2025

M.Sc. 3rd Semester Examination

CHEMISTRY

Paper : CEM - 302

Full Marks : 50 Time : Two Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

(Advance Physical Chemistry-I)

Group - A

Answer any ***four*** questions : 2×4=8

1. An external perturbation, $H' = bx^3$ (where b is a constant) is applied to a linear Harmonic Oscillator. Find the first order correction of energy to its ground state.

2. $S_2(Z)$ operation on a molecule with the axis of rotation as the Z-axis moves a nucleus at (X, Y, Z) to,

   (a) $(-X, -Y, Z)$;

   (b) $(X, -Y, -Z)$;

   (c) $(-X, Y, -Z)$;

   (d) $(-X, -Y, -Z)$.

   Justify your answer.

P.T.O.

3. Write down the steps involved in determining the vibrational modes of a linear molecule using integration method.

4. What is intermediate normalization? Show that, $\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle = 0$; (symbols have their usual significances).

5. The matrix representation of Hamiltonian of a three-level system is given by $H = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$; write down the matrix form of eigen Kets and the corresponding eigen- values of the system.

6. Use Hückel approximation of π-MO and hence obtain the matrix form of the Secular equations for butadiene.

Group - B

Answer any ***four*** questions : 4×4=16

7. Use 3N cartesian coordinate as base vector to obtain the symmetry of the vibrational mode of NH_3.

   (Character table of the required point group is given at the end of the question paper)

8. Symmetry of the vibrational modes of H_2O is, $\Gamma_{vib} = 2A_1 + B_2$. Find, whether the above modes are Raman active or not.

   (Character table of the required point group is given at the end of the question paper).

9. Find the matrix representation of J_z and J^2 operators for an electron having total angular momentum quantum number, $J = 3/2$.

10. Use internal coordinate as base vectors to obtain the symmetry of the vibrational modes of ClF_3 (T-shaped).

    (Character table of the required point group is given at the end of the question paper).

11. Matrix representation of the Hamiltonian of a system is given by, $H = \begin{pmatrix} 2 & 1 \\ 0 & -1 \end{pmatrix}$. Find the eigenvalues and the corresponding eigen vectors of the system.

12. Coefficient matrix of the π-MO of allyl radical is given by,

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & -\frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}$$

    Obtain the total electron charge density on each of the carbon atom of the allyl radical.

P.T.O.

Group - C

Answer any *two* questions : 8×2=16

13. Use degenerate perturbation theory to obtain the splitting of $n = 2$ state of H-atom in presence of an external electrical perturbation, $H' = e.E.Z$ (symbols have their usual significances)

14. The Hamiltonian of a two-level system is given by,

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 4 \end{pmatrix}.$$

A small perturbation is switched on and the matrix form of the perturbation is given by, $V = \begin{pmatrix} a & c \\ c & b \end{pmatrix}$.

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

15. Ground and the excited state of a two-level system is described by $|n>$ and $|k>$ respectively. An oscillatory perturbation, $H' = V\cos(\omega t)$ is applied to the system. Deduce the expression of transition probability $\left(P^{(1)}_{n\to k}\right)$ from state $|n>$ to $|k>$. Justify the idea of induced absorption and induced emission from the above derived expression.

16. Use group theoretical principle to obtain the state of hybridization of central atom in CH_4.

(Character table of the required point group is given at the end of the question paper)

List of Character Tables :

(i)

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		
T_2	3	0	−1	−1	1	(R_x, R_y, R_z) (x, y, z)	(xz, yz, xy)

(ii)

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

P.T.O.

(iii)

	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	$(x,y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

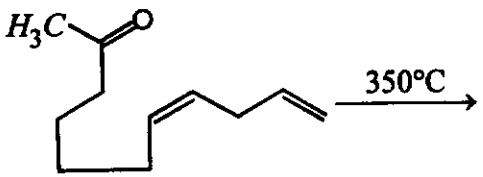
Internal Assessment : 10 marks

(Advanced Organic Chemistry-I)

Group - A

Answer any ***four*** questions : 2×4=8

1. Why Hammett equation is called a linear free energy relationship?
2. Give an example of [9, 9] sigmatropic rearrangement.
3. What were the reasons for choosing the ionizations of meta- and para- substituted benzoic acids as reference reactions by Hammett?
4. What is Tebbe's reagent? What is it used for?
5. Show quantitatively that *p*-nitrophenyl acetic acid is 2.4 times more acidic than phenyl acetic acid. Given : σ_p for $-NO_2$ group = + 0.78; ρ for the ionization of $H-C_6H_4CH_2COOH = +0.49$.
6. Identify the product(s) of the following reaction.



P.T.O.

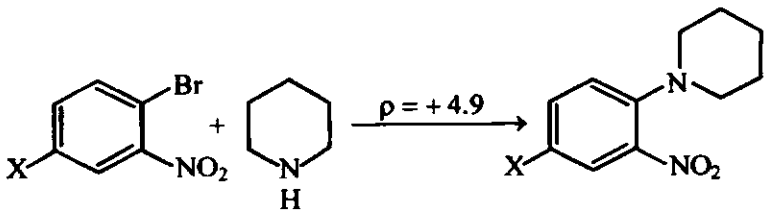
Group - B

Answer any *four* questions : 4×4=16

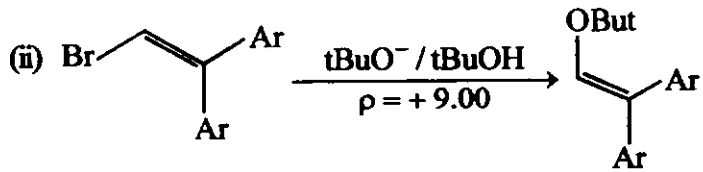
7. State the Grunwald-Winstein equation and explain the terms involved in it. In this context also discuss the significance of the compound parameter *m*.

8. What will you account for the Hammett ρ values in the following reactions?

(i)



(ii)

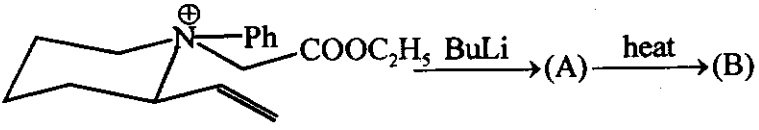


2+2

9. What is Negeshi coupling? Draw the catalytic cycle for Negishi coupling reaction and mention the various steps involved in it. 1+3

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

(i)



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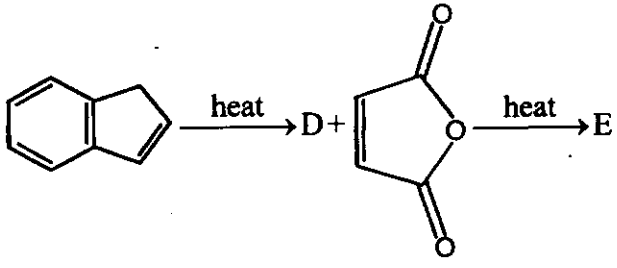


2+2

11. What is Shapiro reaction? Explain with a proper example. Illustrate your answer with suitable mechanism. Comment on the stereoselectivity and regioselectivity of the product(s) formed in Shapiro reaction. 3+1

12. How does ene reaction differ from cycloaddition reaction? Using FMO approach show that thermal ene reactions are symmetry allowed.

Group - C

Answer any *two* questions : 8×2=16

13. (a) Draw the two catalytic cycles for copper catalyzed Sonogashira coupling. What are the drawbacks of using copper as cocatalyst in this reaction?

P.T.O.

(b) How will you prepare 2-substituted benzofuran starting from o-iodophenol? (3+2)+3

14. (a) Examine using PMO approach whether suprafacial and antarafacial [1,5] sigmatropic rearrangements are thermally or photochemically allowed.

(b) 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? 4+(3+1)

15. What do you mean by substituent constant (σ) and reaction constant (ρ) in Hammett equation? Discuss the significance of the Hammett (ρ) values. Give an example of an equation with a small Hammett (ρ) value. How will you ascertain the mechanism of hydrolysis of benzoyl chloride in water using Hammett (ρ) value? 2+2+2+2

16. (a) 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% H_2SO_4.

(b) What is Stille reaction? Draw the catalytic cycle for Stille reaction. 5+3

Internal Assessment : 10 marks

(Advanced Inorganic Chemistry-I)

Group - A (a)

Answer any *two* questions : 2×2=4

1. Explain why the intensity of $A_2 \rightarrow T_2$ electronic transition is around 100 times less than the intensity of $A_2 \rightarrow T_1$ electronic transition in $[CoC_4]^{2-}$ 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		
T_2	3	0	−1	−1	1	(R_x, R_y, R_z) (x, y, z)	(xz, yz, xy)

2. What do you mean by "vibronic polarization"?

3. Though pure *d-d* electronic transitions are symmetry forbidden, most of the coordination compounds exhibit characteristic *d-d* electronic spectral bands. Explain the observation using group theoretical principal.

P.T.O.

Group - A (b)

Answer any *two* questions : 4×2=8

4. With the help of group theory determine the symmetries of normal modes of vibrations of ClF_3 using "Cartesian coordinate method" and "Internal coordinate method". Comment about the results obtained from the two methods. Identify the symmetries of IR and Raman active modes in this molecule. (Given below the character table for C_{2v}).

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

2+1+1

5. Determine the symmetries of the group of orbitals of hydrogen atoms which are effective for σ-bond formation in H_2O molecule. Write the appropriate SALCs for this group of orbitals of hydrogen atoms. Construct a qualitative σ-bonding molecular orbital energy level diagram for H_2O molecule. 2+1+1

6. Show that "exclusion rule" is applicable for SF_6 molecule. (Given below the character table for O_h point group). 4

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		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	$x^2-y^2)$
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		(xy, xz, yz)
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		

Group - A (c)

Answer any *one* question : 8×1=8

7. Establish a correlation diagram for a d^2 ion in an octahedral environment. (Given below the character table for O_h point group).

8. (i) With the help of group theory determine the symmetries of normal modes of vibration of *trans*-$[ML_4X_2]$ molecule using Cartesian coordinate method. Identify the symmetries of IR and Raman active modes.

P.T.O.

(ii) For *trans*-dichloro bis-ethylenediamine cobalt(III) complex the ground state is $^1A_{1g}$ and excited singlet states are $^1A_{2g}$, ^1E_g and $^1B_{2g}$. Show that $^1A_{1g} \rightarrow {}^1A_{2g}$ transition is vibronically allowed with (x, y) polarized light but forbidden with z-polarized light, whereas $^1A_{1g} \rightarrow {}^1E_g$ ransition is vibronically allowed with both (x, y) polarized light and z-polarized light. Given below the character table for D_{4h} point group.

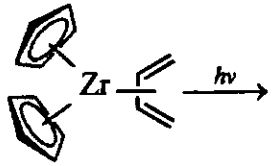
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1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

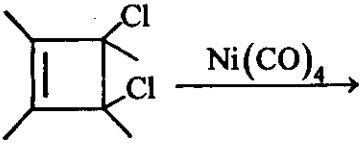
4+4

Group - B (a)

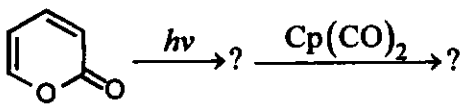
Answer any *two* questions : 2×2=4

9. Write the products of the following reactions :

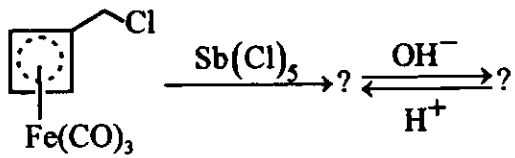
(i) 

(ii) 

10. Complete the following reaction :



11. Complete the following reaction :



P.T.O.

Group - B (b)

Answer any ***two*** questions : 4×2=8

12. (i) Complete the following reaction :

$$W(CO)_6 + NaCp \longrightarrow ? \xrightarrow{H^+} ? \xrightarrow{h\nu} ?$$

Mention the oxidation state of the metal ions for the complexes formed in the above reaction scheme.

(ii) Which product is formed when nickelocene is reacted with $Ni(CO)_4$? 3+1

13. (i) Comment on the fluxional behaviour of $Hg(\eta^1\text{-}CP)_2$.

(ii) What happens when

(a) $MoCl_5$ is treated with NaC_5H_5 and sodium borohydride in THF at low temperature?

(b) $\left[CpFe(CO)_2\right]^-$ is reacted with 2+2

14. Draw the catalytic cycle for BP's 'Cativa process' for the production of acetic acid. 4

Group - B (c)

Answer any ***one*** question : 8×1=8

15. (i) Explain three reaction steps along with the net reaction for the catalytic oxidation of acetylene to acetaldehyde by 'Pd' using $CuCl_2$ as co-catalyst.

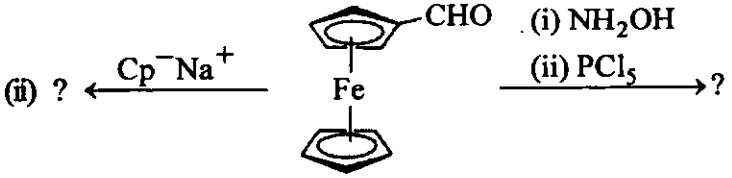
(ii) Draw the catalytic cycle for Wacker Oxidation for the preparation of acetaldehyde. 3+5

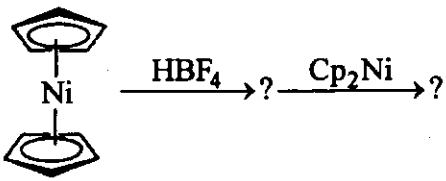
16. Predict the products formed in the following reactions :

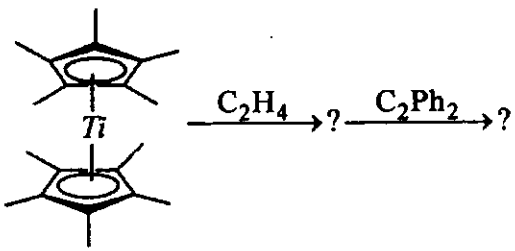
(i) $ZrCl_4(THF)_2 \xrightarrow[\text{[2,2,2]-Crypt.}]{KC_{10}H_8} ?$

1,2-dimethoxyethane

low temp.

(ii) 

(iii) 

(iv) 

Internal Assessment : 10 marks
