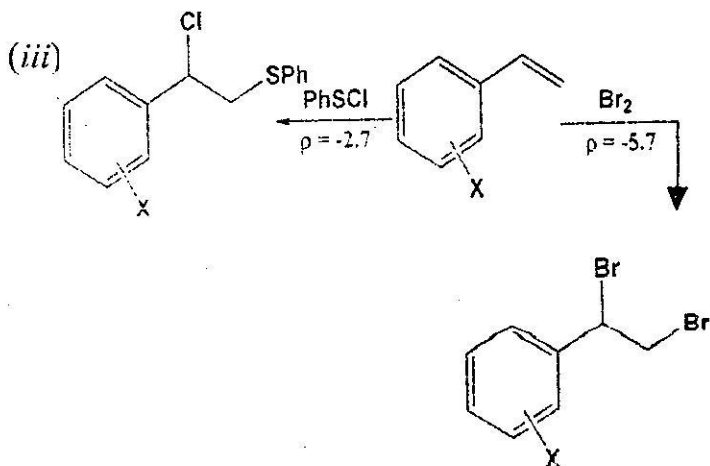
(i)





(c) How will account you for the observed ρ values for the following reactions : 2 + 2 + 4





- (d) (i) Discuss how the ρ value helps us to understand the mechanism of hydrolysis of meta and para substituted methyl and ethyl benzoates in 99.9% H₂SO₄. 5
- (ii) What do you mean by "chelation control" in Heck reaction? Explain with an example. 3

(Inorganic Special)

GROUP – A(a)

Answer any two from the following : 2×2

1. What do you mean by "vibronic polarization" ?
2. Using group theory principles explain the allowedness of d-d electronic transitions in octahedral complexes.
3. Explain why the intensity of $A_2 \rightarrow T_2$ transition around 100 times less than the intensity of $A_2 \rightarrow T_1$ transition in $[\text{CoCl}_4]^{2-}$ anion. Given below the character table for T_d point group.

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	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z) (xz, yz, xy)

GROUP – A(b)

Answer any two from the following : 4×2

4. With the help of group theory determine the symmetries of possible combinations of atomic orbitals of oxygen atoms which are effective for π -bond formation in nitrite anion. Find out the appropriate SALC for these symmetries. Construct qualitative π -molecular orbital energy level diagram for the nitrite anion.

2 + 1 + 1

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

5. With the help of group theory determine the symmetry of vibrational modes of *fac*- $[ML_3X_3]$ molecule using Cartesian coordinate method.

Identify the symmetries of IR and Raman active modes. (Given below the character table for C_{3v}).

3 + 1

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

6. What do you mean by "exclusion rule"? Show that this rule is applicable for *trans*- N_2F_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	

GROUP – A(c)

Answer any **one** from the following : 8×1

7. Construct a correlation diagram for an octahedral coordination compound with d^2 electronic configuration. (Given below the character table for O_h point group).

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_2'$)	i	$6S_6$	$8S_6$	$3C_2$	$6C_4$		
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		(x, y, z)
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		

8. For $trans$ - $[Co(NH_3)_4Cl_2]$ complex the ground state is ${}^1A_{1g}$ and possible excited singlet electronic states are ${}^1A_{2g}$ 1E_g and

${}^1B_{2g}$. Show that pure electronic transitions are forbidden. Determine the vibronically allowed transitions and also find out the effect of polarization of incident radiation on these transitions. (Given that the symmetries of normal modes of vibrations are $2A_{1g}$, B_{1g} , B_{2g} , E_g , $2A_{2u}$, B_{2u} , $3E_u$ for this compound).

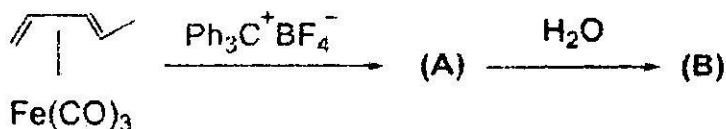
3 + 3 + 2

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		(xz, yz)
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	z	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

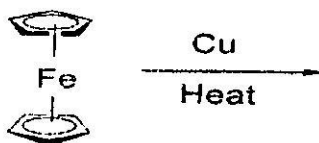
GROUP – B(a)

Answer any two from the following : 2×2

9. Identify (A) and (B) in the following reaction scheme :



10. Complete the following reaction :



11. Write the general formula of four major types of mononuclear cyclopentadienyl complexes and draw their structure.

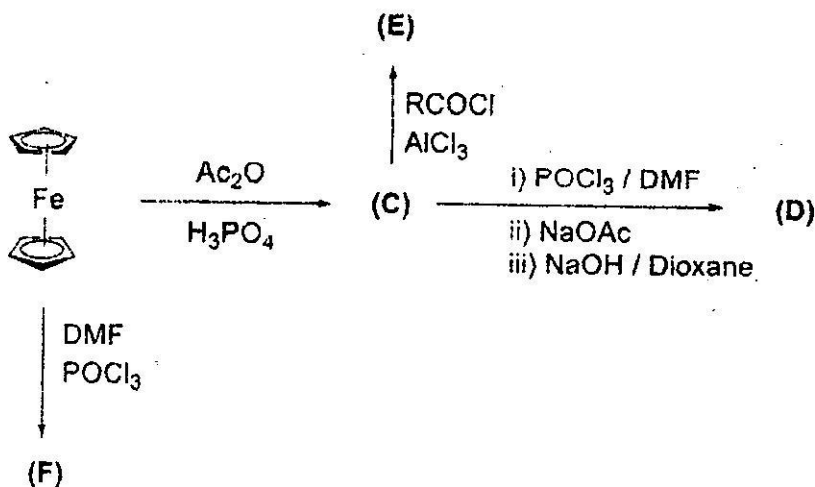
GROUP – B(b)

Answer any two from the following : 4×2

12. (a) What happens when two molecules of Cp_2Ti react with each other ?

- (b) Write down the products formed in the case of the Cp^*_2Ti complex for a similar reaction. 2 + 2

13. Write down the products : (C) to (F). 4



14. (a) Write the products when $[(\text{Cp})\text{Fe}(\text{C}_6\text{H}_6)]^+$ reacts with Na-Hg , DME and NaBH_4 separately.

- (b) What happens when $\text{Cr}(\text{g})$ is reacted with $\text{C}_6\text{H}_3\text{Me}_3(\text{g})$? Write the structure and the TVE of the product. 2 + 2

GROUP – B(c)

Answer any **one** from the following : 8 × 1

15. (a) Mention the essential requirements for the oxidative addition reaction and discuss the stereochemistry regarding this reaction. 2 + 2
- (b) Draw the catalytic cycle for the hydroformylation reaction using $\text{HCo}(\text{CO})_4$ as the catalyst. Mention the formation of the said catalyst from $\text{Co}(\text{CO})_4$ in the scheme. 4
16. (a) Write the structure of the following hydrogenation catalysts : 2 + 2
- Schrock Osborn's catalyst and Mark's catalyst.
- Mention the oxidation state of the metal ions in the complexes.

- (b) Draw the catalytic cycle for the oxidation of ethylene to acetaldehyde by Wacker's process.

4

(Physical Special)

GROUP - A

Answer any four questions from the following :

2×4

1. Number of nodes present in the 1st excited state of π -MO of butadiene is
 - (a) 1
 - (b) 2
 - (c) 3
 - (d) 4
2. What do you mean by π -electron charge density on any atom for a conjugated system ?

3. Write down the standard reduction formula to obtain the irreducible representation from a reducible representation for a linear molecule.
4. Write down the Huckel approximation to solve the π -MO for conjugated polyene.
5. A three levels perturbed system is described by Hamiltonian,

$$H = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 6 \end{pmatrix}$$

Write down the energies and wave functions of the system.

6. Evaluate the commutator, $[J_+, J_-]$

GROUP - B

Answer any **four** questions from the following :

4 × 4

7. Use $\phi = C_1 x(x-1) + C_2 x^2(x-1)^2$ as the trial

wave function for the ground state of a particle having mass 'm' in 1-D box problem. Hence obtain its ground state energy using the Variational principle. Comment on your result.

8. Use group theoretical principle to obtain the state of hybridization of central atom of NH_3 .

Character Table for C_{3v}

A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	R	
E	2	-1	0		$(x^2 - y^2, xy) (xz, yz)$

9. A two-level unperturbed system is described by the following Hamiltonian

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$$

Now a small perturbation represented by $V = \begin{pmatrix} a & c \\ c & b \end{pmatrix}$ is switched on. Obtain the first order correction to its energy eigen values.

10. Symmetries of the vibrational modes of H_2O is A_1 and B_2 . Find whether the above modes are IR active or not.

Character table for C_{2v} point group

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
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

11. Use Huckel approximation to obtain the energies of the π MOs for butadiene system.

12. Matrix representation of the Hamiltonian of a system is the following,

$$H_0 = \begin{pmatrix} 2 & 1 \\ 0 & -1 \end{pmatrix}$$

Obtain the energy eigen values and the eigen vectors of the system.

GROUP – C

Answer any two questions of the following :

8×2

13. Use Huckel theory to obtain the energy and wavefunctions for allyl radical system.
14. The $n = 1 \rightarrow n = 2$ spectral transition line of hydrogen atom split into three well separated lines in presence of an external electric field. Use degenerate perturbation theory to explain the above splitting of spectral line.

15. Use group theoretical principle to obtain the state of hybridization of central atom of $[\text{PtCl}_4]^{2-}$

Character table for D_{4h} point group

	E	$2C_4(z)$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
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	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

16. Use both 3N Cartesian coordinate and Internal coordinate method to obtain the symmetry of the vibrational modes of ML_5 (square pyramid). Comment on your result

Character table of C_{4v} point group is given below.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

[Internal Assessment — 10 Marks]