PG/IIIS/CEM/302/24

M.Sc. 3rd Semester Examination, 2024

CHEMISTRY

PAPER – CEM-302

Full Marks : 50

Time : 2 hours

Answer **all** questions

The figures in the right hand margin indicate marks

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

(Phy. Spl.)

GROUP – A

Answer any **four** questions of the following : 2×4

1. An electron in a hydrogen atom is exposed to a perturbation, $V = V_0 \cos\theta$. Find the first order correction to the ground state energy of the electron.

2. IR active vibrational modes of methane belong to the irreducible representation,
(*a*) $E + A_1$; (*b*) $E + A_2$; (*c*) T_1; (*d*) T_2.
Justify your answer

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)	(xy, xz, yz)

3. The irreducible representation of C_{2h} are A_g, B_g, A_u, B_u. Find the symmetry of the Raman active modes of trans-1,3-butadiene.

4. The matrix representation of Hamiltonian of a two-level system is given by,

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

Write down the expression of energy and eigen ket of each state.

5. Write down the steps involved in determining the vibrational modes of a nonlinear molecule.

6. Which of the following represents the charge density of the central carbon atom of Allyl cation.
(*a*) 0.5; (*b*) 1.0; (*c*) 0.25; (*d*) 0.708.
Justify your answer

GROUP – B

Answer any **four** questions of the following : 4×4

7. Use internal coordinate as base vector to obtain the vibrational mode of CH_2Cl_2. Justify your result.

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. Symmetry of the vibrational modes of NH_3 is, $\Gamma_{vib} = 2A_1 + 2E$. Find, whether the above modes are Raman active or not.
Character table of C_{3v} point group is given below.

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
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)

9. Find the matrix representation of J_z and J^2 operators for an electron having total angular momentum, J = 1.

10. Imagine a system contains two linearly independent kets, $|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.
The specific form of the Hamiltonian is,
$H = \begin{pmatrix} h & g \\ g & h \end{pmatrix}$, where g and h are real constant.

If the system starts at $t = 0$ in state, $|1>$ then find the state of the system at time, t.

11. Matrix representation of the Hamiltonian of a system is given by, $H = \begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}$. Find the eigen values and the corresponding eigen vectors of the system.

12. Obtain the matrix representation of the eigen kets of J_z of an electron whose total angular momentum, $J = 1/2$. Also justify that the eigen ket matrices represent the α and β spin of the electron.

GROUP – C

Answer any **two** questions of the following : 8×2

13. What is Zeeman effect ? Use degenerate perturbation theory to explain the splitting of $np \rightarrow nd$ transition of electron in an atom in presence of an external magnetic field, B_0.

14. 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 the first and second order correction of energy to each level.

15. Consider a π-conjugated linear polyene containing N number of carbon atom and hence deduce the following general expression for its π-MO energy and coefficient of atomic orbitals to form π-MO.

$$E_k = \alpha + 2\beta\cos\left(\frac{k\pi}{N+1}\right); \text{ and } C_{km} = D_k \sin\left(\frac{mk\pi}{N+1}\right)$$

(Symbols have their usual significances)
Deduce the π-MO as LCAO and their energies for allyl radical using the above expressions.

16. Use group theoretical principle to obtain the state of hybridization of central atom of $[PtCl_4]^{2-}$. Also find the hybrid orbitals as the linear combination of atomic orbitals.

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)	

[Internal Assessment — 10 Marks]

(Inorganic Chemistry Special)

GROUP – A(a)

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

1. Why do the configurations 'd^n' and 'd^{10-n}' give identical ligand field terms in any given field symmetry ?

2. Write the all possible term symbols for 'd^2' electronic configuration. How these terms will split in presence of tetrahedral crystal field ?

3. Using group theory how can you explain the intensity of colour of the following complex ions :

   $[Co(H_2O)_6]^{2+}$: light pink

   $[CoCl_4)^{2-}$: deep blue

GROUP – A(b)

Answer any **two** questions of the following : 4×2

4. With the help of group theory determine the symmetrics of the group of orbitals of H-atoms which are effective for the σ-bond formation in H_2O molecule. Construct a qualitative molecular orbital energy level diagram for this molecule.

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 symmetrics of vibrational modes of cis-$[ML_4X_2]$ molecule using Cartesian coordinate method. Identify the symmetrics of IR and Raman active modes in this molecule.

6. Determine the symmetries of the group of orbitals of F atoms which are effective for σ-bond formation in PF_5 molecule. Write the appropriate SALCs for these symmetries. Construct a qualitative σ-bonding molecular orbital energy level diagram for PF_5 molecule. (Given below the character table for D_{3h} point group).

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)

GROUP – A(c)

Answer any **one** question of the following : 8×1

7. (*a*) Establish the relation

(*Continued*)

$$\chi(\alpha) = \frac{\sin\left(l+\frac{1}{2}\right)\alpha}{\sin\left(\frac{\alpha}{2}\right)} \quad (\alpha \neq 0)$$

where the terms have usual significance.

(*b*) Use group theoretical principal to obtain the splitting of d-orbitals of Pt(II) in $[PtCl_4]^{2-}$ anion. (Given below the character table for D_4).

D_4	E	$2C_4$	$C_2\ (=C_4^2)$	$2C'_2$	$2C''_2$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	−1	−1	z, 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)

8. With the help of group theory determine the symmetrics of possible combinations of atomic orbitals of carbon atoms which are effective for π-bond formation in cyclobuta-

diene. Using projection operator method find out the appropriate SALCs for these symmetries. Construct qualitative π-molecular orbital energy level diagram for cyclobutadiene molecule and explain why it is an extremely unstable molecule.

Although cyclobutadiene is unstable, (cyclobutadiene) $Fe(CO)_3$ is a stable molecule-explain. (Given below character table and correlation table). 5 + 3

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		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)	

Correlation table

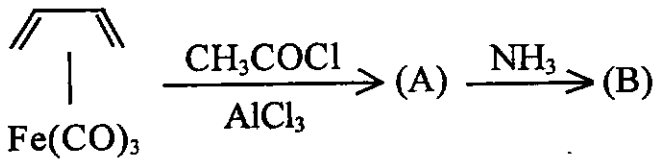
D_{4h}	C_{4v}
A_{2u}	A_1
B_{2u}	B_1
E_g	E

(*Continued*)

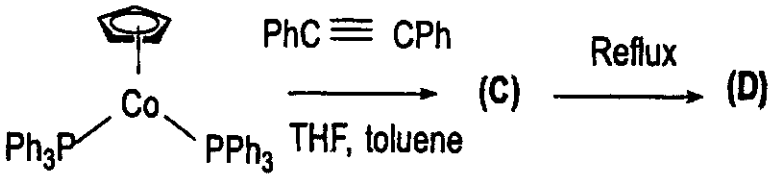
GROUP – B(a)

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

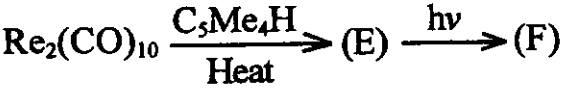
9. Complete the following reaction :



10. Identify 'C' and 'D' in the following reaction :



11. Complete the following reaction :



GROUP – B(b)

Answer any **two** questions of the following : 4×2

12. (*a*) What happens when $Cp_2W(CO)$ uptakes CO ? Discuss the phenomenon.

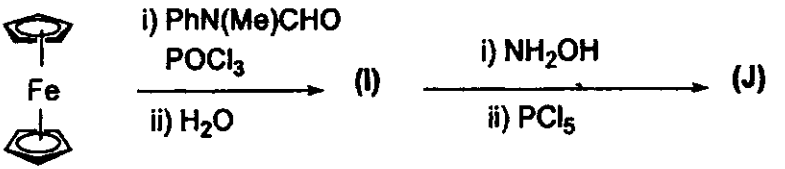
(*b*) Which product is formed when 'borole' is heated with $[Co_2(CO)_8]$ at 60° C in hexane ? Which product is obtained on further heating (160° C) ? $2 + 2$

13. Identify the product in the following reactions : $2 + 2$

(*a*)

$$Cp_2NbCl_5 \xrightarrow[-78°C]{\text{Napthyl Sodium}} (G) \xrightarrow[-50°C]{} (H)$$

(*b*)



14. Complete the following reaction and write the probable structure of 'L'. Mention the oxidation state of 'Re' in the complex 'L'.

$$[(C_6Me_6)_2Re]\ PF_6 \xrightarrow[200^\circ C]{Li(l)} (K) \xrightarrow{Room\ Temp.} (L)$$

GROUP – B(c)

Answer any **one** question of the following : 8×1

15. (*a*) Briefly discuss any two of the 'Insertion reaction', 'β-hydride elimination reaction' and 'alkene isomerization' reaction. 2 + 2

(*b*) Write the catalytic cycle for 'Monsanto acetic acid process'. 4

16. (*a*) Write a short note on 'Oxidative coupling reaction'.

(*b*) What is an 'Orthometallation reaction' ? Give example.

(*c*) Draw the catalytic cycle for hydrogenation using 'Mark's catalyst' ? 2 + 2 + 4

[Internal Assessment — 10 Marks]

(Organic Special)

GROUP – A

Answer any **four** questions : 2×4

1. What is Johnon-Claisen rearrangement ? Explain with a suitable example.

2. Distinguish between Fischer and Schrok carbenes.

3. Give an example each of [9,9] and [4,5] sigmatropic rearrangements.

4. Write down the Yukawa-Tsuno equation and explain the terms involved in it.

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. Discuss the effect of change in solvent polarity on Hammett reaction constant (ρ).

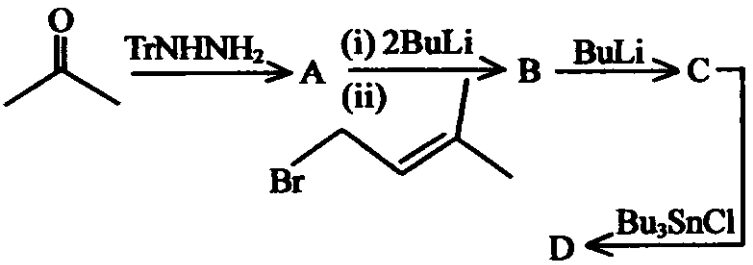
GROUP – B

Answer any **four** questions : 4×4

7. What is Petasis reagent ? How is it synthesized ? Discuss the synthetic utility of this reagent. 1 + 1 + 2

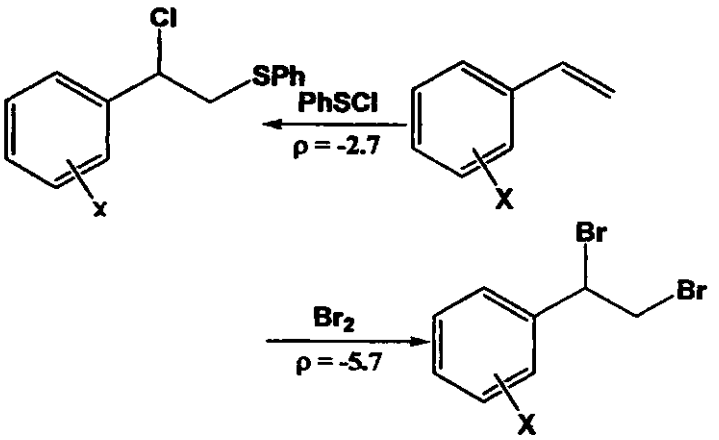
8. Using both FMO and PMO approach show that suprafacial [1,5] sigmatropic rearrangements are thermally allowed.

9. Predict the products of the following reactions with plausible mechanism and describe the stereochemistry of the product (if applicable) :



10. Draw the catalytic cycle for the Suzuki reaction. Discuss the role of base in this reaction.

11. How will you account for the Hammett ρ values in the following reactions ?



12. What is ene reaction ? Why ene reactions take place at higher temperatures compared to Diels-Alder reaction ? Using FMO approach show that thermal ene reactions are symmetry allowed.

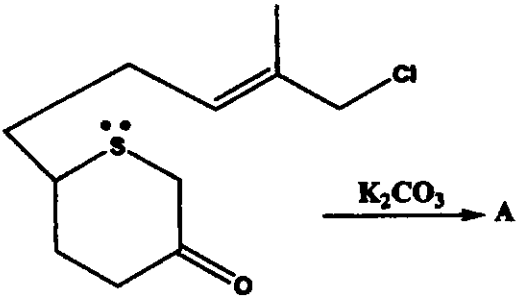
GROUP – C

Answer any **two** questions : 8×2

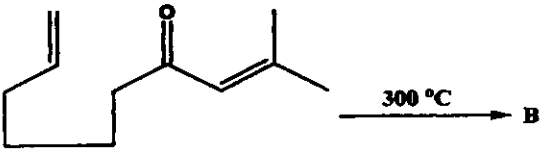
13. State the reasons for the popularity of the palladium complexes in organic synthesis. Draw the catalytic cycle for Heck reaction. Discuss the regioselectivity of Heck reaction with respect to electron donating and electron attracting substituents. $3 + 2 + 3$

14. Predict the product(s) of the following reactions with plausible mechanism : 2×4

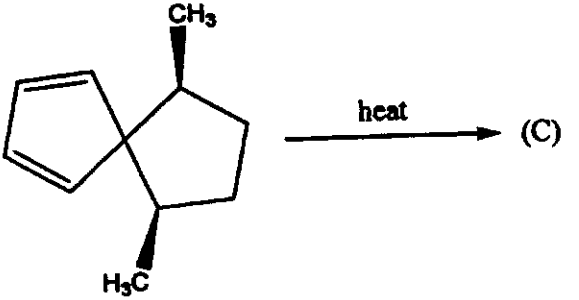
(*i*)



(*ii*)



(*iii*)



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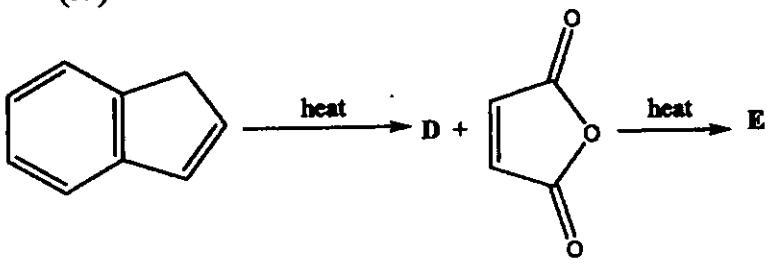
(*iv*)



15. (*i*) How will you account for the observation that alkaline hydrolysis of ethylesters 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 ?

(*ii*) Discuss the nature of Hammett plots for the acetolysis of 3-aryl-2-butyl brosylates. 4 + 4

16. (*i*) Draw the catalytic cycle for Buchwald-Hartwig amination. Discuss the advantages and drawbacks of this reaction. How Buchwald has diverged from Hartwig subsequently for this type of reactions ? 5

(*ii*) Write down Taft's equation and explain the terms involved in it. Discuss the drawbacks of this equation. 3

[Internal Assessment — 10 Marks]
