

**M.Sc. 3rd Semester Examination, 2018**

**CHEMISTRY**

**PAPER – CEM-301**

*Full Marks : 40*

*Time : 2 hours*

*The figures in the right-hand margin indicate marks*

*(Physical Special)*

**GROUP—A(a)**

Answer any two questions of the following :  $2 \times 2$

1. For particle in a 1-dim box problem in  $(0, L)$ , the approximate wave function is given by,

$$\psi = x\left(\frac{L}{2} - x\right)(L - x).$$

The average energy  $\bar{E}$  for such a system will obey,

$$(a) \frac{h^2}{8mL^2} < \bar{E} < \frac{h^2}{2mL^2}$$

( Turn Over )

$$(b) \bar{E} > \frac{h^2}{2mL^2}$$

$$(c) \frac{h^2}{4mL^2} < \bar{E} < \frac{h^2}{2mL^2}$$

$$(d) 0 < \bar{E} < \frac{h^2}{8mL^2}$$

2. For some one electron system with  $l = 0$  and  $m = 0$ , the function  $N_0 e^{-\sigma}$  and  $N_1 (2 - \sigma) e^{-\sigma/2}$  refer respectively to the ground ( $E_0$ ) and first excited energy ( $E_1$ ) levels. If the trial wavefunction  $N_2 (3 - \sigma) e^{-\sigma}$  yields an average energy  $\bar{E}$ , it will satisfy,

$$(a) \bar{E} \geq 0$$

$$(b) 0 \leq \bar{E} \leq E_0$$

$$(c) \bar{E} \geq E_1$$

$$(d) E_0 < \bar{E} \leq E_1$$

3. A particle executing SHM is subjected to an external perturbation,  $V = Cx^3$  (where 'C' is a constant). Find the first order correction to energy for its  $n = 5$  state.
4. Write down the expression of the Hamiltonian operator and wave-functions for  $A_2$  spin system.

GROUP-A(b)

Answer any two questions of the following :  $2 \times 2$

5. If  $\hat{H}$  is the Hamiltonian operator and  $\hat{R}$  is any symmetry element of the point group of a molecule, then  $[\hat{H}, \hat{R}] = 0$ . Justify or criticize the statement.
6. What is Linear function space ? Illustrate with an example.
7. What is meant by accidental degeneracy ? Give one such example.
8. Write down three Pauli spin matrices which serve as basis for all  $2 \times 2$  matrix having zero trace.

## GROUP-B(a)

Answer any two questions of the following : 4 × 2

9. The trial wave function of a system is expanded as,

$$\Psi_t = C_1\phi_1 + C_2\phi_2$$

The matrix elements of the Hamiltonian are given by,

$$\langle \phi_1 | H | \phi_1 \rangle = 0$$

$$\langle \phi_1 | H | \phi_2 \rangle = 2$$

$$\langle \phi_2 | H | \phi_1 \rangle = 2$$

$$\langle \phi_2 | H | \phi_2 \rangle = 3$$

Find the approximate ground state energy of the system using linear variational principle.

10. Write down the Hamiltonian and wave functions for  $A - X$  spin system and hence obtain the 1st order correction to its ground state energy.

11. Ground state trial wave function for particle in 1-dim box problem (with unit length  $a = 1$ ) is given by,

$$\phi = C_1 x(a-x) + C_2 x^2(a-x)^2$$

Use variational principle to show that the obtained energy is greater than the exact energy.

12. State and proof Eckart's theorem.

GROUP-B(b)

Answer any two questions of the following :  $4 \times 2$

13. The first order transition probability from state,  $|n\rangle$  to state  $|k\rangle$  for a two level system is given by,

$$P_{n \rightarrow k}^{(1)} = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{kn}t'} H'_{kn} dt' \right|^2$$

where  $H'_{kn} = \langle k | H' | n \rangle$ .

Use  $H'$  as time dependent oscillating perturbation and hence deduce the expression of transition probability. Comment on your result.

14. Show that each non-degenerate MO of a molecule belonging to a particular point group serves as a basis for one-dimensional IR of the point group.

15. Consider a particle in 1-D box of length 'a' and its potential is given by,

$$\begin{aligned} V(x) &= \infty ; x < 0 \\ &= \infty ; x > a \\ &= 0 ; 0 \leq x \leq a/2 \\ &= V_1 ; a/2 \leq x \leq a \end{aligned}$$

Consider  $V_1$  as the perturbing potential and hence obtain the first order correction to its ground state energy.

16. A normalized state  $\phi$  is constructed as a linear combination of ground state  $\psi_0$  and first excited state  $\psi_1$  with energies  $1/2$  and  $3/2$  respectively. If the average energy of the state,  $\phi$  is  $\langle E \rangle = 7/6$ , then find the probability of  $\psi_0$  in  $\phi$ .

## GROUP-C

Answer any two questions of the following : 8 × 2

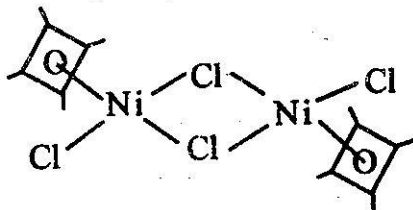
17. State Hückel approximations for linear conjugated system and hence deduce the expression of energies and wave functions of  $\pi$  MO for Allyl radical.
18. Write down the steps involved for the determination of symmetry of vibrational modes of a linear molecule using integration method and hence obtain the symmetry of vibrational modes of HCN. Character table of  $C_{\infty v}$  point group is given below :

$C_{\infty v}$	$E$	$2C_{\infty}^{\theta}$	$2C_{\infty}^{\theta+\phi}$	.....	$\infty J_{\nu}$		
$A_1$	1	1			1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1			-1	$R_z$	
$E_1$	2	$2\cos\theta$			0	$(x, y)(R_x, R_y)$	$(xz, yz)$
$E_2$	2	$2\cos 2\theta$			0		$(x^2 - y^2, xy)$
$E_3$	2	$2\cos 3\theta$			0		
...	.....	.....	.....	.....	.....		

19. Deduce the expression of Fermi Golden rule.  
Comment on the final form of the expression.
20. Use linear variational principle to obtain the energy states of electron of H-atom in presence of an external magnetic field.

(Inorganic Special)

1. Answer any *two* questions : 2 × 2
- (a) Explain the 'turnstile mechanism' for (1, 3-butadiene) Fe(CO)<sub>3</sub> complex. 2
- (b) How will you synthesize

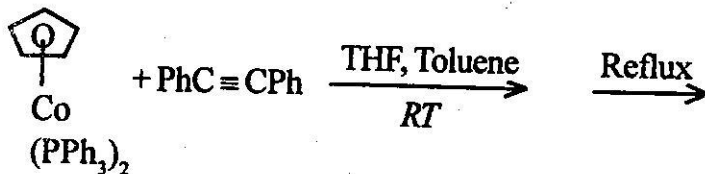


via dehalogenation of dihalocyclobutane starting from Ni(CO)<sub>4</sub>? 2

- (c) 'Although being highly poisonous, C<sub>p</sub>Tl is one of the well-utilized C<sub>p</sub> precursors'— Why? 2



(d) Complete the following reaction : 2



2. Answer any *two* questions : 4 × 2

(a) What is catalytic converter ? Schematically present the design of the device. What are the tasks of a catalytic converter ? 4

(b) ' $(\eta^4 - \text{C}_4\text{H}_4) \text{Fe}(\text{CO})_3$  is diamagnetic' – Discuss in the light of MO-theory. 4

(c) bis (hexamethyl) rhenium is unstable in monomeric form at room temp. Write down the products when  $[(\text{C}_6\text{Me}_6)_2\text{Re}] \text{PF}_6$  is treated with Li(I) at  $200^\circ \text{C}$ . Also mention the complex formed when the product is cooled to room temp. Draw the probable structure of the final product. 4

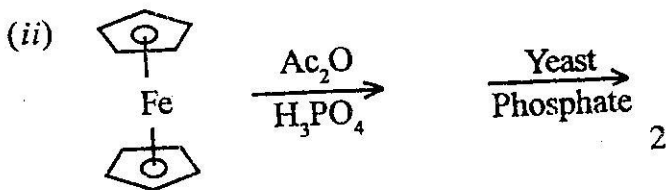
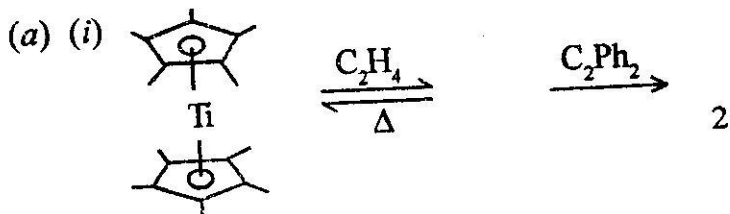
(d) (i) Mention the essential requirements for oxidative addition reaction. 2

(ii) What is orthometallation reaction?  
Cite one example of such reaction.

2

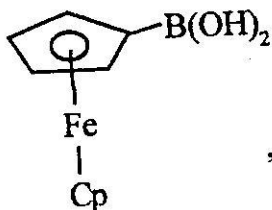
3. Answer any *one* question :

8 × 1



(iii) Schematically present the catalytic cycle of Monsanto's acetic acid synthesis. 4

(b) (i) How ferrocene boronic acid,



can be synthesized from ferrocene ?  
What will be the product when  
ferrocene boronic acid is treated with  
 $\text{Cu}(\text{OAc})_2$  ? 2+1

(ii) What will be Produced if ferrocene is  
treated with  $\text{POCl}_3$  in presence of  
DMF ? 1

(iii) Schematically present the catalytic  
cycle of Pd-catalysed Wacker Oxidation  
process. 4

4. Answer any *two* of the following questions :  $2 \times 2$

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

(b) Show that the  $f$ -orbital whose angular wave  
function is constant times  $\sin^2\theta \cos\theta \sin 2\phi$   
is  $f_{xyz}$  orbital.

(c) What do you mean by "Exclusion rule" ?

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

5. Answer any *two* of the following questions :  $4 \times 2$

(a) Use group theoretical principal to obtain the splitting of  $d$ -orbitals of Pt(II) in  $[\text{PtCl}_4]^{2-}$  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	$(x, y)$ $(R_x, R_y)$	$(xz, yz)$

(b) Establish the relation

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

where the terms have usual significance.

- (c) With the help of group theory determine the symmetry of vibrational modes of *fac*-[ML<sub>3</sub>X<sub>3</sub>] molecule using Cartesian coordinate method. Identify the symmetry of IR and Raman active modes in this molecule. (Given below the character table for C<sub>3v</sub>).

C <sub>3v</sub>	E	2C <sub>3</sub>	3σ <sub>v</sub>		
A <sub>1</sub>	1	1	1	z	x <sup>2</sup> + y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	R <sub>z</sub>	
E	2	-1	0	(x, z)(R <sub>x</sub> , R <sub>y</sub> )	(x <sup>2</sup> - y <sup>2</sup> , xy)(xz, yz)

- (d) With the help of group theory determine the symmetries of the group of orbitals of H-atoms which are effective for the σ-bond formation in NH<sub>3</sub> molecule. Construct a qualitative molecular orbital energy level diagram for this molecule.
6. Answer any *one* of the following questions : 8 × 1
- (a) Applying group theory justify that electrocyclic reaction of *cis*-butadiene must occur via conrotatory mechanism under thermal

condition but disrotatory mechanism under photochemical condition. (Given below the character table and correlation table).

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$		
$A_1$	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	$y, R_x$	$yz$

$C_{2v}$	$C_2$	$\sigma(xz)$ $\sigma(yz)$	
		$C_s$	$C_s$
$A_1$	$A$	$A'$	$A'$
$A_2$	$A$	$A''$	$A''$
$B_1$	$B$	$A'$	$A''$
$B_2$	$B$	$A''$	$A'$

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

( 15 )

(Organic Special)

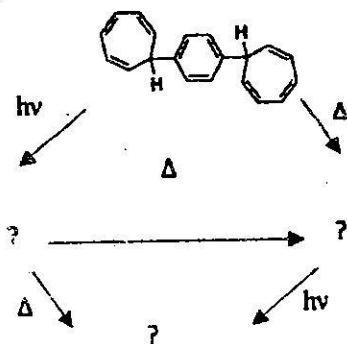
GROUP-A

Answer any **four** questions : 2 × 4

1. Why Wittig rearrangement is suppressed in case of benzyl alkyl ethers of arenechromiumtricarbonyl complexes ? 2
2. What do you mean by chelation control in Heck reaction ? Illustrate your answer with an example. 2
3. Why a mixture of THF and di-*n* butyl ether is used as the medium of thermolysis for the synthesis of arenechromium tricarbonyl complexes ? 2
4. State the basic differences between Fischer and Schrock carbenes. 2
5. How do you explain with proper example the effect of solvent on  $\rho$  value ? 2
6. What is Tebbe's reagent ? 2

7. State the Grunwald-Winstein equation ? 2

8. Predict the product/s for the following reactions and also write down the mechanism for the reaction : 2



GROUP-B

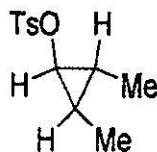
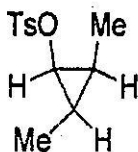
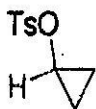
Answer any four questions : 4 × 4

9. (a) Discuss the physical significance of  $\rho$ . What does positive and negative sign of  $\rho$  indicate ? 2

(b) Explain the relative rate of solvolysis for



the following substrates with proper mechanism : 2



10. (a) Explain why the first order rate of the solvolysis of (benzylchloride)  $\text{Cr}(\text{CO})_3$  is  $10^5$  times superior than the solvolysis of uncomplexed benzyl chloride. 2
- (b) State the reasons for the popularity of the palladium complexes in organic synthesis. 2
11. (a) What are the drawbacks of using copper(I) cocatalyst in Sonogashira reaction ? 2
- (b) Why the substitution is strongly favoured at meta- with minor ortho- substitution in benzenechromiumtricarbonyl complexes carrying a single resonance donor substituent ? 2

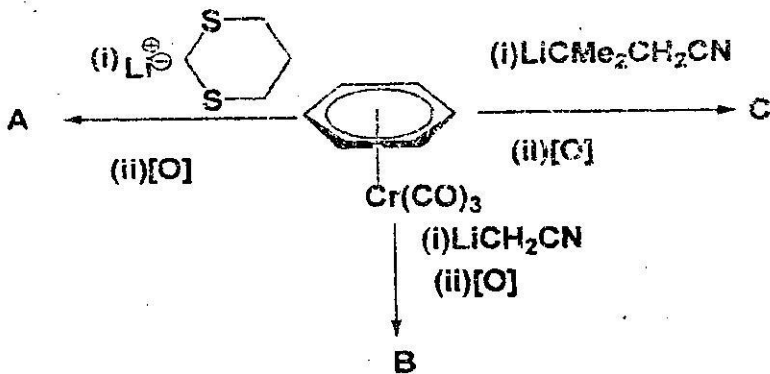
12. Write short notes on :

2 + 2

- (i) Yukawa-Tsuno equation  
 (ii) Petasis reagent.

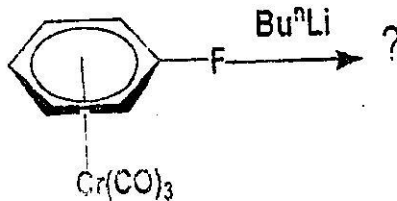
13. (a) Predict the product/s A, B, C for the following reactions :

2

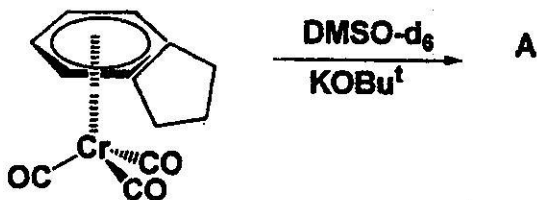


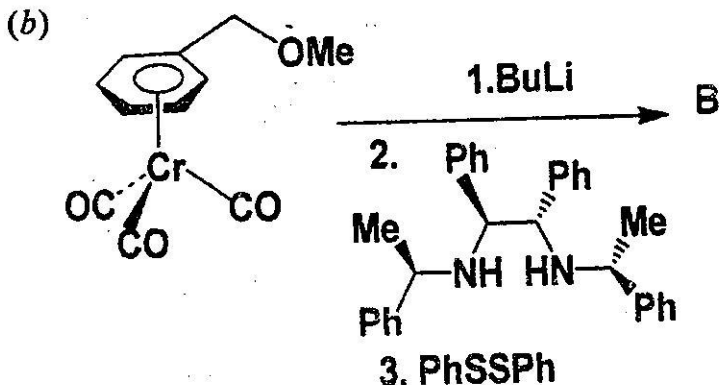
(b) Predict the product of the following reaction with plausible mechanism :

2



14. What happens when chromium tricarbonyl complexes of arylidene derivatives, derived from benzosuberone are treated with ethyl acetoacetate in presence of base. Illustrate your answer with proper reaction mechanism. 4
15. (a) A linear Hammett plot is obtained in the alkaline hydrolysis of *p*- and *m*- substituted benzoic acid esters while the Hammett plot of similar esters in 99.9 %  $H_2SO_4$  consists of two straight lines of positives and negative slopes meeting at zero. Explain. 2
- (b) What do you mean by photochromium? Explain the phenomenon with proper examples. 2
16. (a) Predict the product of the following reactions with proper justification :  $1\frac{1}{2}$





Comment on the enantiometric excess of the product formed.

$2\frac{1}{2}$

### GROUP-C

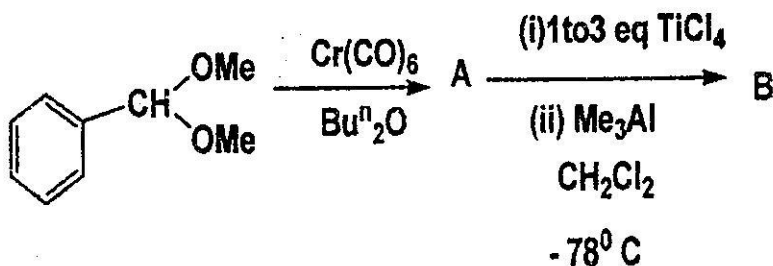
Answer any **two** questions :  $8 \times 2$

17. (a) Write down the synthetic steps involved with proper mechanism the synthesise [6]-radialene from cyclododeca 1, 5, 9-triayne. 3
- (b) How does the curved Hammett plot obtained by plotting logarithms of rate constants of solvolysis of 3-aryl-2-butylbrosylaytesin

acetic acid, obtained by titrating the p-bromobenzene sulphonic acid formed, against the  $\sigma$ -values of the substituents on the aromatic ring establish the formation of a phenonium intermediate. 3

- (c) What is Nysted reagent? State the synthetic use of Nysted reagent giving proper reaction mechanism. 2

18. (a) Explain the formation of the products A and B with proper justification : 2

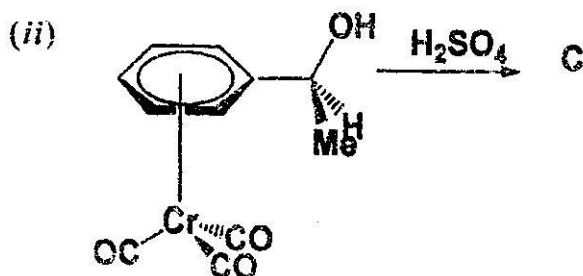
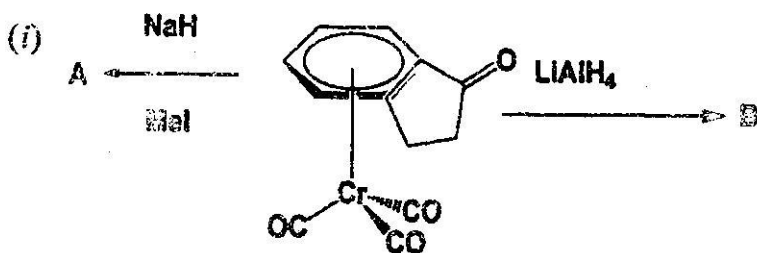


- (b) How you can configure the proper reaction mechanism for a particular reaction using Hammett  $\rho$  value? 3

(c) Site proper example for each of the following type of reaction and justify your answer : 3

- (i) Reaction having large negative  $\rho$  value and (ii) Reactions with small  $\rho$  values.

19. (a) Identify the products in the following reaction with plausible mechanism : 2 + 2



- (b) Outline the various steps involved in the catalytic Heck olefination reaction. Also comment on the regioselectivity of the reaction in presence of electron rich and electron withdrawing groups. 4
20. (a) How will you synthesize 2-substituted benzofurans from *o*-iodo phenol?  $2\frac{1}{2}$
- (b) Give a schematic representation of the proposed mechanism for the two catalytic cycles of Sonogashira reaction.  $2\frac{1}{2}$
- (c) What happens when chromium tricarbonyl complex of fluorene is treated with base followed by methyl iodide at  $-40^{\circ}\text{C}$ ? Also predict the product with proper justification when the temperature is increased to  $-20^{\circ}\text{C}$  prior to addition of methyl iodide? 3
-