M.Sc. 3rd Semester Examination, 2022

CHEMISTRY

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

PAPER – CEM-302(CCAE)

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

(*Inorganic Special*)

GROUP–A(a)

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

1. What do you mean by "vibronic coupling" ?

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

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 $[CoCl_4]^{2-}$ 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** of the following questions : 4×2

4. What do you mean by "exclusion rule" ? Show that this rule is applicable for ML_6 octahedral

compound. (Given below the character table for O_h point group). 1 + 3

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		$(2z^2-x^2-y^2,\ x^2-y^2)$
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		

5. With the help of group theory determine the symmetries of the group of orbitals of H-atoms which are effective for σ-bond formation in NH_3 molecule. Write the appropriate SALCs for these symmetries. Construct a qualitative σ-bonding molecular orbital energy level diagram for NH_3 molecule. (Given below the character table for C_{3v} point group). 4

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. Establish the relation

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

where the terms have usual significance. 4

GROUP–A(c)

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

7. 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. 8

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)	

8. Establish a correlation diagram for a d^2 ion in an octahedral environment. (Use the character table for O_h point group given in Question No. **4**). 8

GROUP–B(a)

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

9. Explain the 'β-hydrogen elimination' reaction in the light of organometallic chemistry.

10. How ferrocene boronic acid can be synthesized from ferrocene ?

11. Comment on the magnetic behaviour of manganocene.

GROUP–B(b)

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

12. Discuss the catalytic cycle of Rh-catalyzed 'Monsanto acetic acid synthesis'. 4

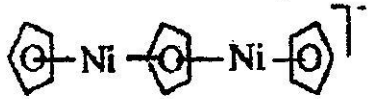
13. What is oxidative addition reaction ? Maintain the important features for this reaction. Write down the essential requirements for this type of reaction. $1 + 2 + 1$

14. Discuss the catalytic cycle for the hydroformylation using $HCo(CO)_4$ as catalyst. 4

GROUP–B(c)

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

15. (*a*) Starting from nickelocene, how will you synthesize the following species ?



(*b*) What is orthometallation reaction ? Write an example of such reaction.

(*c*) Write down the structure of two hydrogenation catalysts rather than Wilkinson's catalyst.

(*d*) Write explanatory note on 'alkyl/hydrogen migration'. 2 + 2 + 2 + 2

16. Write down the complete reaction(s) for the production of CH_3CHO from C_2H_4 by Wacker process. Write the rate equation for this process. Indicating role of $CuCl_2$, discuss the catalytic cycle of Wacker process. 1 + 1 + 6

(*Organic Special*)

GROUP – A

Answer any **four** questions : 2×4

1. Distinguish between Fischer and Schrok carbenes with suitable examples.

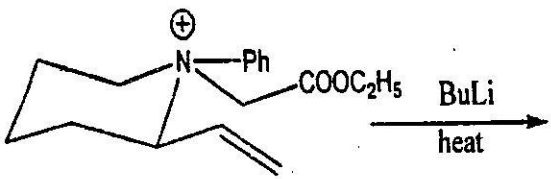
2. What do you mean by Hammett substituent constant, σ, (sigma) ?

3. What do you mean by working and auxiliary ligands ? Illustrate with suitable examples.

4. The displacement of iodide from EtI by phenoxide anions has a ρ value of exactly -1.0 – Justify the observation.

5. Using PMO method show that suprafacial [1, 3] sigmatropic rearrangement is photochemically allowed.

6. Identify the products of the following reaction.



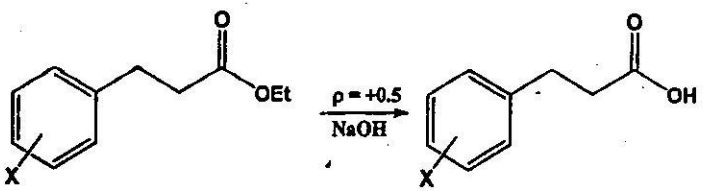
GROUP – B

Answer any **four** questions : 4×4

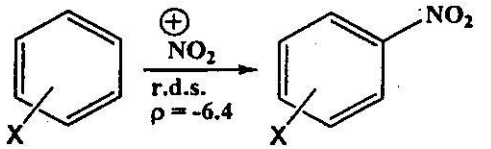
7. What do you mean by σ^+ and σ^- values ? Explain with suitable examples. 4

8. What will you account for the Hammett ρ values in the following reactions : 2 + 2

(*i*)



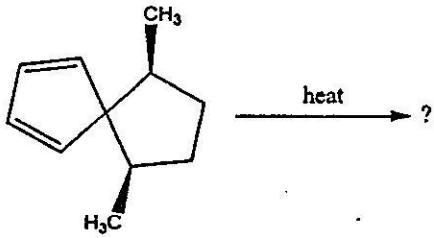
(*ii*)



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

10. Predict the product(s) of the following reactions with plausible mechanism : 2 + 2

(*i*)



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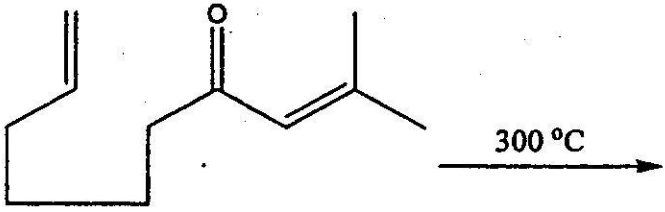


11. Usong FMO approach show that [1, 5] sigmatropic rearrangements are thermally allowed and photochemically forbidden. 4

12. Draw the catalytic cycle for Heck reaction. Discuss the regioselectivity of Heck reaction with respect to electron donating and electron attracting substituents. 4

GROUP – C

Answer any **two** questions : 8×2

13. (*a*) Discuss the nature of the Hammett plot for the hydrolysis of ArCOOR in 99.9% H_2SO_4. 5

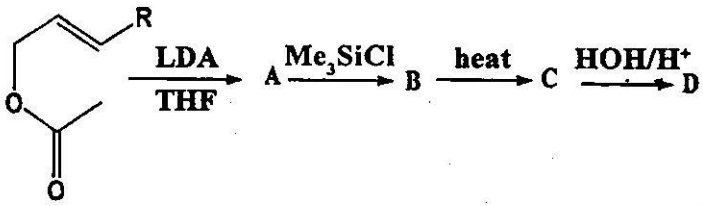
(*b*) Explain the Yukawa-Tsuno equation with a suitable example. 3

14. (*a*) What is ene reaction ? Give an example of a Lewis acid catalyzed ene reaction. Using FMO approach show that these reactions are symmetry allowed. 1 + 1 + 2

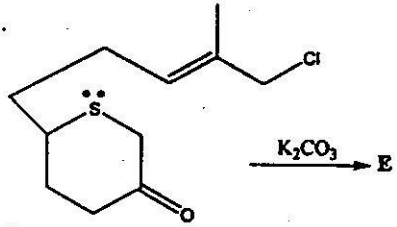
(*b*) What is meant by "chelation control" in Heck reaction ? How "chelation control" *vs* "ligand control" influences the regioselectivity of the product in Heck reaction ? Explain with proper examples. 4

15. Identify the products (**A**, **B**, **C** and **D** for the following reaction. 2×4

(*i*)



(*ii*)



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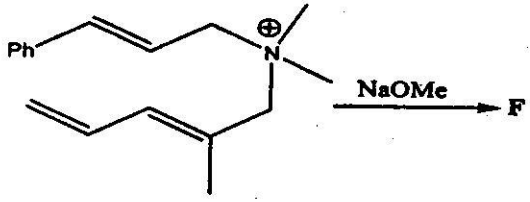
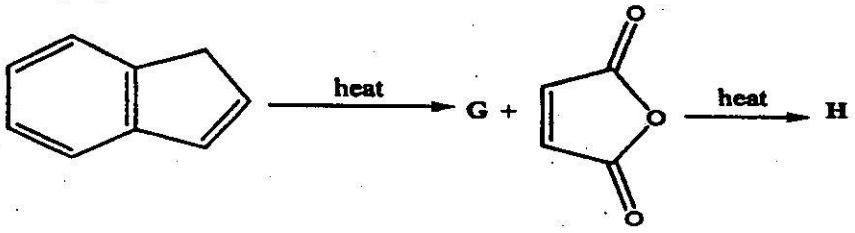


(*iv*)



16. What is Buchwald-Hartwig amination ? Draw the catalytic cycle for this reaction. Discuss the advantages and drawbacks of this reaction. How Buchwald has diverged from Hartwig subsequently for this type of reactions ? $2+2+3+1$

(Physical Special)

GROUP – A

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

1. Write down the expression of the first order correction to wavefunction in time independent degenerate perturbation theory.

2. Hamiltonian of a two-level system is given by the following matrix,

$$H_0 = \begin{pmatrix} 2 & 0 \\ 0 & 4 \end{pmatrix}$$

Find the energy eigen values and eigen ket of each state.

3. Use internal coordinate system to obtain the reducible representation of H_2O.

4. Obtain the first order correction to ground state energy, when a perturbation, $H' = Cx$(C is a constant) is applied to a linear Harmonic Oscillator.

5. Write down the standard reduction formula used in group theory for non-linear molecules.

6. The irreducible representation of trans-1, 3-butadiene are A_g, B_g, A_u and B_u. Find the IR active modes of trans-1, 3-butadiene.

GROUP – B

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

7. Use group theoretical principle to obtain the vibrational modes of NH_3. Following is the character table of C_{3v} point group.

Character table for point group C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components
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) $(x^2 - y^2, xy)(yz, xz)$

8. Deduce the expression of first order correction to energy using time independent degenerate perturbation theory.

9. Calculate the first order correction to energy of the *n*th state of Harmonic oscillator whose centre of potential has been displaced from 0 to L.

10. Describe the methodology to obtain first order correction to energy of each level for a doubly degenerate state.

11. A two level unperturbed system is described by the Hamiltonian,

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

Now a small perturbation is switched on and is given by,

$$V = \begin{pmatrix} a & c \\ c & d \end{pmatrix}$$

Find the second order correction to energy of each level.

12. Describe a scheme to diagonalize the matrix form of the following equation in a n-dimentional space.

$$HC = \lambda C.$$

GROUP – C

Answer any two questions of the following : 8×2

13. Describe the procedure and hence obtain the state of hybridization of central atom using group theoretical principle.

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)

14. Use the first order degenerate perturbation theory to obtain the spliting of spectral line ($n = 1$ to $n = 2$ transition) of Hydrogen atom in presence of an external electric field in the Z direction.

15. Find the matrix representation of angular momentum operator J^2 and J_z for $j = 3/2$ state.

16. Find the matrix representation of operator J_x for $j = 1$ level.