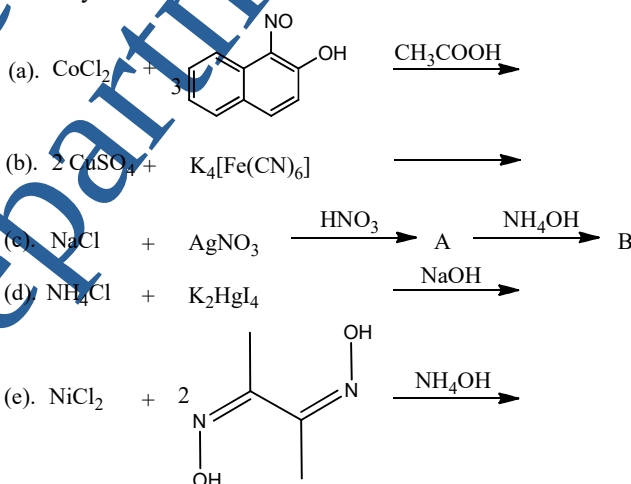


*(Attempt any 12 questions: Each Question carries 5 marks)*

- Answer the following questions with explanation? (a) Compare the melting point of  $\text{AgNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$  (b) Among  $\text{CaCl}_2$  and  $\text{MgCl}_2$  which compound will form harder crystal lattice? (c) Arrange following in correct order of increasing C–O bond length of  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$  (1.5 + 1.5 + 2 marks)
- (a) Derive an equation (Born-Landé) for the theoretical calculation of lattice energy. (b). Draw shape of following molecules using VSEPR theory:  $\text{PCl}_3\text{F}_2$ ,  $\text{XeF}_6$ . (3+2 marks)
- (a) When a mole of crystalline  $\text{NaCl}$  is prepared from 1 mole of  $\text{Na(s)}$  and half a mole of  $\text{Cl}_2(\text{g})$ , 410 kJ of heat is produced. The heat of dissociation of  $\text{Cl}_2(\text{g})$  is  $242 \text{ kJ mol}^{-1}$  and the electron affinity of  $\text{Cl}(\text{g})$  is  $368 \text{ kJ mol}^{-1}$ . The sublimation energy of  $\text{Na(s)}$  is  $109 \text{ kJ mol}^{-1}$  and the ionization energy of  $\text{Na(g)}$  is  $495 \text{ kJ mol}^{-1}$ . Calculate the lattice energy of  $\text{NaCl}$  from this data. (b) Show the linear combination of p-p, and p-d orbitals pictorially. (3+2 marks)
- (a) Is  $\text{O}_2^-$  diamagnetic or paramagnetic? Justify your answer using molecular orbital diagram. (b) Predict hybridization in following molecules (a) Xenon of  $\text{XeOF}_4$  (b) Nitrogen of  $\text{RCH=N-CH}_3$  (c) In C2-C3 carbon of . (2+3 marks)
- (a) The wavelengths of two photons are 2000 Å and 4000 Å respectively. What is the ratio of their energies? (b) The minimum energy necessary to overcome the attractive force between the electron and the surface of silver metal is  $7.52 \times 10^{-19} \text{ J}$ . What will be the maximum kinetic energy of the electrons ejected from silver metal which is being irradiated with UV light having a wavelength of 360 Å. (c) Name the scientist who discovered photo electric effect. (2+2+1 marks)
- (a) How many d orbitals are there? Give their names and draw their orbital representations. (b) Find the ground state term symbol for the atom of atomic number 9 and 22. (3+2 marks)
- (a) Calculate the effective nuclear charge for the atomic number 14 and 34. (b) Arrange 3<sup>rd</sup> period elements of periodic table in increasing order of ionization energy and justify your answer? (1.5 + 1.5 + 2 marks)
- (a) Compare first and second Ionization Energy of Cr and Mn with proper justification of your answer? (b) Write short note on lanthanoid contraction. (3+2 marks)
- (a) Define the conjugate acid and conjugate base pair concept of Brownsted-Lowery theory with suitable example. (b) State the formula and the name of the conjugate acid of each of the following bases: (a)  $\text{HCO}_3^-$  (b)  $\text{HPO}_4^{2-}$  (c) Define amphoterism with suitable examples? (2 + 1 + 2 marks)
- Derive Henderson Hasselbalch Equation for the dissociation of a weak acid. Explain how it helps to determine pKa (acid dissociation constant)? (5 marks)
- Define indicator. Write structure, observed colour change with pH, and chemical reactions involved during titration for the following indicators: (a) Phenolphthalein at pH 9; (b) Methyl Orange at pH 5. (1+2+2 marks)
- (a) An ammonia solution has a hydroxide-ion concentration of  $1.9 \times 10^{-3} \text{ M}$ . What is the pH of the solution? (b) Calculate the  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH in 0.10 M  $\text{HCl}$ . (2+3 marks)
- (a) What are super acids. (b) Write the Hammett acidity function expression with meaning of each term. (c) Name four super acids with their  $\text{H}_0$  values. (1 + 2 + 2 marks)
- Draw the structures of magneson and cupferon. Explain their applications in semi-micro inorganic qualitative analysis? (5 marks)
- Write the complete following reactions in your answer sheets: (1\*5 marks)



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**CENTRAL UNIVERSITY OF RAJASTHAN**

Department of Chemistry, School of Chemical Sciences and Pharmacy

End of Semester Examination, Date: 5<sup>th</sup> December, 2019

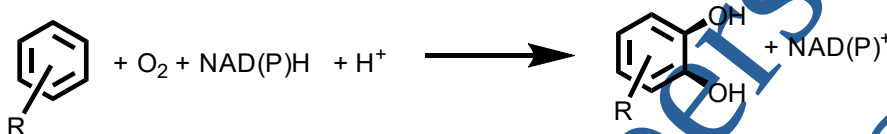
Course Name: Basic BIOINORGANIC CHEMISTRY; Course Code: CHM-504

Time: 2-5 PM

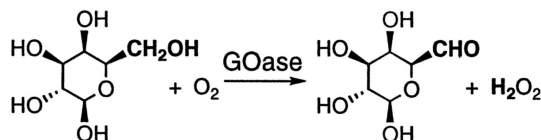
Max. Marks: 60

**(Attempt any 12 Questions, each question carries 5 marks)**

- (a) Arrange following in the decreasing order of O-O stretching frequency:  $O_2$ ,  $O_2^+$ ,  $O_2^-$ ,  $O_2^{2-}$ . (b) Derive Hills equation and show the graphs which helps in evaluating cooperativity. (2+3)
- Describe one model systems for the mimic of haemoglobin, hemocyanin and hemerythrin. (5)
- Which metalloenzyme can catalyse the following reaction? Describe the active site and mechanism. (5)



- (a) Write the principle for using a "contrast agent" in magnetic resonance imaging with the structures for two MRI contrast agents. (b) How Wilson disease occurs? Discuss in brief with cause, mechanism and possible treatments. (3+2)
- Discuss the catalytic cycle and the "active oxygen species" to carry out the monooxygenation of substrates in Cytochrome-P450 class of enzyme? (5)
- (a) Write a role of metal ions in the pathogenesis, possible treatments for Alzheimer's disease. (b) Write a short note on Parkinson Disease. (3+2)
- Discuss the various spectroscopic and other techniques used for determining the active site structure determination for an intradiol dioxygenase. (5)
- Identify the metalloenzyme capable of catalysing the following reaction and write down the catalytic cycle:



(5)

- "I am a metalloenzyme responsible for the synthesis of a pigment responsible for your skin colour, browning of fruits etc. and I have two catalytic cycles within my mechanism", Who am I? Can you write my active site structure and mechanism? (5)
- (a) What is the role of superoxide dismutase in our body, describe how it works? (b) Comment on the different types, structure and functions of iron-sulphur proteins. (2+3)
- Write a brief note on the discovery of Cis-DDP. Write the detailed mechanism of action of drug with a mention of side effects. (5)
- (a) What is the principle of PET imaging? Which imaging technique is more sensitive between PET and SPECT and why? (b) Why  $^{64}\text{Cu}$  should be beneficial over  $^{18}\text{F}$  as radiotracer in PET imaging? (3+2)
- (a) Write the active site structure of Horseradish peroxidase, how is it different from the one in chloroperoxidase? (b) How the active site structure of Alcohol dehydrogenase looks like, describe its mechanism also. (2.5+2.5)
- How the three classes of Cu metalloenzymes are different from each other both in structure and spectroscopic features? Give at least one example of each. (5)
- Draw the Vitamin B12 active site structure and discuss the mechanism of the chemical reaction catalysed by it. (5)

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**CENTRAL UNIVERSITY OF RAJASTHAN**

Department of Chemistry, School of Chemical Sciences and Pharmacy  
M.Sc. (2Y, 5Y, 3Y); End of Semester Examination, Date: 01<sup>st</sup> May, 2019  
Course Name: Coordination Chemistry; Course Code: CHM-405

**Time: 2-5 PM**

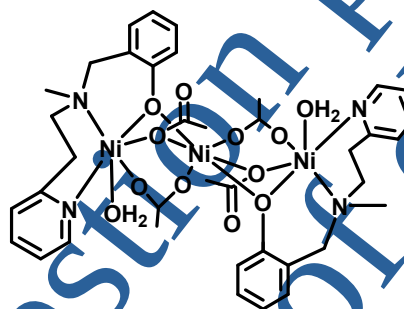
**Max. Marks: 60**

**(Q1 is compulsory; Attempt any other 10 Questions carrying 5 marks each)**

1. Find out for which system the given table of microstates corresponds to? Can you reduce the table to its constituent free ion terms? **(10)**

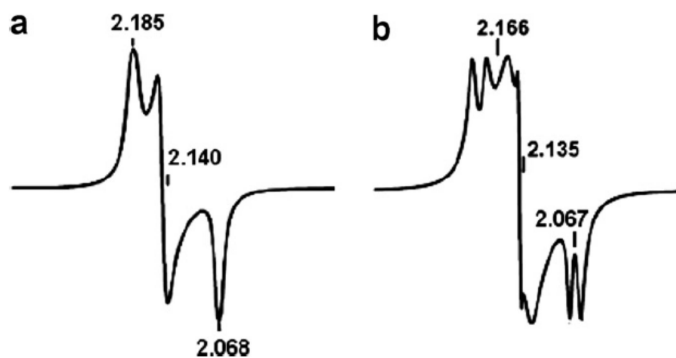
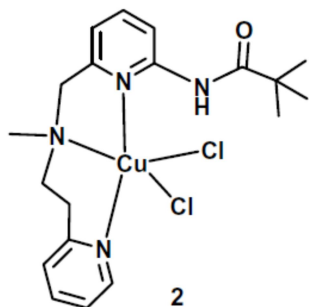
		$M_L$								
		4	3	2	1	0	-1	-2	-3	-4
$M_S$	1		1	1	2	2	2	1	1	
	0	1	2	3	4	5	4	3	2	1
	-1		1	1	2	2	2	1	1	

2. The compound  $\text{trans-Fe}(\text{O-phen})_2(\text{NCS})_2$  has a magnetic moment of 0.65 BM at 80K, increasing with temperature to 5.2 BM at 300K. Assuming a spin-only magnetic moment, calculate the number of unpaired electron at these temperatures. How the increase in magnetic moment with temperature could be explained at these two temperatures? **(2.5+2.5)**
3. Calculate the diamagnetic correction to magnetic susceptibility for the following molecule (Pascal's constants are given at the end) **(5)**



4. Draw the single Orgel diagram for  $d^2, d^7, d^3, d^8$  systems in tetrahedral and octahedral ligand field. How many absorption bands are expected for  $\text{Ni}^{2+}$  complex? **(5)**
5.  $\text{Ni}^{2+}$  is having two unpaired electrons but its magnetic moment is higher than spin-only. Can you suggest a reason for that? (ii) Show the calculation for getting  $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ . **(2.5+2.5)**
6. What is Curie law? Derive the magnetization and magnetic susceptibility expressions for an isolated  $S = \frac{1}{2}$  system with no orbital contribution. **(5)**
7. (i) Define  $A, I_a, D$  and  $I_d$  mechanisms of substitution in square planar complexes. Can you suggest the situations in which these will be favoured or disfavoured? (ii) Write a short note on Trans Effect with its application in inorganic reaction mechanism. **(2.5+2.5)**
8. (i) What is Nephelauxetic effect? (ii) Draw the MO diagram for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and explain the spin state and magnetic property for the same. **(1+4)**
9. (i) Why  $\text{KMnO}_4$  solutions are deep purple in colour but  $\text{MnSO}_4$  gives only light pink solution? (ii) Calculate the spin-only magnetic moment for the complexes:  $[\text{MnCl}_6]^{4-}$  and  $[\text{Mn}(\text{CN})_6]^{4-}$ . (iii) Which of these two complexes should absorb higher wavelengths of incident radiation? **(2+2+1)**
10. (i) What are spin and Laporte selection rules, explain with examples? (ii) What is heavy atom effect? (iii) Determine the ground state terms for the following configurations:  $d^8$  (Oh symmetry) and  $d^5$  (HS and LS) (Oh symmetry). **(2.5+1+1.5)**
11. (i)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  spectra has an absorption band at  $\sim 520$  nm and in addition has a closely associated shoulder band. How would you explain it? (ii) Draw the d-orbital splitting for an Oh symmetry reducing to z-in and z-out. **(3+2)**

12. Explain the number of lines observed in the X-band EPR spectra of the following complex at 298 K (a) and 120 K (b) (ref: *Inorg. Chim. Acta* 361, 2008, 2768). (5)



13. i) What are stepwise and overall stability constants? Establish a relation between them. (ii) What is the utility of HYSS program? (4+1)
14. What do you understand by Thermodynamic and Kinetic stability of a metal complex? When do you call a complex inert or labile? (5)
15. Discuss and in detail the outer sphere and inner sphere mechanism of electron transfer with examples? How to differentiate between the two mechanisms? (5)

Table of Pascal's constants:

Atoms, $\chi_A$		Bonds, $\chi_B$			
Atom	$\chi_A (\times 10^{-6} \text{ cm}^3 \text{ mole}^{-1})$	Atom	$\chi_A (\times 10^{-6} \text{ cm}^3 \text{ mole}^{-1})$	Bond	$\chi_B (\times 10^{-6} \text{ cm}^3 \text{ mole}^{-1})$
H	-2.93	F	-63	C=C	+5.5
C	-6.00	Cl	-20.1	C≡C	+0.8
C (aromatic)	-6.24	Br	-30.6	C=N	+8.2
N	-5.57	I	-44.6	C≡N	+0.8
N (aromatic)	-4.61	Mg <sup>2+</sup>	-5	N=N	+1.8
N (monamide)	-1.54	Zn <sup>2+</sup>	-15	N=O	+1.7
N (diamide, imide)	-2.11	Pb <sup>2+</sup>	-32.0	C=O	+6.3
O	-4.61	Ca <sup>2+</sup>	-10.4		
O <sub>2</sub> (carboxylate)	-7.95	Fe <sup>2+</sup>	-12.8		
S	-15.0	Cu <sup>2+</sup>	-12.8		
P	-26.3	Co <sup>2+</sup>	-12.8		
		Ni <sup>2+</sup>	-12.8		

Also given that:

$$k = 1.38 \times 10^{-16} \text{ erg/K}$$

$$\mu_B = 9.274 \times 10^{-21} \text{ G cm}^3$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

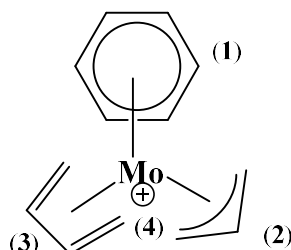
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Time: 3 h

Max. Marks: 60

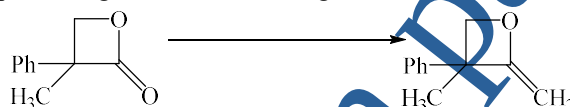
**PART A (Attempt any Seven Questions)**

1. (a) The following compound can undergo nucleophilic addition at position 1, 2, 3 and 4. This addition of nucleophile on alkene is possible due to umpolung effect. Which of the position will be fastest nucleophilic (Nu<sup>-</sup>) attack? Sketch the structure of the product after nucleophilic attack. [2]



- (b) Arrange the following in order of their increasing  $\nu_{C-O}$  stretching frequency.  $[Mn(CO)_6]^+$ ,  $[Cr(CO)_6]$ ,  $[V(CO)_6]^-$ , CO and  $[Ti(CO)_6]^{2-}$ . [2]

- (c) Write the structure of most appropriate reagent for the following transformation. [1]



2. (a) Predict the product from the given sets of reagents: [3]

(i) Ferrocene, acetylchloride,  $AlCl_3$  (1:2:2 ratio)

(ii) Ferrocene, *n*-BuLi, TMEDA

(iii) Ferrocene, HCHO,  $HNMe_2$ , AcOH

- (b) What is carbenoid? Give an example of carbenoid. [2]

3. (a) Give the total metal electron counts, and metal  $d^n$  numbers for the following complexes. [1x3=3]

(i).  $K[PtCl_3(C_2H_4)] \cdot H_2O$

(ii).  $(PPh_3)AuCl_4$

(iii).  $Pd(PPh_3)_4$

- (b) What is Hapticity and Denticity? Explain with examples. [2]

4. (a) What is the difference between Nuclear Transmutation and Nuclear Fission? Explain with examples. [2]

- (b) Discuss the application isotope in chemical reaction pathway and structural determination. [2]

- (c) What is the end of the product of  $4n+2$  series? Write the number of ' $\alpha$ ' and ' $\beta$ ' particles are emitted in this series. [1]

5. (a). Define Law of radioactivity. Derive the equation  $N = N_0 e^{-\lambda t}$ , where N is the number of particles at any instant and  $N_0$  is number of particles at time  $t = 0$ . [3]

- (b). How boron is used for the treatment of brain cancer? Explain. [2]

6. (a) A freshly prepared isolated sample of  $^{90}Sr$  was found to have an activity of  $9.8 \times 10^5$  disintegrations per minute at 1.00 PM on December 3, 1992. At 2.15 PM on December 17, 1993, its activity was determined and found to be  $2.6 \times 10^4$  disintegrations per minute. Calculate the half-life of  $^{90}Sr$ . [2]

- (b) How old is the sample of wood whose  $^{14}C$  content is found to be 43% that of a living tree? The half-life of  $^{14}C$  is 5730 years. [2]

- (c) What radionuclide is used for lungs and liver disease diagnosis? [1]

7. (a) Write the difference between half-life and average life of radioactive substance. [2]

(b) A sample to be used for medical imaging is labeled with  $^{18}F$ , which has a half-life of 110 minutes. What percentage of the original activity in the sample remains after 300 minutes? Calculate the average life of  $^{18}F$ . [3]

8. (a) Cobalt-60 is used in the radiation therapy of cancer. How it can be synthesized from cobalt-59? Write the nuclear reaction. [2]

- (b) Write the difference between isotone and isobar (with examples). [2]

- (c) Radon-222, which is found in the air inside houses built over soil containing uranium, has a half-life of 3.02 days. How long before a sample decreases to  $\frac{1}{64}$  of the original amount? [1]

**PART B (Attempt any five Questions)**

9. (i) What is octahedral site preference energy (OSPE)? Calculate OSPE for  $d^1$  and  $d^9$  systems. (2.5)  
(ii) Calculate the difference between CFSE of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . (2.5)
10. Write the main postulates of CFT. It is observed that crystal field splitting in tetrahedral ligand field is  $\sim 0.44\Delta_o$  ( $\Delta_o$  = Octahedral splitting). Explain why? (2+3)
11. What are spinels? How CFSE helps in predicting the structure of spinels? Predict the structure of  $\text{Mn}_3\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ . [5]
12. Draw the complete splitting diagram as per CFT for the square pyramidal, trigonal bipyramidal, tetrahedral and square planar geometries. [5]
13. (i)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  spectra has an absorption band at  $\sim 520$  nm and in addition has a closely associated shoulder band. How would you explain it? (3)  
(ii) Draw the  $d$ -orbital splitting for an octahedral symmetry reducing to  $Z$ -in and  $Z$ -out. (2)
14. Define Bioinorganic Chemistry with its scope. Classify the elements which are biologically important. (5)
15. (i) Write Jahn-Teller theorem. (1)  
(ii) Draw the graph of lattice energy for divalent transition metal ions, justify your answer. (4)

Model Question Papers  
Department of Chemistry



CENTRAL UNIVERSITY OF RAJASTHAN

Department of Chemistry, School of Chemical Sciences and Pharmacy  
End of Semester Examination-From-Home (EoS-EFH), 19 January 2021  
Course Name: ORGANOMETALLIC CHEMISTRY; Course Code: CHM-501

Time: 10.00 AM – 01.00 PM.

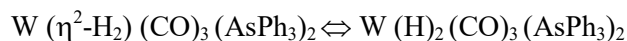
Max. Marks: 60

**Exam-from-home mode**

**SECTION A**

*(Q1 to Q6: Attempt any Five questions; Each Question carries 3 marks)*

1. Assign the oxidation states,  $d^n$  configurations, and electron counts for the two species shown below, which are equilibrium in solution.



2. A complex has the empirical formula  $(PPh_3)Re(CO)_3Cl$ . How could it attain the 18-electron configuration without requiring any additional ligands?
3. Write the increasing order of  $\nu_{CO}$  stretching frequency for following species:  
 $[Cr(CO)_6]$ ,  $[Ti(CO)_6]^{2-}$ ,  $[Mn(CO)_6]^+$ ,  $CO$ ,  $[Fe(CO)_4]^+$ ,  $[V(CO)_6]^-$
4. Reaction of  $[Cr(CO)_6]$  with  $LiC_6H_5$  gives X, which reacts with  $[Me_3O][BF_4]$  to give Y. Write the structures of X and Y.
5. Two electron electrochemical reduction of the 18-electron cation  $[(\eta^5-indenyl)_2V(CO)_2]^+$  is reversible while the same reduction of the complex  $[Cp_2V(CO)_2]^+$  leads to the cleavage of a molecule of CO. Give reasons.
6. What are the factors which facilitate the reductive elimination? Explain with examples.

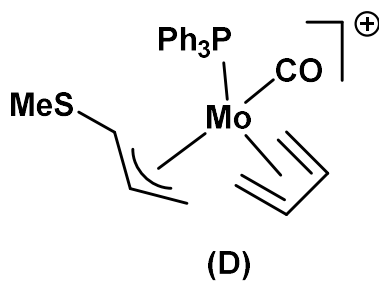
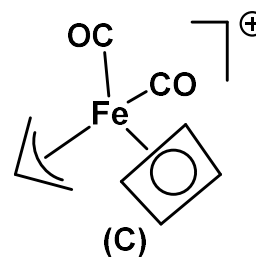
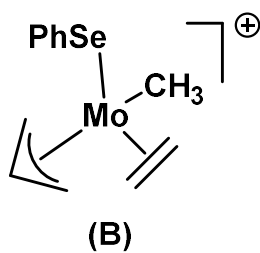
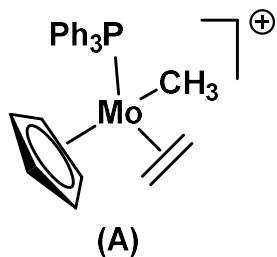
**SECTION B**

*(Q7 to Q10: Attempt any three questions; Each Question carries 15 marks)*

7. (a) Analyse and give your thoughts on the following sentences by using suitable examples. (10)  
***N-heterocyclic carbene ligand is a ubiquitous ligand in organometallic chemistry. This ligand is a phosphine substitutes in catalytic applications.***  
(b) Suggest an efficient method for preparing  $Cp(CO)_3MoCH_3$  from  $Cp(CO)_3MoH$ . (3)  
(c) A Schrock type carbene based reagent used for converting carbonyl groups to methylene group. Name the reagent and discuss its synthesis. (2)
8. (a) What are the various factors favoured for the  $X_2$ -type bonding in metal-olefin complex? Explain with suitable examples. (5)  
(b) Draw a diagram that illustrates the bonding and back-bonding interactions for a metal-alkyne complex. (5) (c) What is the difference between classical metal carbonyls and non-classical metal carbonyls? Give examples. (3)  
(d) Why palladium-allyl complexes are more reactive? (2)
9. (a) Give an example of organometallic compound which shows like a molecular propeller. Discuss its fluxionality behaviour. (5)  
(b) Trihaptoallyl-palladium chloride complex is fluxional in nature. What you will expect from its variable temperature  $^1H$  NMR spectrum data? Explain with diagram. (5)  
(c) What is metal hopping? Can you observe this fluxional behaviour in variable temperature NMR data? (5)

10. Write the expected product after a **hydride ion** attack on each of the following:

(5x3=15)



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Model Question Papers  
Department of Chemistry



### Exam-from-home mode

#### Section A

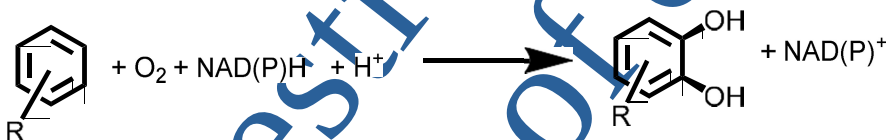
(Attempt any 5 Questions, each question carries 3 marks)

1. Describe one structural and functional model systems of myoglobin and hemocyanin. Write the name of scientist discovered these.
2. What are the elements being used to develop metal complexes for anticancer activity and why? (b) Write the detailed mechanism of action of drug cisplatin.
3. Show how to derive the Hills equation and the graphs using it that helps in evaluating cooperativity in dioxygen binding in hemoglobin.
4. Write the principle for using a "contrast agent" in magnetic resonance imaging with the structures for two MRI contrast agents.
5. What are the evidences and hypothesis for the roles of metal ions in the pathogenesis of Alzheimer's disease? Suggest a possible treatment method with justification.
6. How the three classes of Cu metalloenzymes are different from each other both in structure and spectroscopic features? Give at least one example of each.

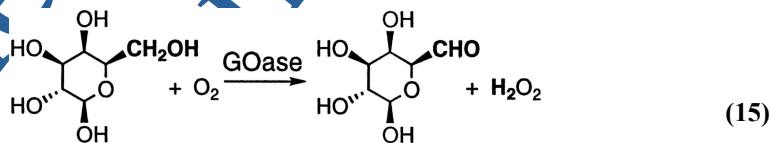
#### Section B

(Attempt any 3 Questions, each question carries 15 marks)

7. (a) See the reaction given below and suggest a metalloenzyme that can catalyse this reaction. Describe the active site and most plausible mechanism. (8)



- (b) Why is CYP450 so important? Discuss the catalytic cycle and the "active oxygen species" to carry out the monooxygenation of substrates in Cytochrome-P450 class of enzyme? (7)
8. Describe the information obtained from various spectroscopic and other techniques used for determining the active site structure determination for an intradiol dioxygenase (15)
9. Carefully see the reaction given below and write the detailed mechanism of a metalloenzyme capable of catalysing such reactions.



10. (a) "I am a metalloenzyme having two catalytic cycles within my mechanism. I help in the synthesis of a pigment responsible for your skin colour, browning of fruits etc.". Who am I and which pigment I am talking about? Can you write my active site structure and detailed mechanism? (10)
- (b) What is the principle of PET imaging? Which imaging technique is more sensitive between PET and SPECT and why? (5)

**CENTRAL UNIVERSITY OF RAJASTHAN**

Department of Chemistry, School of Chemical Sciences and Pharmacy

M. Sc. (2Yr), Int. M.Sc. B. Ed. (3Yr), Int. M.Sc. (5Yr); End of Semester Examination, 12<sup>th</sup> Dec. 2019

Course Name: GREEN CHEMISTRY; Course Code: CHM-619

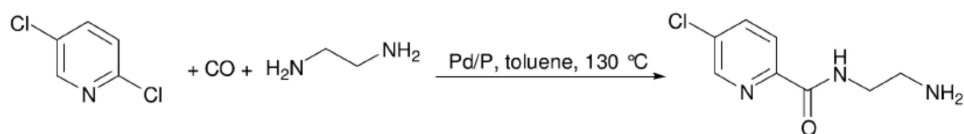
**Time: 2.00 PM. to 5.00 P.M.**

**Max. Marks: 60**

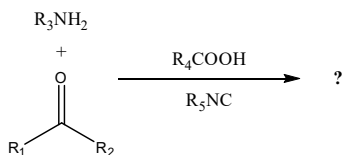
*(Attempt any twelve questions; Each Question carries 5 marks) [12x5=60 marks]*

1. Analyze the *green route* of producing Ibuprofen, discussing the reaction pathway to be followed and in which ways it is better than the traditional method of synthesizing the same. [5]
  2. (a). In 1990, Haber et al. developed the synthesis of aniline from nitrobenzene by electrochemical reduction. Write all the intermediates formed from the above reaction. [2]  
 (b). Explain the following: (i). Hazard and Risk, (ii) Non-covalent derivatization. [2+1]
  3. (a). What is reverse phase transfer catalysts? How it is different from normal phase transfer catalysts? Explain with examples. [3]  
 (b). Give an example of surfactant. Discuss its role in organic reaction with example. [2]
  4. (a). Describe the pathways which should be followed to synthesize the *n*-nonane from 5-hydroxymethyl-2-furfural (HMF). [3]  
 (b). Highlight the differences between *microwave heating* and *conventional heating*. [2]
  5. (a). Write the various factors influences the reactivity and selectivity in catalytic hydrogenation reaction by heterogeneous catalyst. [3]  
 (b). Sketch the structure of Grubb's second generation catalyst for metathesis reaction. [2]
  6. (a). An industrial process (Wacker oxidation process) used for the synthesis of acetaldehyde from ethylene by palladium catalyst and copper as co-catalyst. Draw the catalytic cycle. [3]  
 (b). What is supercritical fluid? Draw the phase diagram of carbon dioxide. [2]
  7. (a). Define the turnover number of an enzyme. 1.5 gm of an enzyme (Molecular weight-32000), in presence of excess substrate catalyzes at a rate of 3.2 mol substrate/min. Calculate the TON. [1+2]  
 (b). Calculate the atom economy and Reaction Mass Efficiency (RME) of the following reaction. [1+1]
- 
8. Explain the consequences (*cons* and *pros*) of using solvents in chemical reactions. How would you rationalize water as green solvents? [3+2]
  9. (a). Is the use of ultrasound for doing a chemical reaction really a green chemistry? Explain by using the principles of Green Chemistry. [2]  
 (b). Discuss the following multicomponent reactions with mechanism, [3]  
     (i) Passerini reaction,                      (ii). Biginelli reaction. .
  10. (a). Discuss the different categories in which EPA honors winners for the Presidential Green chemistry award. [2]  
 (b). Provide the greener route of synthesizing the following compounds. [1.5+1.5]  
     (i) Indigo,      (ii). Lexan

11. (a). Calculate the Atom economy, Reaction Mass efficiency and carbon efficiency in the following reaction. [3]



- (b). DuPont has won the 2003 Presidential Green Chemistry award for the manufacture of a polymer. Draw the structure of polymer and explain its synthesis. [2]
12. (a). Write the differences between cationic clays and anionic clays. How is it different from zeolites in terms of structural arrangement? [2]
- (b). Define the following terms: (i) SEALINE™, (ii) Risk assessment. [1.5+1.5]
13. (a). Predict the product in the following reaction, and suggest the mechanism of the product formation. [4]



- (b). Define combinatorial chemistry. How is it different from conventional strategies? [1]
14. Define and interpret the 10<sup>th</sup> and 11<sup>th</sup> principles of Green Chemistry with suitable examples. [5]

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CENTRAL UNIVERSITY OF RAJASTHAN  
DEPARTMENT OF CHEMISTRY

End of Semester Examination  
Int. M.Sc. (5 yr) Chemistry; Semester V

Course Code: CHM-302

Course Name: Organic Chemistry-II

PART A

Time allowed: 40 min

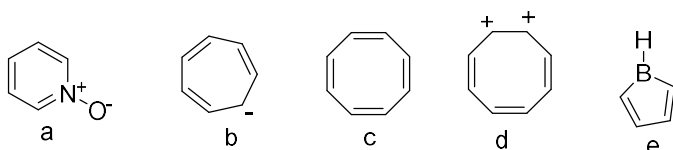
Max marks: 20

Answer ANY 4 questions

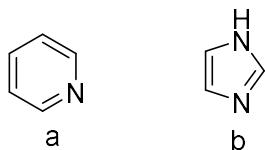
(5 marks × 4 = 20)

1: What is aldol reaction? Explain with examples and write the mechanisms for both acid and base catalyzed aldol reaction. (5)

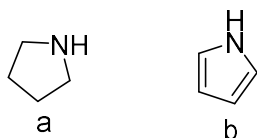
2: Indicate the given compounds as aromatic/non-aromatic/anti-aromatic. (5)



3: a) Which among these will have high basicity and why? (3)



b) Which among these will have low pKa value and why? (2)

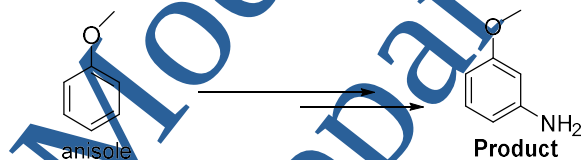


4: a) Write the structure of pentaerythritol. How it can be synthesized? Name the reaction. (3)

b) Will p-nitrobenzaldehyde give benzoin condensation? Provide suitable explanation. (2)

5: a) What are benzyne? Write any two ways to synthesize benzyne. (3)

b) How to synthesize the product in given reaction starting from anisole? (2)



**PART B**

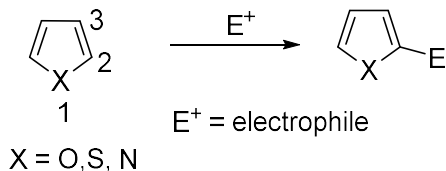
Time allowed: 80 min

Max marks: 40

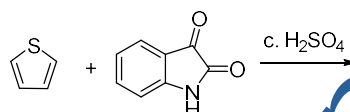
Answer ANY 2 questions

(20 marks × 2 = 40)

6. (a) Explain the reason for site of electrophilic reactions occurring at 2-position instead of 3-position in 5-membered heterocycles. (5)



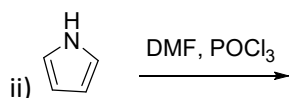
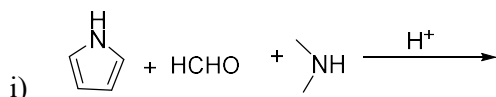
- (b) Write the product obtained in following reaction along with reaction mechanism. (5)



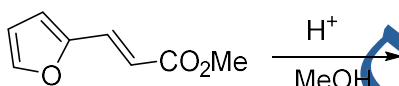
- (c) How to synthesize 2-amino pyridine from pyridine? What is the name and mechanism of the reaction? (5)

- (d) What is Ehrlich test? Write the reaction and mechanism. (5)

7. (a) Write the product and mechanism of following reaction. Also mention the name of reaction. (10)



- (b) Write the product and mechanism of the given reaction (10)



8. (a) Write Fisher-Indole synthesis along with mechanism. (5)

- (b) Write Hantzsch Synthesis of Pyridine along with mechanism. (5)

- (c) Which among the pyrrole, thiophene, and furan is (10)

i) most aromatic and why?

ii) most reactive towards electrophilic aromatic substitution and why?

Time allowed: 3 h

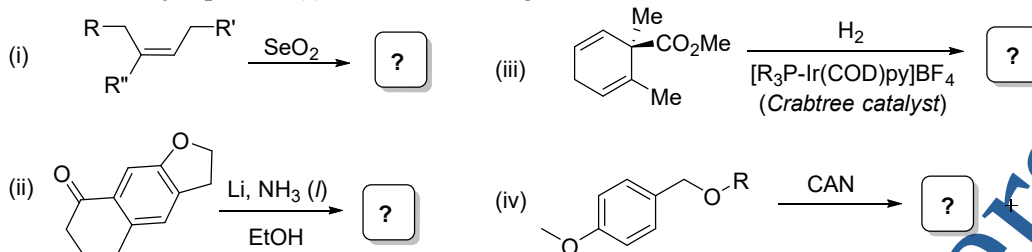
Max marks: 60

Answer ANY 12 questions

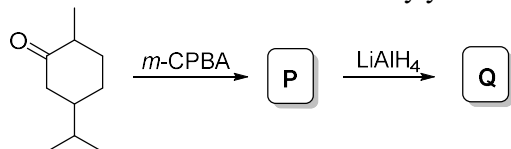
(5 marks × 12 = 60)

(For subdivisions where individual marks are not specified, total marks of the question shall be divided equally).

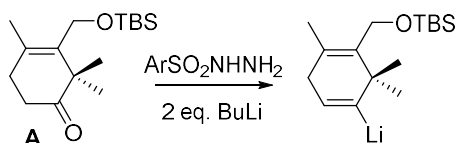
1. Predict the major product(s) of the reactions given below:



2. Identify **P** and **Q** in the sequence given below. Outline a mechanism for the formation of **P**. What would be the minor product of this transformation? Justify your answer.

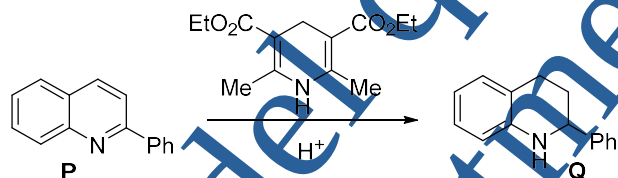


3. (i) In Nicolaou's total synthesis of taxol (Ref.: *J. Am. Chem. Soc.* **1995**, *117*, 653) the carbonyl group in **A** was converted into a nucleophilic vinyl Lithium species (shown below). Outline a mechanism for the reaction and also identify the name of the reaction. (2.5)

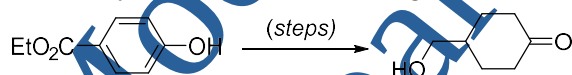


(ii) Bring out the major chemoselectivity difference between  $\text{LiBH}_4$  and  $\text{BH}_3$  as reducing agents using suitable examples. Why is this difference observed? (2.5)

4. (i) Outline a mechanism for the conversion of **P** to **Q**. What is this method of reduction called? What would be the most appropriate reagent for converting **Q** back to **P**? (3.5)



(ii) How can you execute the following transformation (outline the steps): (1.5)

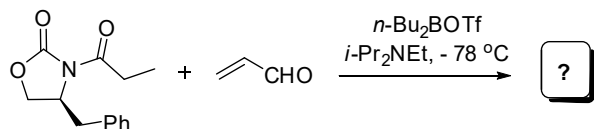


5. An optically active compound **A** ( $\text{C}_{10}\text{H}_{16}$ ) undergoes the reactions shown below. Deduce the structure of **A**, **B**, **C** and **E** from the given data and assign the configuration of **A**.

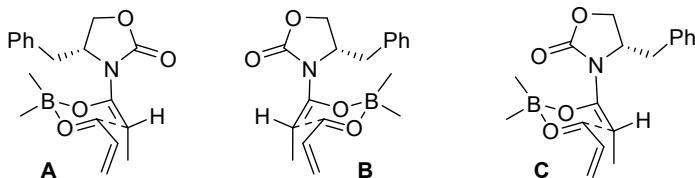




6. David Evans used his asymmetric aldol protocol in the enantioselective total synthesis of the marine natural product (+)-calyculin A (Ref: *J. Am. Chem. Soc.* **1992**, *114*, 9434). The key reaction in the synthesis is shown below. Answer the questions that follow based on the same:



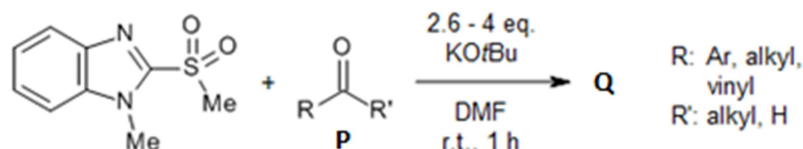
- (i) Which of the 3 non-chelated transition states shown below represents the correct and most favourable one for the reaction? Justify by elucidating why the other two T.S.'s are unfavourable.



The Bu groups on the Boron are not displayed for better clarity

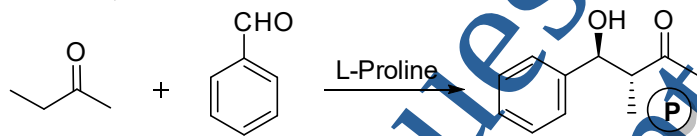
- (ii) Illustrate the structure of the product with the correct absolute stereochemistry in its open chain conformation. Mark the product as the *syn* or *anti* diastereomer.

7. zsasssdddaysyysqwqqaKaori Ando *et al* developed a practical olefination reaction under mild conditions using benzimidazol-2-yl sulfone reagent (Ref.: *Org. Lett.* **2015**, *17*, 2554). Predict the structure of **Q** and outline a step-wise mechanism for this conversion, clearly illustrating the intermediates and the side-products.

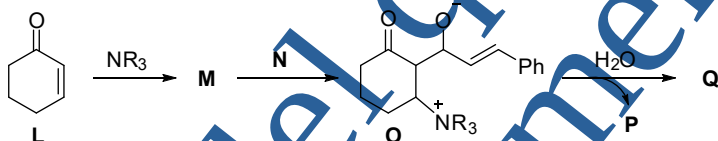


8. (i) Bring out the two major features of the Shibasaki aldol reaction that distinguishes it from other aldol addition methods. (2)

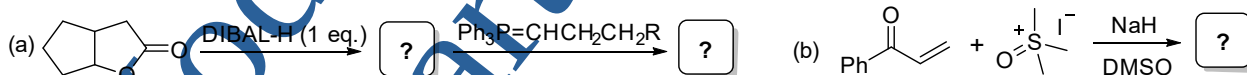
- (ii) Provide a suitable mechanism for the reaction given below. Write the structure of any two other possible products of the reaction (at least one of them SHOULD NOT be a stereoisomer of **P**). (3)



9. (i) Identify the missing reagents/products in the scheme given below (2)

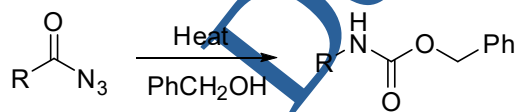


- (ii) Predict the products (*with the correct stereochemistry wherever appropriate*) (3)

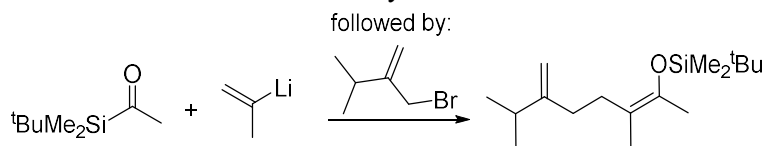


10. (i) What do you expect when  $\alpha$ -chloro cyclohexanone reacts with NaOMe in MeOH? Outline a suitable mechanism and identify the name of the reaction.

- (ii) Outline a suitable mechanism and identify the name of the reaction given below:



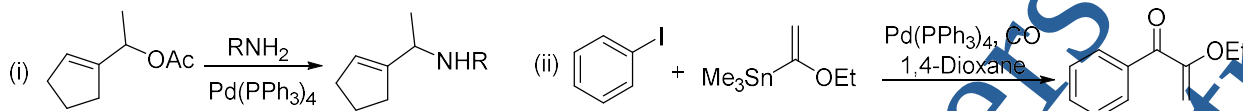
11. (i) Outline a mechanism and identify the name for the reaction shown below: (2.5)



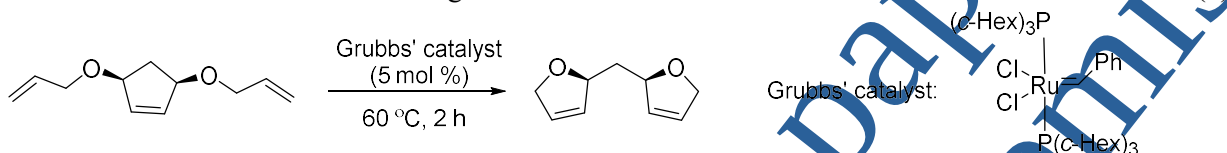
(ii) Predict the products and identify the name (wherever appropriate): (2.5)



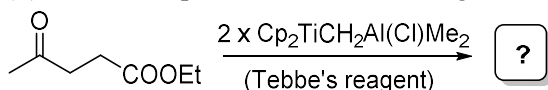
12. Illustrate a suitable mechanism for the conversions shown below:



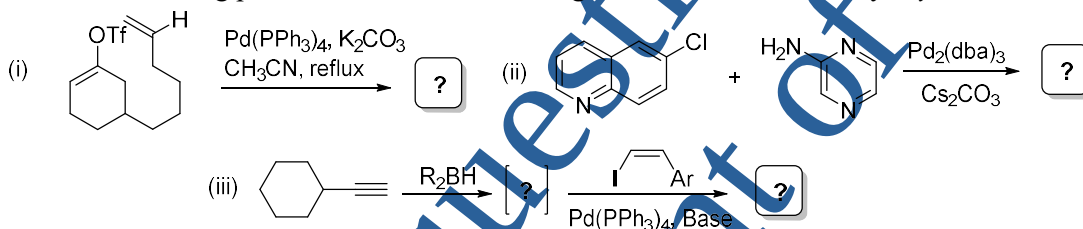
13. Outline a mechanism for the reaction given below: (4)



(ii) Predict the product of the reaction given below: (1)



14. Predict the missing products of *all* the reactions given below. Also identify *any two* named reactions.



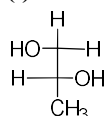
15. Predict the product and outline a suitable mechanism (first 2 catalytic cycles) for the reaction shown below (*short form of the catalyst may be used*):



**PART A**

*(Q1 to Q6: All questions are compulsory; Each Question carries 3 marks)*

- Draw structures for each of the following: (a) 4-chloro-3,5-dimethylphenol; (b) cyclopropyl propyl ether; (c) bromopropanone
- (i) Which of the following sodium fusion extract of organic compound gives brilliant violet color with sodium nitroprusside solution?  
 A) Urea                      B) Thiourea                      C) Benzoic acid                      D) Aniline  
 (ii) Which compound does not give a positive result in the Lassaigne's test for nitrogen?  
 A) Aniline                      B) Glycerin                      C) Benzamide                      D) Urea  
 (iii) Which compound gives violet colour with neutral ferric chloride solution?  
 A) Acetic acid                      B) Methylamine                      C) Monohydroxybenzene                      D) Ethyl alcohol
- (i) Correct IUPAC name of the following molecule is

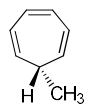


- A) (1R,2R)-Propanediol    B) (R)-1,2-Propanediol    C) (1S,2S)-Propanediol    D) (S)-1,2-Propanediol

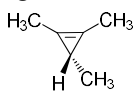
- (ii) Among the following molecules, the compound having most acidic hydrogen is



(i)



(ii)



(iii)



(iv)

- A) (i)                      B) (ii)                      C) (iii)                      D) iv

- (iii) What is Lucas reagent?

- A) A solution of sodium carbonate, sodium citrate and copper (II) sulphate  
 B)  $\text{ZnCl}_2$  in Conc. HCl    C) 2,4-Dinitrophenyl hydrazine    D) Ammonical  $\text{AgNO}_3$

- (i) Which statement is correct regarding inductive effect?  
 A) Inductive effect operates only in saturated compounds containing at least one polar sigma bond while electromeric effect occurs in unsaturated compounds containing at least one double or a triple bond which may or may not be polar in nature.  
 B) Inductive effect is a permanent effect and involves the mere displacement of sigma electrons while electromeric effect is a temporary one and involves the cleavage of a multiple bond with complete transfer of a shared pair of electrons to one of the bonded atoms.  
 C) Inductive effect does not require any outside attacking reagent for its operation while electromeric effect takes place only in the presence of an attacking reagent.  
 D) Above All  
 (ii) The following arrow indicates

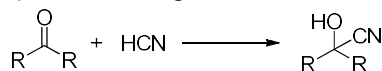


- A) Resonating structures    B) Equilibrium    C) Inductive effect    D) Reversible reaction

- (iii) A sample of pure (S)-2-butanol was placed in a 5.0 cm polarimeter tube. Using the D line of a sodium lamp, the observed rotation at 20 °C was  $\alpha = +104^\circ$ . The density of this compound is 0.312 g ml<sup>-1</sup>. What is the specific rotation of (S)-2-butanol?

- A) +104°    B) +208°    C) +666°    D) +333°

- Addition of sodiumcyanide to acetone (finally quench the reaction with dil.HCl) gives two structures **C** and **D** due to attack of cyanide on front or back face of the acetone molecule.  
 (a) Draw the structures of **C** and **D**    (b) Give the stereochemical relationship between **C** and **D**
- (i) In the organic chemistry lab two test tubes are labeled as maleic acid and fumaric acid. What would be your observation while adding  $\text{Br}_2$  in  $\text{CCl}_4$  to the test tubes containing maleic acid and fumaric acid?  
 A) Both maleic acid and fumaric acid can decolorizes bromine solution.  
 B) Maleic acid decolorizes bromine solution whereas fumaric acid cannot.  
 C) Fumaric acid decolorizes bromine solution whereas Maleic acid cannot.  
 D) Both maleic acid and fumaric acid **cannot** decolorizes bromine solution.  
 (ii) The rate of  $\text{S}_\text{N}2$  reaction depends upon the concentration of  
 A) Alkyl halide only    B) Base only    C) Both alkyl halide and base    D) None of the reactants  
 (iii) The following reaction is an example of .....

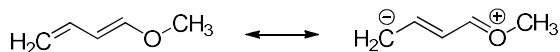


- A) Substitution    B) rearrangement    C) elimination    D) addition

PART B

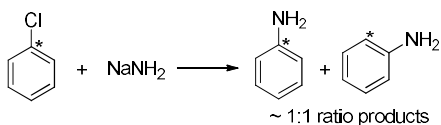
(Q7 to Q13: Attempt any SIX questions; Each Question carries 5 marks)

7. (i) The following equation is an example of



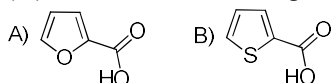
A) Inductive effect B) Electromeric effect C) Mesomeric effect D) Hyperconjugation

(ii) The reactive intermediate involved in the following reaction is

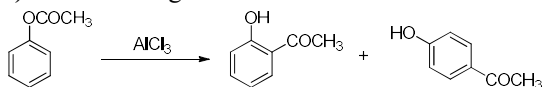


A) Radical B) Carbocation C) Carbanion D) Benzyne

(iii) Which of the following acid is more acidic? Justify your answer.

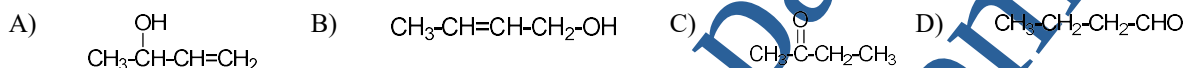


(iv) The following reaction is known as



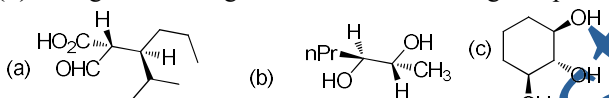
A) Fries rearrangement B) Hofmann rearrangement C) Curtius rearrangement D) Cope Rearrangement

(v) Compound X (C<sub>4</sub>H<sub>8</sub>O) forms a phenylhydrazone and gives negative results for iodoform test. Then the compound 'X' is

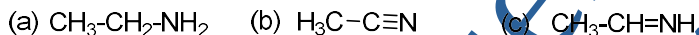


8. (i) What is the expected observed rotation of a 1.0x10<sup>-4</sup> M methanol solution of the potent anticancer drug Taxol? Specific rotation of this material: [α]<sub>D</sub><sup>20</sup> = -50.0° and the solution placed in a 10-cm-long Polarimeter cell. Taxol has a molecular weight of 853.93 g/mole. (2M)

(ii) Assign R/S configuration for the following compounds. (3M)



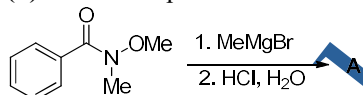
9. (i) Arrange the following nitrogen containing compounds in decreasing order of basicity. (1M)



(ii) Draw the structures for the following. (3M)

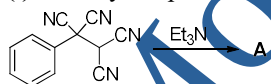


(ii) Predict the product A in the following reaction. (1M)

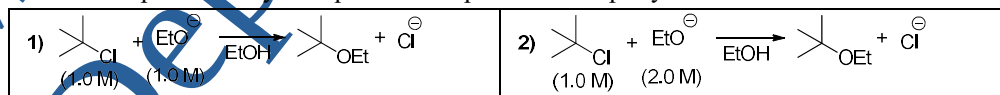


10. Enantiomers could not possible to separate by using normal separating techniques such as silica gel column chromatography. However, for example using (R,R)-(+)-Tartaric acid as a resolving agent we could able to resolve (R)-2-butanol and (S)-2-butanol from its racemic mixture. Give all the reactions involved in this resolution process.

11. (i) Identify the product A and propose a suitable mechanism for the following reaction. (2M)

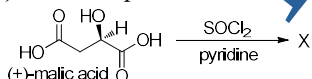


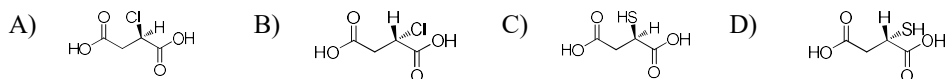
(ii) Which S<sub>N</sub>1 reaction of each pair would you expect to take place more rapidly?



A) Reaction 1 B) Reaction 2 C) Reaction 1 and 2 takes place with same rate D) None of the above

(iii) The final product obtained in the following reaction is X. What is X?





(iv) Identify the correct statements from the following.

- (i) In E2 reaction compound containing protium (H) reacts seven times as fast as the compound containing deuterium (D).  
 (ii) E1 elimination reaction proceeds in two steps.  
 (iii) Reactivity of R-X toward E2 reaction is  $3^\circ > 2^\circ > 1^\circ$   
 (iv) In dehydrohalogenation the preferred product is the alkene that has the less number of alkyl groups.

- A) i, iii      B) iii, ii      C) i, ii, iv      D) i, ii, iii

12. (i) What type of compounds responds to biuret test?

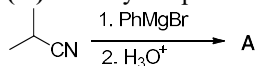
- A) Aliphatic diamide      B) Aromatic ketone      C) Aromatic diamide      D) Aliphatic ketone

(ii) Which one of the following does **not** give precipitate with ammonical cuprous chloride?

- A)  $\text{CH}_3\text{CH}_2\text{-C}\equiv\text{CH}$       B)  $\text{H}_3\text{C-C}\equiv\text{CH}$       C)  $\text{HC}\equiv\text{CH}$       D)  $\text{H}_3\text{C-C}\equiv\text{C-CH}_3$

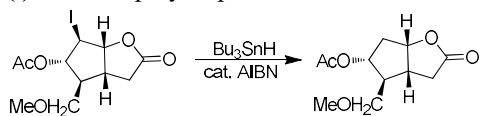
(iii) Predict the major product obtained from the bromination ( $\text{Br}_2$  in  $\text{CCl}_4$ ; 1 equiv.) of acetylenedicarboxylic acid.

(iv) Identify the product **A** in the following reaction.



(v) What kind of species is responsible for the appearance of blue colour in dry THF solvent in the presence of benzophenone and sodium?

13. (i) Write step by step mechanism for the following reaction. (3M)



(ii) Propose a suitable mechanism of Wittig reaction with an example. (2M)

### PART C

(Answer ANY ONE of the following questions, O14 or O15)

14. (a) In organic chemistry the curly arrow represents the ..... (fill in the blank). Indicate the formation of bonds in the following complex using curly arrow. (a)  $\text{Et}_2\text{OBF}_3$  (b)  $\text{BF}_3\text{Me}_2\text{S}$  (1.5M)

(b) Identify the electrophile and nucleophile from the following (a)  $\text{R}_3\text{N}$ ; (b)  $\text{R}_2\text{S}$ ; (c)  $\text{AlCl}_3$  (1.5M)

(c) How could you synthesize 1,2-diphenylethyne from 1,2-diphenylethene in two-step reaction? Propose a step-by-step mechanism. (3M)

(d) Draw the potential energy diagram of cyclohexane ring flip and explain relative stability and energies of all the major conformers involved in the process. (4M)

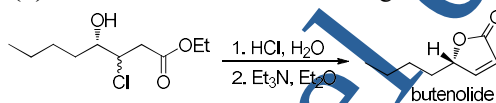
(e) An unknown alkene with the formula  $\text{C}_8\text{H}_{16}$  was found, on oxidation with hot basic permanganate, to yield a three-carbon carboxylic acid (propanoic acid) and a five-carbon carboxylic acid (pentanoic acid). What was the structure of this alkene?

(f) Propose a method to synthesize but-1-yne from acetylene. (1M)

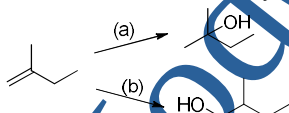
(OR)

15. (a) Draw the structures for the following. (a) (2S,3R)-3-bromo-2-butanol; (b) (4S,3S)-4-hydroxy-3-iodo-pentanoic acid (2M)

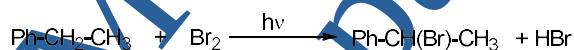
(b) Write the mechanism indicating all the steps clearly for the following transformation. (3M)



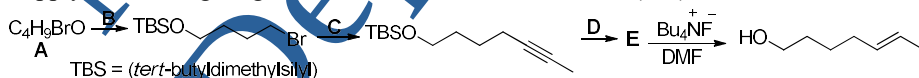
(c) What conditions would you use for each reaction? (2M)



(d) Propose a mechanism for the following substitution reaction. (3M)



(e) Supply the missing reagents and intermediates **B-E**. (2M)



TBS = (tert-butylidimethylsilyl)

\*\*\*\*\*

**CENTRAL UNIVERSITY OF RAJASTHAN**

**Department of Chemistry**

M.Sc. / Int. M.Sc. Chemistry; Semester III/ IX

End of Semester Examination; Date: 06/12/2019

**Time: 3 hr** CHM-622: Natural Products – Biosynthesis and Advances in Total Synthesis

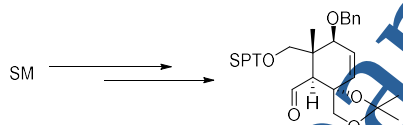
**Max. Marks: 60**

**PART-A (Attempt Q1)**

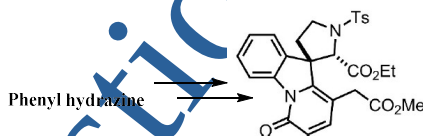
- Attempt the following: (5 M)
  - Which compound confers to 'For its molecular size it is the most complex substance known' as by mentioned Sir Robert Robinson?
  - Pelletier and Caventou reported the isolation of Strychnine in the year-----.
  - Taxol inhibits cell division by inhibition of microtubule formation. (**True/False**)
  - Taxol is isolated from plant-----.
  - Name the botanist involved in collection of plants as part of NCI program that led to discovery of Taxol.

**PART-B (Q2 to Q5: Attempt any THREE questions. Each Question carries 5 marks.)**

- Write the Retrosynthetic analysis of Strychnine.
- Write the synthesis for given aldehyde as delineated in Nicolaou's approach. Discuss the key reaction mechanisms and stereochemistry obtained at appropriate steps.

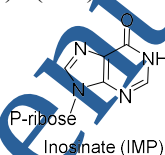


- Write the structure of Taxol with defined stereochemistry. Give key synthons required for the assembly of Taxol in Nicolaou's approach. (2.5 M)
  - Write a short note on history of Taxol and comment on its biological activity. (2.5 M)
- Complete the given synthetic scheme. Discuss the key reaction mechanisms and stereochemistry obtained at appropriate steps in this Woodward's approach toward Strychnine.

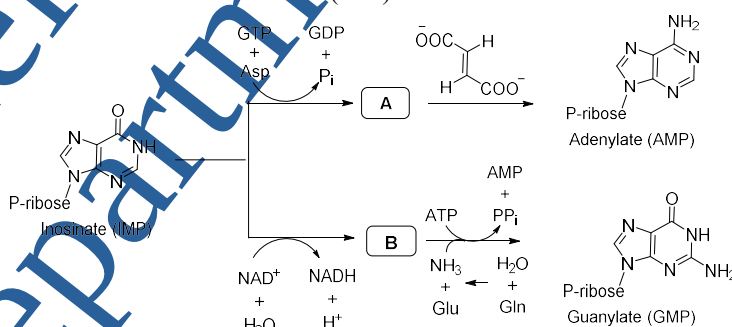


**PART-C (Q6 to Q15: Attempt any EIGHT questions. Each Question carries 5 marks.)**

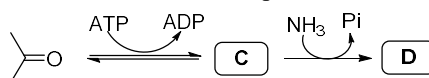
- Discuss the De novo purine biosynthesis of inosinate (IMP). (5 M)



- Find out the structure of A & B show in the below scheme. (3 M)

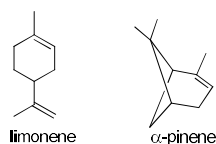


- A phosphorylation followed by displacement reaction has been depicted below. Identify the compounds C & D. (2 M)

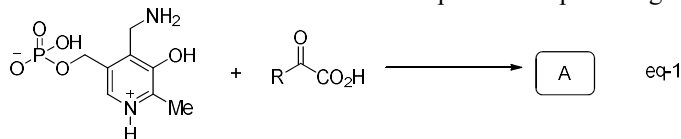


- Outline the biosynthesis of monoterpenes limonene and  $\alpha$ -pinene by mevalonic acid-isopentylpyrophosphate pathway. Chemical structures of limonene and  $\alpha$ -pinene are shown here for your reference. (5 M)

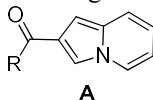




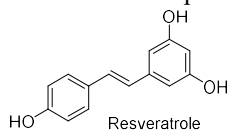
9. (i) Identify the product formed in the aminotransferase reaction shown in eq-1 with emphasizing reaction mechanism.



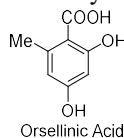
- (ii) Provide the retrosynthetic analysis and synthetic plan for the target molecule A.



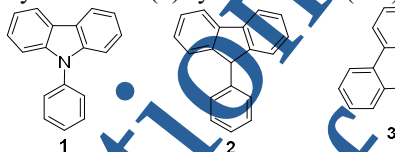
10. (i) Resveratrole (shown below) is a compound in red grape skins that has been suggested as one of the compounds in red wine that protects against heart disease. How do plants synthesize resveratrole? Explain with mechanism. (3 M)



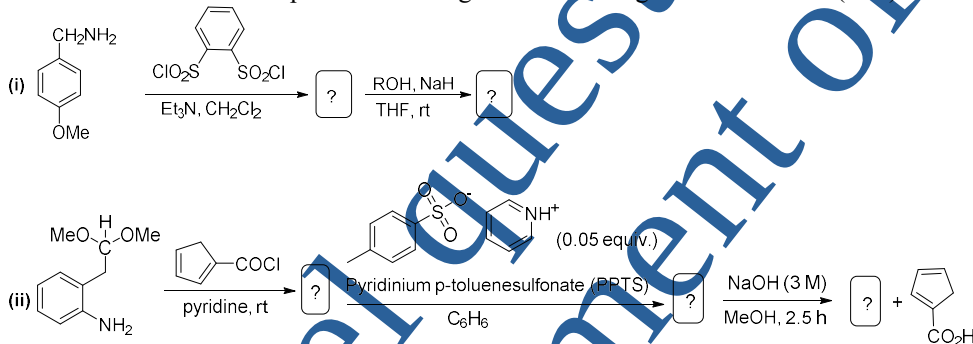
- (ii) Outline the biosynthesis of Orsellinic acid. (Hint: start from Acetyl-CoA and Malonyl-CoA). (2 M)



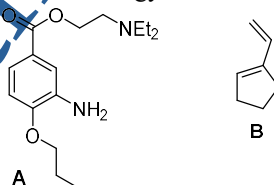
11. The following molecules (1, 2 & 3) could be accessed from single starting precursor dibenzothiophene. Identify the suitable coupling partners and propose a mechanism for the N-arylcarbazole (**1**) synthesis. (5M)



12. Write the structures of the products missing in the following transformations. (5 M)



13. Outline the appropriate retrosynthetic analysis and synthetic strategy to the following target materials (**A** & **B**). (3 + 2)



14. (i) Among *cis* & *trans*-1,2-dimethyl cyclohexane, which one could be resolvable at room temperature? Justify your answer. (2M)  
 (ii) Draw most stable conformation of 1,3-dihydroxy cyclohexane, 1,2-dichloro cyclohexane, and ((1S,3R)-1-(*tert*-butyl)-3-methyl)cyclohexane. (3M)

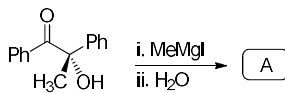
15. (i) Compare the rate of oxidation of *cis* & *trans*-4-(*tert*-butyl)cyclohexanol in the presence of  $\text{CrO}_3$ . Find the reason for it. (2.5 M)

- (ii) In compounds shown below, the rate of saponification reaction is faster with compound **B** than for compound **A**. Why?

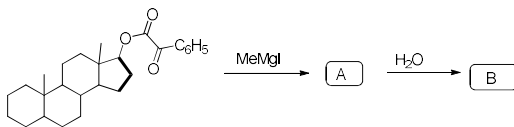


16. (i) Define the Curtin–Hammett principle. Prove it with an example of methylation of 8-methyl-8-azabicyclo[3.2.1]octane. (3M)  
 (ii) What is anomeric effect? Explain with an example. (2M)

17. (i) Write the structure of major stereoisomer that is obtained from the reaction shown below with the help of Cram's model. (sketch the appropriate Cram's model). (2M)



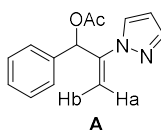
- (ii) Identify the major products **A** & **B** with emphasizing the stereochemistry using prelog's model. (sketch the appropriate Prelog's model). (3M)



18. (i) Illustrate the following with a suitable example. (3M)

- (a) Pseudo asymmetric centre  
 (b) Molecule having an achirotopic point but stereogenic.  
 (c) Topicity of faces

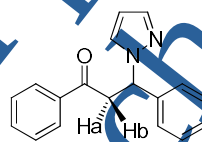
- (ii) What is the topic relation between Ha & Hb shown in the compound **A**. Predict the multiplicity of peaks that may be observed for Ha & Hb in <sup>1</sup>H NMR. (2M)



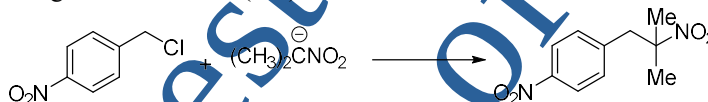
19. (i) Write a short note on the stereochemistry of ansa compounds and biphenyls with a suitable example. (3M)  
 (ii) Amines undergo rapid inter conversion whereas phosphorous compounds do not and enantiomers of phosphorous compounds could be isolable. Explain the reasons behind it. (2 M)

20. (i) What is the topic relation between Ha & Hb? On the basis of <sup>1</sup>H NMR data provided below, identify the approximate chemical shift value of Ha & Hb. (2M)

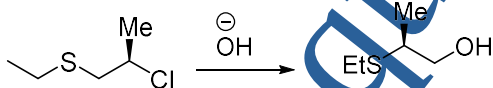
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.60–7.50 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 4H), 7.31–7.26 (m, 1H), 6.24 (s, 1H), 6.13 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.50 (dd, *J* = 8.4, 17.6 Hz, 1H), 3.65 (dd, *J* = 5.2, 17.6 Hz, 1H)



- (ii) Highly substituted carbon skeletons could not be accessible by normal S<sub>N</sub>2 process but it can be obtained by S<sub>RN</sub>1 reactions. Propose a mechanism for the following S<sub>RN</sub>1 reaction. (3M)



21. (i) Deduce the mechanism for the following transformation (considering stereochemical aspects). (2M)



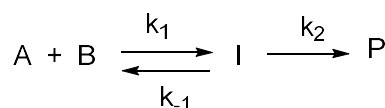
- (ii) Identify the products **A**, **B**, and **C** that are obtained in the following reactions and also emphasize on mechanism and stereochemistry of product formation. (3M)



22. (i) Isotopes can also be used to solve mechanistic problems that are non-kinetic. The following is an example. Deduce a suitable reaction mechanism for a reaction shown below. (3M)



- (ii) Derive the rate equation for the following general reaction on the basis of steady-state approximation. (2M)



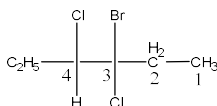
23. (i) Menthyl chloride and neomenthyl chloride undergo E2 elimination to provide the corresponding olefins. Identify all the possible olefins by clearly showing mechanism (chair conformation). (2M)



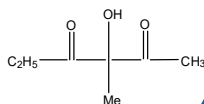
**PART A (Q1 to Q15: All questions are compulsory. Each Question carries 1 mark)**

1. The number of stereogenic centres in the following molecule is.....

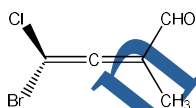
2. The C-2 carbon in the following molecule is achirotopic and non-stereogenic. (True / False)



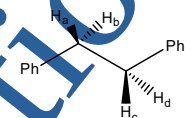
3. The maximum number of stereoisomers that are possible to be obtained by NaBH<sub>4</sub>-mediated reduction of both the carbonyl groups in the following molecule is .....



4. The absolute configuration of the following molecule is.....



5. The pro-R hydrogens in the following molecule are



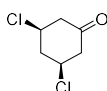
a) H<sub>a</sub> and H<sub>b</sub>

b) H<sub>a</sub> and H<sub>c</sub>

c) H<sub>b</sub> and H<sub>d</sub>

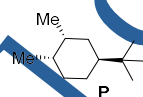
d) H<sub>b</sub> and H<sub>c</sub>

6. During reduction with NaBH<sub>4</sub>, the addition of hydride from the *re* face of the molecule shown below gives rise to *r*-alcohol.



(True / False)

7. In the preferred conformation of **P**

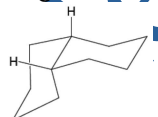


a) Both the methyl groups are equatorial

b) Only one methyl group equatorial

c) Both the methyl groups are axial

8. The number of extra gauche butane interactions in the following molecule as compared to two cyclohexane chair forms is



a) 2

b) 3

c) 4

d) 7

9. If..... contribution is zero than Yukawa-Tsuno equation is equal to Hammett equation!

10. Hammett studied .....deprotonation as the standard reaction to calculate substituent constant ( $\sigma$ ).

11. The reaction shown below for conversion of compound **C** to compound **D** can be classified as

a) E1 elimination reaction    b) E2 elimination reaction    c) E1CB elimination reaction

12. Based on Hammond postulate, a highly exothermic reaction will have.....transition state.

13. Write the structure of more stable product obtained from the reaction of PhCHO with (CH<sub>3</sub>)<sub>2</sub>C=CH(CH<sub>3</sub>) under hv condition.

14. Provide an example for chiral spirane.

15. The energy difference between the preferred conformations of *cis* & *trans*-1,2-dimethylcyclohexane is

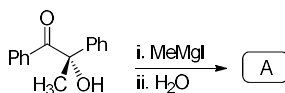
a) 2.7 kcal/mol    b) 1.8 kcal/mol    c) 3.6 kcal/mol

PART B (Q16 to Q27: Attempt **any NINE** questions. Each Question carries 5 marks.)

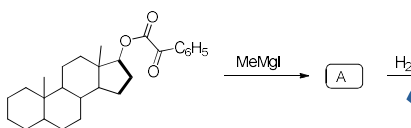
16. (i) Among *cis* & *trans*-1,2-dimethyl cyclohexane, which one could be resolvable at room temperature? Justify your answer. (2M)  
 (ii) Draw most stable conformation of 1,3-dihydroxy cyclohexane, 1,2-dichloro cyclohexane, and ((1*S*,3*R*)-1-(*tert*-butyl)-3-methyl)cyclohexane. (3M)
17. (i) Compare the rate of oxidation of *cis* & *trans*-4-(*tert*-butyl)cyclohexanol in the presence of CrO<sub>3</sub>. Find the reason for it. (2.5 M)  
 (ii) In compounds shown below, the rate of saponification reaction is faster with compound **A** than for compound **B**. Why? (2.5 M)



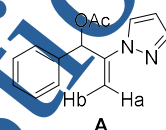
18. (i) Define the Curtin–Hammett principle. Prove it with an example of methylation of 8-methyl-8-azabicyclo[3.2.1]octane. (3M)  
 (ii) What is anomeric effect? Explain with an example. (2M)
19. (i) Write the structure of major stereoisomer that is obtained from the reaction shown below with the help of Cram's model. (sketch the appropriate Cram's model). (2M)



- (ii) Identify the major products **A** & **B** with emphasizing the stereochemistry using prelog's model. (sketch the appropriate Prelog's model). (3M)

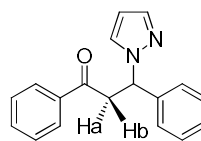


20. (i) Illustrate the following with a suitable example. (3M)  
 (d) Pseudo asymmetric centre  
 (e) Molecule having an achirotopic point but stereogenic.  
 (f) Topicity of faces  
 (ii) What is the topic relation between Ha & Hb shown in the compound **A**. Predict the multiplicity of peaks that may be observed for Ha & Hb in <sup>1</sup>H NMR. (2M)

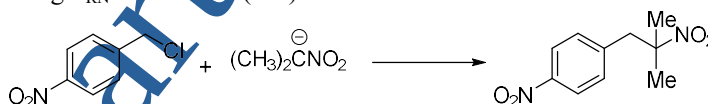


21. (i) Write a short note on the stereochemistry of ansa compounds and biphenyls with a suitable example. (3M)  
 (ii) Amines undergo rapid inter conversion whereas phosphorous compounds do not and enantiomers of phosphorous compounds could be isolable. Explain the reasons behind it. (2M)
22. (i) What is the topic relation between Ha & Hb? On the basis of <sup>1</sup>H NMR data provided below, identify the approximate chemical shift value of Ha & Hb. (2M)

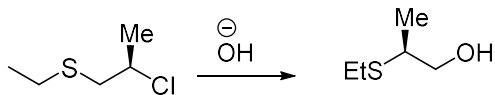
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.60–7.50 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 4H), 7.31–7.26 (m, 1H), 6.24 (s, 1H), 6.13 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.50 (dd, *J* = 8.4, 17.6 Hz, 1H), 3.65 (dd, *J* = 5.2, 17.6 Hz, 1H).



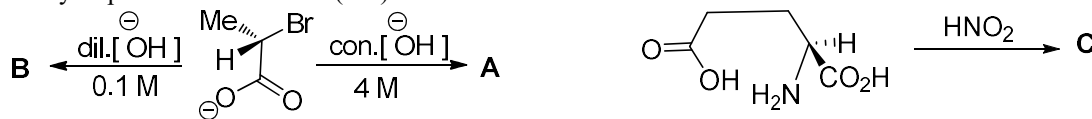
- (ii) Highly substituted carbon skeletons could not be accessible by normal S<sub>N</sub>2 process but it can be obtained by S<sub>RN</sub>1 reactions. Propose a mechanism for the following S<sub>RN</sub>1 reaction. (3M)



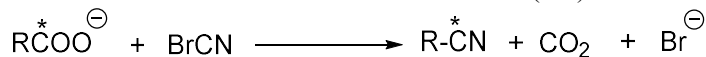
23. (i) Deduce the mechanism for the following transformation (considering stereochemical aspects). (2M)



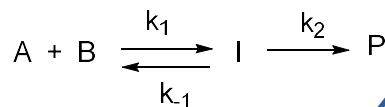
(ii) Identify the products **A**, **B**, and **C** that are obtained in the following reactions and also emphasize on mechanism and stereochemistry of product formation. (3M)



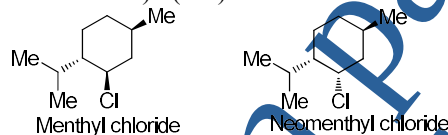
24. (i) Isotopes can also be used to solve mechanistic problems that are non-kinetic. The following is an example. Deduce a suitable reaction mechanism for a reaction shown below. (3M)



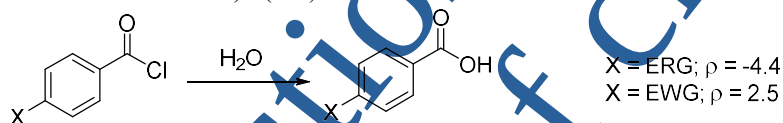
(ii) Derive the rate equation for the following general reaction on the basis of steady-state approximation. (2M)



25. (i) Menthyl chloride and neomenthyl chloride undergo E2 elimination to provide the corresponding olefins. Identify all the possible olefins by clearly showing mechanism (chair conformation). (2M)



(ii) Draw the Hammett plots and suggest the suitable mechanism for the reactions shown below on the basis of given data. ( $\rho$  values should be correlated to the mechanism). (3M)

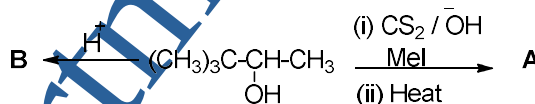


26. (i) What are Hammond postulate? Sketch the potential energy diagram of exothermic and endothermic reactions. (2M)

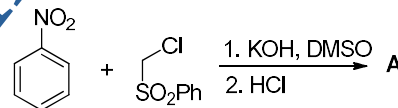
(ii) Reaction of  $O^{18}$  labelled deuterated propargyl alcohol **A** with  $SOCl_2$  provided the  $\alpha,\beta$ -unsaturated carbonyl compound **B** in which  $O^{18}$  labelled oxygen has not been incorporated while deuterium is incorporated. Keeping these observations, propose a mechanism for the reaction shown below. (Hint: [3,3] sigma tropic rearrangement). (3M)



27. (i) Identify the major product **A** and **B** obtained from the following transformation by clearly indicating transition states/intermediates. (2M)



(ii) What is vicarious nucleophilic substitution reaction? Identify the product **A** of reaction shown below and propose a step by step mechanism. (3M)



\*\*\*\*\*



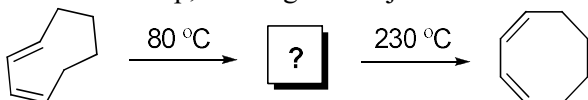
Time allowed: 3 h

Max marks: 60

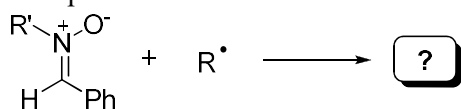
Answer ANY 12 questions

(5 marks × 12 = 60)

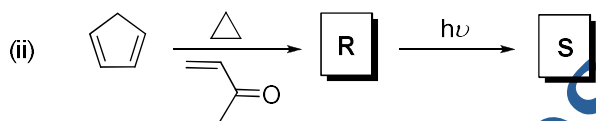
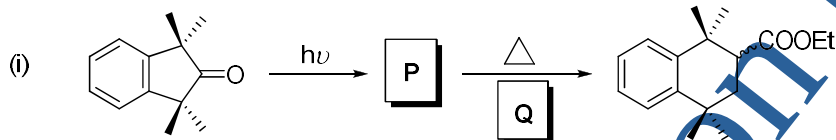
1. (i) Predict the product of the 1<sup>st</sup> step in the reaction shown below and classify it appropriately. Comment on the concerted nature of the 2<sup>nd</sup> step, offering a brief justification. (4)



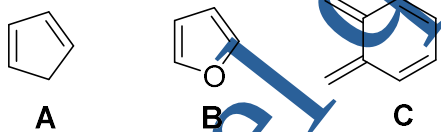
- (ii) Why are nitrones used as spin trapping reagents for the study of free radicals in EPR spectroscopy? Illustrate using the example of a reaction between the nitron shown below and any R<sup>•</sup>: (1)



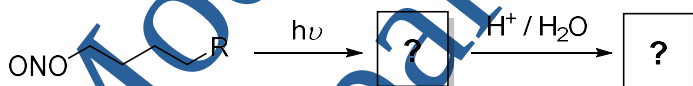
2. Identify P, Q, R & S in the following transformations:



3. (i) Predict the product (with stereochemistry) for the CON rotatory and DIS rotatory cyclisation of (2E,4Z,6E)-octa-2,4,6-triene; which path will be followed for a photochemical reaction?  
(ii) What will be the order of reactivity of A, B and C in the Diels-Alder reaction? Justify.

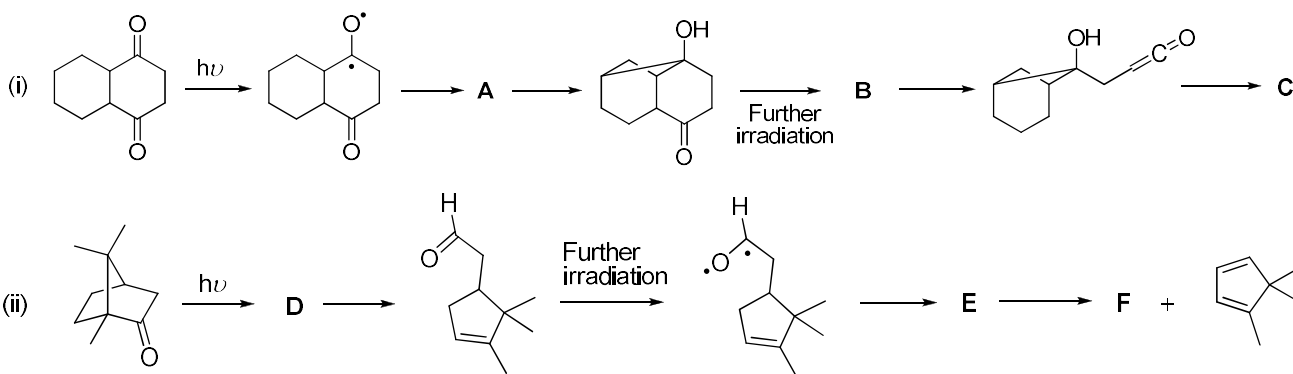


4. (i) Identify the missing intermediate & product of the reaction given below. Give an appropriate name and outline the mechanism of the reaction. (3)



- (ii) When a bottle of benzaldehyde is left open in the laboratory, some of it gets oxidised to benzoic acid. Outline a suitable mechanism for this process involving free radicals. (2)

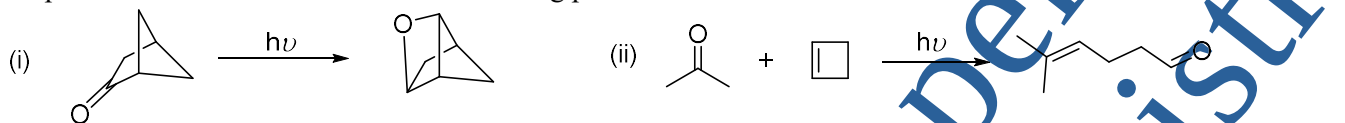
5. Identify the plausible intermediates/products which are missing in the reaction sequences depicted below, illustrating mechanisms for the formation and subsequent reactions of the same. Also name the reaction steps wherever appropriate.



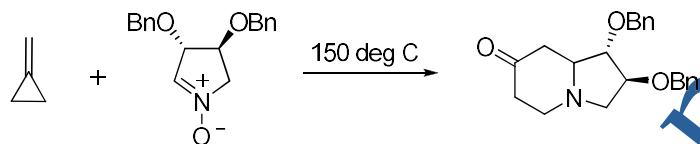
6. Account for the following with suitable justification and illustrations:

- (i) The extra stabilization offered by adjacent pi-donors is lower for a free radical as compared to a carbocation.  
 (ii) *o*-Methyl benzophenone is used in the plastics & dyes industry to protect light sensitive materials.

7. Propose a suitable mechanism for the following photochemical transformations:

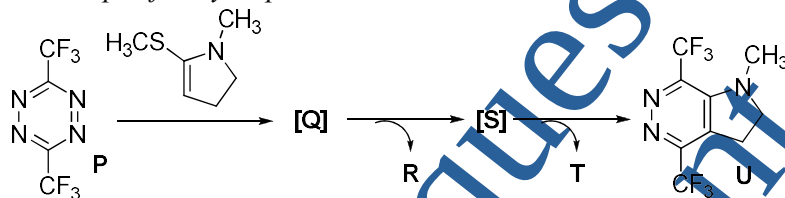


8. Propose a suitable mechanism for the reactions shown below:

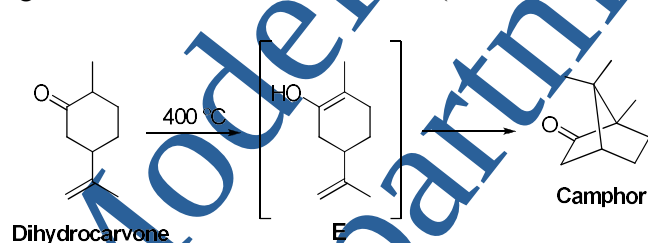


**Hints:** (i) [3+2] cycloaddition; (ii) weak O-N bond; (iii) fragmentation and recombination

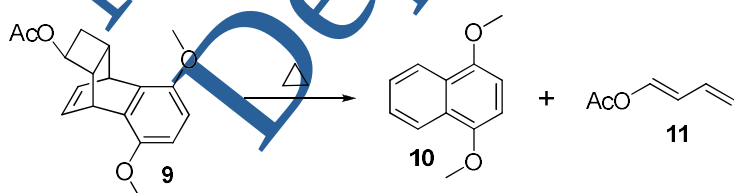
9. Identify **Q**, **R**, **S** & **T** in the following transformation. Classify the reactions involved in the conversion of **P** to **Q** and **Q** to **S** as specifically as possible.



10. (i) An effective synthetic method for the synthesis of camphor involves heating dihydrocarvone to 400 °C, which undergoes the reaction via the enol form ('E' in the scheme given below). Outline a suitable mechanism for this reaction. (3)

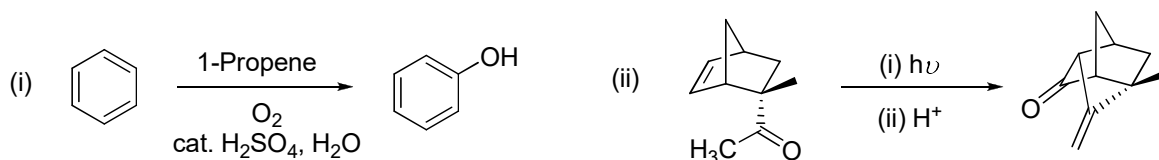


(ii) Outline a suitable mechanism for the following reaction (with the intermediates) (2)

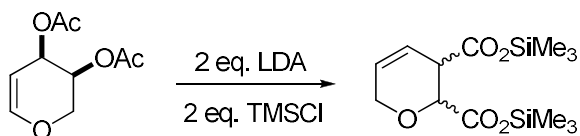


11. Outline a detailed mechanism for the reactions shown below:

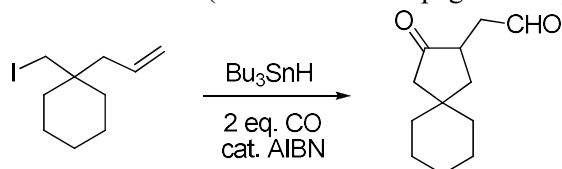
(3 + 2)



12. The following transformation takes place by one or more sigmatropic rearrangements. Identify the reactions and predict the stereochemistry of the substituents in the product.

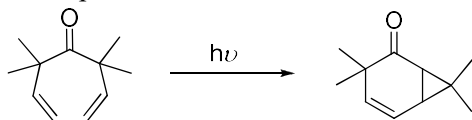


13. Outline a mechanism (Initiation and Propagation steps only) for the reaction given below:

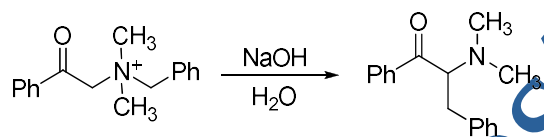


**Hint:** A free radical can form a bond with the C atom of carbon monoxide when taken as  $[O=C:]$

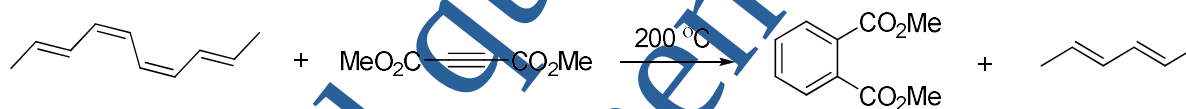
14. (i) Outline a plausible mechanism for the transformation shown below: (3)



- (ii) Elucidate the mechanism of the reaction given below and identify the name of this reaction. (2)



15. The following reaction takes place in 5 steps, with a combination of electrocyclic, cycloaddition and retro-cycloaddition reactions. Identify the steps and show that all the 5 steps obey the Woodward-Hoffmann rules:



**CENTRAL UNIVERSITY OF RAJASTHAN  
DEPARTMENT OF CHEMISTRY**

**End of Semester Examination (Online)**  
M.Sc. / Int. M.Sc. B.Ed. / Int. M.Sc. Chemistry; Semester III / IX

**Course Code: CHM-502**

**Course Name: Pericyclic Reactions and Photochemistry**

**Date: 21<sup>st</sup> Jan 2021**

**Time allowed: 3 hrs**

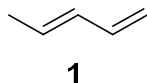
**Max marks: 60**

**PART A**

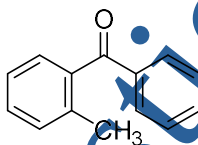
Answer **ANY 5** questions

(3 marks × 5 = 15)

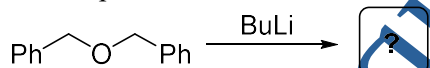
1. If you were asked to attribute the phenomenon of glow-in-the-dark toys to fluorescence or phosphorescence, which would you pick? Offer a justification based on excited states.
2. (i) Justify why *trans*-piperylene **1** is more reactive in the Diels-Alder reaction than the *cis* counterpart. (ii) How would the reactivity of **1** compare with that of cyclopentadiene as a diene for the Diels-Alder reaction? Justify your answer.



3. *o*-Substituted benzophenone (shown beside) is used as a light trapping source in the dye industry to protect the colours and sensitive materials from getting decomposed by light. Offer a mechanistic explanation for this application. What is the type of reaction involved?



4. Predict the product and illustrate the mechanism for the reaction given below; identify the named reaction.



5. Predict the product (with stereochemistry) for the CON rotatory and DIS rotatory cyclisation of (2*Z*,4*Z*,6*E*)-octa-2,4,6-triene. What can you comment on the reactivity of (2*Z*,4*E*,6*Z*)-octa-2,4,6-triene for undergoing a similar transformation?
6. Outline the initiation and propagation steps in the chain mechanism for the reaction shown below:

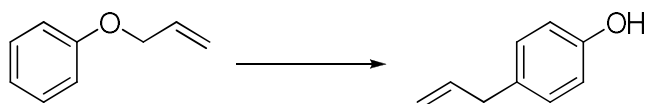


**PART B**

Answer **ANY 3** questions

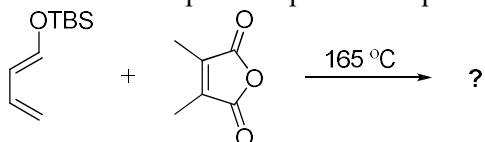
(15 marks × 3 = 45)

7. (i) A small amount of 4-allylphenol is often obtained during the Claisen rearrangement of allyl phenyl ether. Two different mechanisms involving sigmatropic migrations are possible for this transformation – one is a single step while the other is a 2-step mechanism. Illustrate both the possible mechanisms and determine which is the more likely of the two, with justification. (5)

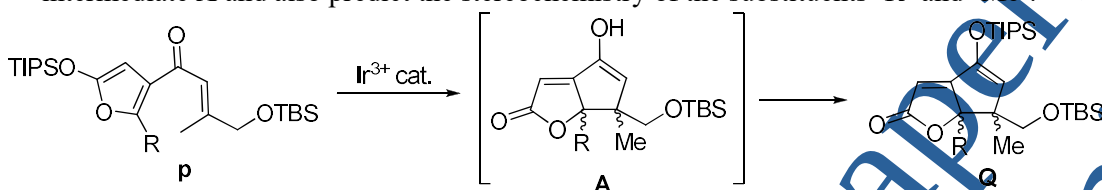


(ii) The structurally unique natural product Merrillactone A, identified as a potent neurotropic factor, has been synthesized by two separate groups – Danishefsky *et al* and Frontier *et al*. Interestingly, both routes involved a key pericyclic reaction as detailed below:

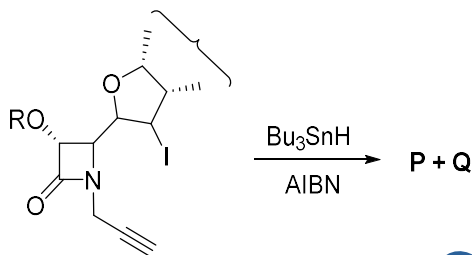
a) Danishefsky's synthesis (Ref. *J. Am. Chem. Soc.* **2002**, 124, 2080) started with the Diels-Alder reaction shown below. You are required to predict the product with the correct regio- and stereochemistry.



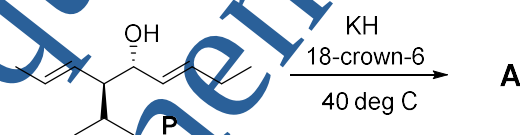
b) Frontier's synthesis (Ref. *J. Am. Chem. Soc.* **2007**, 129, 498) involved a Nazarov cyclization, involving the elimination of a silyl group, as shown below. You are required to outline a mechanism for the formation of intermediate **A** and also predict the stereochemistry of the substituents 'R' and 'Me'.



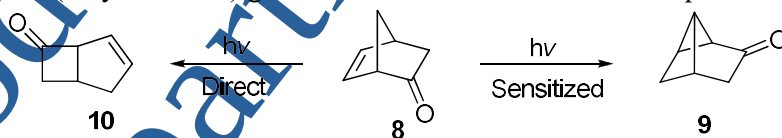
(iii) Jayanthi *et al* synthesized polycyclic  $\beta$ -lactams utilizing the intramolecular radical cyclisation of N-propargyl substituted azetidin-2-ones (Ref.: *Synlett* **2004**, 1249). Depict the structure of the 2 products **P** and **Q** and name them appropriately.



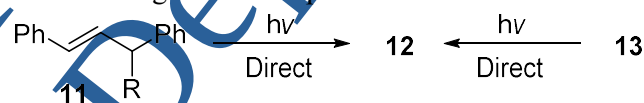
8. (i) Predict the product **A** with the correct stereochemistry in the reaction of **P** below, corroborating it with the appropriate Transition State(s) and brief comments.



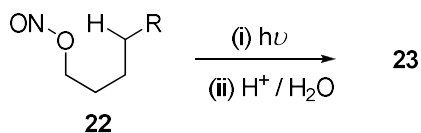
(ii) Outline the mechanism for the rearrangement of bicyclic ketone **8** to tricyclic ketone **9**. What mechanism/rearrangement (only the name) gives rise to the isomeric ketone **10** upon direct irradiation? (4)



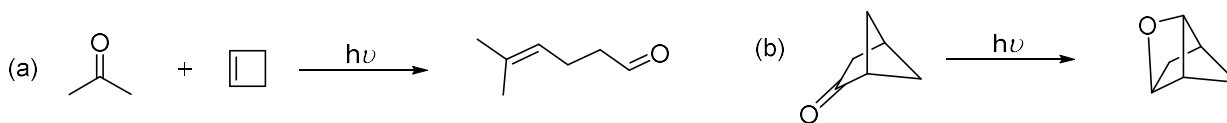
(iii) Based on a similar rearrangement as above, predict the structure of **12** in the reaction below. What other starting material **13** can be used to get the same product under similar conditions? (4)



9. (i) Predict the product of the reaction shown below, providing a suitable mechanism.

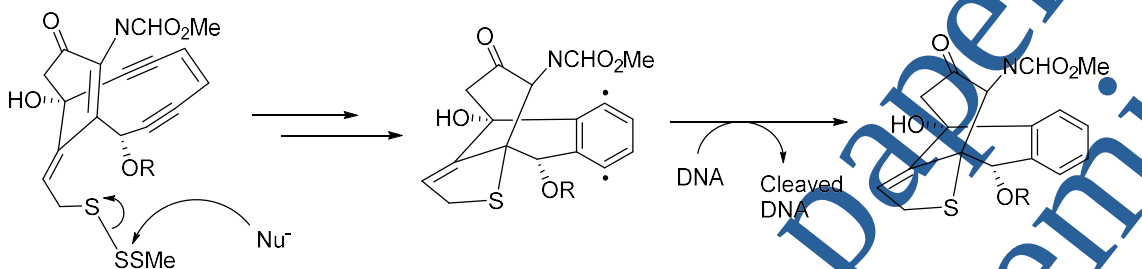


(ii) Propose a suitable mechanism for the following photochemical transformations: (5)



(iii) When a bottle of benzaldehyde is left open in the laboratory, some of it gets oxidised to benzoic acid. Outline a suitable mechanism for this process involving free radicals. (5)

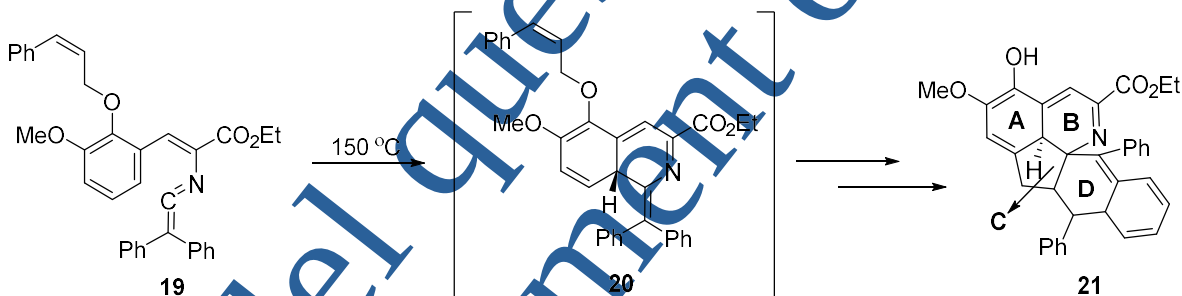
10. (i) Two types of carbocyclic ring formations are involved in the biological action of the drug calicheamicin, leading to the formation of the diradical species that effects a DNA cleavage. Identify both these cyclisations and illustrate the mechanism, clearly numbering the atoms involved. The first step – generation of a thiolate triggered by a Nu<sup>-</sup> – has been indicated. (6)



(ii) Molina and co-workers reported this domino reaction sequence (*J. Org. Chem.* 1991, 56, 4008) for the construction of complex ring systems. Provide a mechanism to account for this **multi-step transformation**. Name each of the steps appropriately, including the 1<sup>st</sup> step of the transformation. The 1<sup>st</sup> step, which leads to intermediate **20**, has been illustrated. (9)

**Hints:**

- Different types of pericyclic reactions are involved.
- The last step involves a double bond of one of the Ph groups in a pericyclic reaction, leading to the formation of ring C and ring D in a single step.





**Central University of Rajasthan**  
**Department: Chemistry**  
**Course Code: CHM-404**  
**(Group Theory and Molecular Spectroscopy)**



**End of Semester Examination (EoSE)**




**Date: 20-03-2021**

**Total marks: 60**

**Time: 14:00 – 17:00 hrs.**

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**Part-A**

Answer any 5 questions. Each question carries 3 marks (5 x 3 = 15)

1. Identify the point group of each of the following: (3 x 1 = 3)
- a)  b)  c) 
2. Arrange the following molecules categorically in "Abelian", "Non-abelian" and "cyclic" group:
- a) cis-dichloroethylene    b) cyclopropanol    c) trans-1,2-dichlorocyclopropane (1 x 3 = 3)
3. What kind of rotor of the following molecules (1 x 3 = 3)
- (a) a molecule mainly has  $4C_2$ ,  $1\sigma_h$ ,  $C_4$ ,  $4\sigma_v$  these symmetry elements  
(b) a molecule mainly has  $C_2$ ,  $1\sigma_h$ ,  $2\sigma_v$  these symmetry elements  
(c) a molecule mainly has  $5C_2$ ,  $1\sigma_h$ ,  $2\sigma_v$ ,  $3C_4$  these symmetry elements
4. What are the point group notation of the sub-groups in  $D_3$  point group? (1 x 3 = 3)
5. Arrange the following bonds in descending order based on the vibrational frequency and justify your answer.
- a) C-C    b) C-F    c) O-F    d) P-Cl (1 x 3 = 3)
6. Define the mutual exclusion principle. Among the following molecules which will satisfy this rule
- a) acetylene    b) sulphur dioxide    c) cyclobutane    d) benzene (3)

**Part-B**

Answer any 3 questions. Each question carries 15 marks (3 x 15 = 45)

7. (a) Construct the character table for a pyridine molecule and find out the number of IR vibrational, Microwave rotational mode and corresponding irreducible representation for the same. (13)
- (b) Identify the Mullikan notation for the following irreducible representation (2)

E	$C_n$	$nC_2$	i	$\sigma_h$
1	1	-1	-1	-1

8. (a). The internuclear distance of a  $^{12}\text{C}^{16}\text{O}$  molecule is  $1.13 \text{ \AA}$ . Calculate the angular velocity of this molecule in the first excited rotational level and find out the energy in *erg* (unit) for the transition  $J = 4$  to  $J = 5$ . (8)

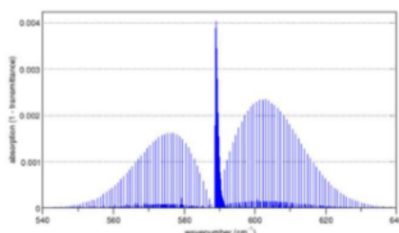
(b). What is the relation among three different moment of inertias ( $I_a$ ,  $I_b$  &  $I_c$ ) of the following molecules?

a)  $\text{PCl}_5$     b)  $\text{HNC}$     c)  $\text{CH}_2\text{Cl}_2$     d) sulfur chloride pentafluoride (1 x 4 = 4)

(c). If the reduced mass of a diatomic molecule is doubled without changing the force constant, then what happen to frequency. (3)

9.(a).  $\text{HCl}$  show instance absorption at  $2886\text{cm}^{-1}$ , a weaker one at  $5668\text{cm}^{-1}$  and very weak at  $8347\text{cm}^{-1}$ . Calculate the percentage of decrease of oscillation frequency of harmonic oscillator with respect to anharmonic oscillator at the first excited vibrational energy state. (8)

(b).



The above ro-vibrational spectra obtained for a molecule. What could be the possibilities of shape of this molecule? Justify your answer. (4)

(c). Let assume you have a molecule which exhibit three characteristic vibrations at the wavenumbers  $2200\text{cm}^{-1}$ ,  $1180\text{cm}^{-1}$  and  $585\text{cm}^{-1}$ . However, in the experimental result it was obtained three peaks appear around  $1195\text{cm}^{-1}$ ,  $1155\text{cm}^{-1}$  and  $2200\text{cm}^{-1}$ . Why the instrument is not giving the peaks at their respective position. (3)

10.(a). A  $20491\text{cm}^{-1}$  Laser light was used to excite  $^{16}\text{O}=\text{O}$  molecule to obtain Rotational Raman Spectra of  $\text{O}_2$  has 1<sup>st</sup> Stoke line at  $20479\text{cm}^{-1}$ . Find the bond length of the  $^{16}\text{O}=\text{O}$  molecule and next rotational stoke line position (3+3=6)

(b). Which type of vibrational spectroscopy technique (IR or Raman or both) would you use to measure the vibrational frequency of the following bonds:

a) The  $\text{C}=\text{C}$  symmetric stretching and bending for *trans*-1,2-dichloroethene molecule

b) The  $\text{C}=\text{O}$  stretch in  $\text{CO}$  (2+1=3)

(c). Draw the different polarizable ellipsoid structures for various mode for vibration of a  $\text{SO}_2$  molecule. (6)

Central University of Rajasthan  
Department: Chemistry  
Course Code: CHT-305 and ICHT-905:  
(Solid State, Surface and Material Chemistry)



End of Semester Examination (EoSE)

Date: 20-01-2021

Total marks: 60

Time: 10:00 – 13:00 hrs.

Part-A

Answer any 5 questions. Each question carries 3 marks (5 x 3 = 15)

1. What are the fundamental difference among “Crystal”, “Amorphous” and “Quasicrystal”. (3)
2. Draw the Stereogram of the given point group (222), (mm2), (mmm) individually. (3)
3. What is the effect of increasing temperature on an anti-ferro magnetic material? What is the main difference between soft and hard magnet? (2+1)
4. What is Quantum dots? For a particular Quantum dot system, the emission peak appears at 550, 600 and 650 nm for three different sizes of quantum dots. Arrange this quantum dot’s size based on their emission peak. (2+1)
5. How the temperature will vary with pressure for a specific adsorption process (3)
6. Calculate how long a hydrogen atom will remain on the surface of a solid at 298K if its desorption energy is:  
(a) 15 KJ mol<sup>-1</sup> (b) 150 KJ mol<sup>-1</sup>. Assume that  $\tau_0 = 0.1$ ps. (3)

Part-B

Answer any 3 questions. Each question carries 15 marks (3 x 15 = 45)

- 7.(a). What is the *intrinsic* and *extrinsic* semiconductor? Graphically represent how the temperature effect can lead to transform from intrinsic to extrinsic semiconductor. Why “*exhaustion*” range is so much important for device fabrication. (8)  
(b). Let’s assume you have a sample of TiO<sub>2</sub> nanotube on a glass surface. What kind of instruments you would use to determine surface roughness, morphology, and structure separately? Justify your answer. (7)
- 8.(a). Assuming a crystal structure having three-2 fold, two-4 fold, five-2 fold rotational axes, 8m, six-4 rotoinversion and eight-6 rotoinversion symmetries, Calculate the order of the point group. (6)  
(b). Identify the “Schonflies” notation from the given “Hermann-Mauguin” notation: i) 4/m, ii) 4 2 m, iii) 4/m 2/m 2/m, iv) 222 v) 4mm vi) mm2 (6)

(c). Find out the symbol of the "SPACE GROUP", considering the following information respectively

i) primitive unit cell contains one  $2_1$  screw axis and point group notation is  $2/m$ .

ii) body centered unit cell contains one  $4_2$  and one  $2_1$  screw axis and point group notation is  $422$ .

iii) face centered unit cell contains one diagonal glide plane, one glide plane along "a" axis and point group notation is  $mm2$ . (3)

9.(a). Explain about the concept of "DOMAIN" in ferro/ferri magnetic material. Explain the nature of the hysteresis of the plot magnetic flux density vs. magnetic field strength. (6)

(b). What do you mean by "PLANER DEFECT" and "BULK DEFECT" (4)

(c). Find out the "SHORT FORM" of "Hermann-Mauguin" notation of the given "Space group" notation and mention the meaning of each symbol in the respective space group.

i)  $I41/acd$  ii)  $Fd\bar{3}$  iii)  $P2/c$  iv)  $Cc$  v)  $I2_13$  (5)

10.(a). Briefly explain about the working principle of i) SEM (Scanning Electron Microscope), ii) TEM (Tunneling Electron Microscope) and iii) AFM (Atomic Force Microscope) (3 x 2 = 6)

(b). Define "Anti-ferroelectricity", "Pyroelectricity", "Piezoelectricity". (3)

(c). At  $0^\circ\text{C}$  and 1 atm pressure, the volume of  $\text{N}_2$  gas required to cover a sample of silica gel, is found to be  $130 \text{ cm}^3 \text{ gm}^{-1}$ . Calculate the surface area per gram of silica gel. (Area occupied by  $\text{N}_2$  molecule is  $0.162 \text{ (nm)}^2$ ) (6)

Central University of Rajasthan  
School of Chemical Sciences and Pharmacy  
Department of Chemistry  
M. Sc (Sem. I) & Int. M. Sc. B. Ed (Sem. I): End of Semester Examination

Course: CHM403 (Quantum chemistry)  
March 15, 2021

Maximum Marks: 60  
Time: 02:00 PM - 05:00 PM

**Part-A**                      **Answer any 5 questions out of 6**                      **Max. Marks: 15**

1. Are the following operators are Hermitian:  $i\left(\frac{d}{dx}\right)$ ,  $i\left(\frac{d^2}{dx^2}\right)$ . [3]
2. Explain why each of the following integrals must be zero, where the functions are hydrogenlike wave functions: (a)  $\langle 2p_1 | L_z | 3p_1 \rangle$ ; (b)  $\langle 3p_0 | L_z | 3p_0 \rangle$ . [3]
3. Prove that the degree of degeneracy of an energy level  $n$  in a Hydrogen atom is  $n^2$ ? [3]
4. Which of the following operators meet the requirements for a quantum-mechanical operator that is to represent a physical quantity: (a)  $( )^{1/2}$ ; (b)  $d/dx$ ; (c)  $d^2/dx^2$  [3]
5. The  $J = 0$  and  $J = 1$  transition for carbon monoxide ( $^{12}C^{16}O$ ) occurs at  $1.153 \times 10^5$  MHz. Calculate the bond length in carbon monoxide. No need to work out the numerical. Write the working equation, substitute the quantities and bring them into MKS units and leave it. [3]
6. Suppose that at time  $t'$  a hydrogen atom is in a nonstationary state with [3]

$$\Psi = \frac{1}{\sqrt{6}}(2p_1) - i\frac{1}{\sqrt{2}}(2p_0) - \frac{1}{\sqrt{3}}(3d_1)$$

then evaluate  $\langle \Psi | \hat{L}_z | \Psi \rangle$

**Part-B**                      **Answer any 3 questions out of 4**                      **Max. Marks: 45**

1. True or False. Question in bold Mandates an explanation or illustration through an example. [1]
  - (a) In both classical and quantum mechanics, knowledge of the present state of an isolated system allows its future state to be calculated [1]
  - (b) Every linear combination of eigenfunctions of the Hamiltonian is an eigenfunction of the Hamiltonian [1]
  - (c) If the state function is not an eigenfunction of the operator  $A$ , then a measurement of the property  $A$  might give a value that is one of the eigenvalues of  $A$  [1]
  - (d) If two Hermitian operators do not commute, then they cannot possess common complete set [1]
  - (e) If two Hermitian operators commute, then every eigenfunction of one must be an eigenfunction of the other [1]

- (f) The normalized state function  $\Psi$  is dimensionless (that is, has no units) [2]
- (g) The state function  $\Psi$  can never be negative [2]
- (h) The value zero is never allowed for an eigenvalue [2]
- (i) The wavelength of the particle-in-a-box absorption transition from quantum number  $n$  to  $n + 1$  decreases as the value of the quantum number  $n$  increases must be an eigenfunction of the other, [2]
- (j) If  $c$  is a constant, and if  $\langle cm|\hat{f}|n \rangle = \langle m|\hat{f}|cn \rangle$ , then  $c$  must be real [2]
2. (a) Describe the constraints that the Born interpretation puts on the acceptable wavefunction? [5]
- (b) Show that the expressions for kinetic energy and potential energy for a harmonic oscillator have the units of energy (joules). [3]
- (c) Derive the expression for Schrodinger equation of simple Harmonic oscillator? What are the approximations were made in solving the Schrodinger equation? Obtain the wavefunction of first excited state from the recursion relations and obtain the normalization constant? [6]
3. For  $He^+$  cation, answer the linked questions
- (a) Write the Hamiltonian for internal motion in hyperspherical coordinates [2]
- (b) Write the eigen functions and energies for two lowest levels [5]
- (c) Is  $\Psi_t = e^{-\alpha r^2}$  a valid function for the ground state wavefunction? Explain [3]
- (d) The parameter  $\alpha$  in the above question can be obtained by Variational theory. First set  $l = 0$  in the Hamiltonian. Evaluate [3]

$$W = \frac{\int_r \int_\theta \int_\phi \Psi_t^* H \Psi_t d\tau}{\int_r \int_\theta \int_\phi \Psi_t^* \Psi_t d\tau}$$

- (e) Find the  $\alpha$  at which  $W$  is minimum. Then  $\Psi_t = e^{-\alpha r^2}$  will be a solution to the Hamiltonian of  $He^+$ . [2]

4. In molecular spectroscopy, the nuclear motion (particularly vibrations) of a diatom is modelled by solving nuclear Schrödinger equation. The answer the following liked questions

(a) Write the generalized Hamiltonian for a diatom ? [2]

(b) Born-Öppenheimer approximation allow you to replace all electronic terms and nuclear repulsion terms with intermolecular potential energy surface. One such surface is Morse potential. [1]

$$V(x) = D [1 - e^{-\beta x}]^2$$

where  $D$  and  $\beta$  are constants.

Write the resultant Hamiltonian after replacing all electronic terms and nuclear repulsion terms with Morse potential.

(c) The separation of translational and internal degree of freedom was taught to you in the class. Apply the analogy here and separate translational and internal degree of freedom. Just be very brief, full derivation is not needed. Show the frame of reference, center of mass etc. [3]

(d) Expand  $e^{-\beta x}$  in power series around  $x$  and show that the Hamiltonian operator for the nuclear motion is [4]

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4 + \dots \quad (1)$$

Where  $a$ ,  $b$  and  $c$  are constants. Give the expression for the constants  $a$ ,  $b$  and  $c$  in terms of  $D$  and  $\beta$ .

(e) What is the ground state  $\Psi_0$  and its energy  $E_0$  for the Hamiltonian [2]

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + ax^2$$

(f) Non-degenerate perturbation theory allow you to treat the Hamiltonian Eq. 1 and get the correction to the energy of the ground state. Calculate the first order correction ( $E^1$ ) from  $bx^3 + cx^4$ . [3]

$$E^1 = \frac{\int_{-\infty}^{\infty} \Psi_0^* (bx^3 + cx^4) \Psi_0 dx}{\int_{-\infty}^{\infty} \Psi_0^* \Psi_0 dx}$$



$$\int x \sin bx \, dx = \frac{1}{b^2} \sin bx - \frac{x}{b} \cos bx \quad (\text{A.1})$$

$$\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin (2bx) \quad (\text{A.2})$$

$$\int x \sin^2 bx \, dx = \frac{x^2}{4} - \frac{x}{4b} \sin (2bx) - \frac{1}{8b^2} \cos (2bx) \quad (\text{A.3})$$

$$\int x^2 \sin^2 bx \, dx = \frac{x^3}{6} - \left( \frac{x^2}{4b} - \frac{1}{8b^3} \right) \sin (2bx) - \frac{x}{4b^2} \cos (2bx) \quad (\text{A.4})$$

$$\int x e^{bx} \, dx = \frac{e^{bx}}{b^2} (bx - 1) \quad (\text{A.5})$$

$$\int x^2 e^{bx} \, dx = e^{bx} \left( \frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3} \right) \quad (\text{A.6})$$

$$\int_0^{\infty} x^n e^{-qx} \, dx = \frac{n!}{q^{n+1}}, \quad n > -1, q > 0 \quad (\text{A.7})$$

$$\int_0^{\infty} e^{-bx^2} \, dx = \frac{1}{2} \left( \frac{\pi}{b} \right)^{1/2}, \quad b > 0 \quad (\text{A.8})$$

$$\int_0^{\infty} x^{2n} e^{-bx^2} \, dx = \frac{1 \cdot 3 \cdots (2n-1)}{2^{n+1}} \left( \frac{\pi}{b^{2n+1}} \right)^{1/2}, \quad b > 0, n = 1, 2, 3, \dots \quad (\text{A.9})$$

$$\int_t^{\infty} z^n e^{-az} \, dz = \frac{n!}{a^{n+1}} e^{-at} \left( 1 + at + \frac{a^2 t^2}{2!} + \cdots + \frac{a^n t^n}{n!} \right), \quad n = 0, 1, 2, \dots, a > 0 \quad (\text{A.10})$$

Figure 1: Some integrals may be useful to solve the problems quickly.

Central University of Rajasthan  
School of Chemical Sciences and Pharmacy  
Department of Chemistry  
Integrated M. Sc (Sem. III): End of Semester Examination

Course: ICHT-301 (Physical Chemistry-I)  
January 18, 2021

Maximum Marks: 60  
Time: 10:00 AM - 13:00 PM

**Part-A**                      **Answer any 5 questions out of 6**                      **Max. Marks: 15**

1. 100 Liters of ideal gas allowed to expand isothermally against constant pressure of 1 atm until its volume becomes doubled. Calculate the work done  $w$ , heat energy  $q$  and change in enthalpy  $\Delta H$ ? [3]

2. The Joule-Thomson coefficient of a gas can be expressed as [3]

$$\mu_{JT} = - \left( \frac{1}{C_p} \right) \left( \frac{\partial H}{\partial P} \right)_T$$

At 3000C in the pressure range 0 to 60 atm, the Joule-Thomson coefficient of  $N_2$  can be represented by the equation,  $\mu_{JT} = [0.0142 - 2.60 \times 10^{-4} P]$  K atm<sup>-1</sup>. Calculate  $H$  when ten moles of  $N_2$ , a van der Waals gas expands isothermally at 3000C from 45 atm to 40 atm. Given  $C_p = 7/2R$

3. Explain how the internal energy and entropy depends on temperature? [3]

4. What are exact and inexact differentials? What is their significance in Thermodynamics? [3]

5. Derive the expression for the efficiency of a reversible Carnot heat engine? [3]

6. What happens to the temperature (increases, decreases or unchanged) during an adiabatic expansion and give reason? [3]

**Part-B**                      **Answer any 3 questions out of 4**                      **Max. Marks: 45**

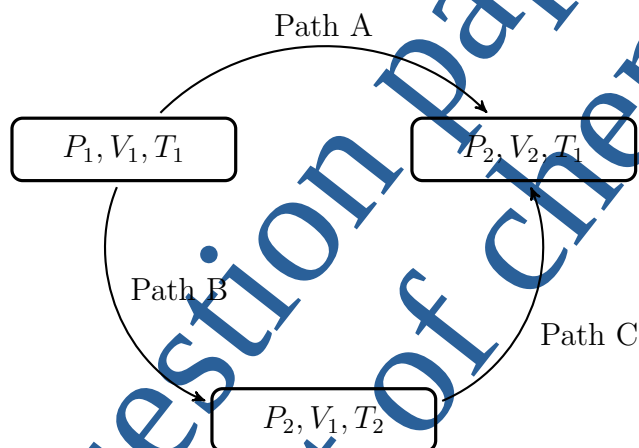
1. (a) The SI units of parameters **a** and **b** of the equation of state of a gas  $P = \frac{RTe^{\frac{a}{RTV_m}}}{V_m - b}$  are? [2]

(b) The critical constants of ethane are  $P_c = 28.40$  atm,  $V_c = 218$  cm<sup>3</sup> mol<sup>-1</sup>, and  $T_c = 155.4$  K. Calculate the parameters **a** and **b** of the equation of state  $P = \frac{RTe^{\frac{a}{RTV_m}}}{V_m - b}$ ? [3]

(c) A real gas behaves as a perfect gas when? [1]

- A. Temperature approaches zero
- B. Pressure approaches zero
- C. Both temperature and pressure approaches zero
- D. None of the above

- (d) If the state function of a gas is given by  $P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$  then calculate thermodynamical properties (a) isothermal reversible work done, (b) change in enthalpy, (c) change in entropy and (d) the internal pressure  $\pi_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$ . [9]
2. (a) An ideal gas in an initial state  $(P_1, V_1, T_1)$  converted into final state  $(P_2, V_2, T_1)$  through isothermal reversible process (Path A). The final state can also be achieved by (i) Path B: reversible process at constant volume to form an intermediate state  $(P_2, V_1, T_2)$  and (ii) Path C: conversion of the intermediate state  $(P_2, V_1, T_2)$  into the final state through another reversible process at constant pressure. Please see the figure given below. Calculate the  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta S$  for the paths A and (B+C)? [10]



- (b) How is the entropy calculated experimentally? [5]
3. (a) Derive the expressions for work done in reversible and irreversible expansion of an ideal gas. In which process, more work can be realized. Give your reasoning? [5]
- (b) The molar heat capacity of a substance is represented in the temperature range 298 K to 400 K by the empirical relation  $C_{p,m} = (14 + bT)$  J K<sup>-1</sup> mol<sup>-1</sup>, where  $b$  is a constant. The molar enthalpy change when the substance is heated from 300 K to 350 K is 2 kJ mol<sup>-1</sup>. Calculate the value of  $b$  upto two decimal places. [3]
- (c) The molar enthalpy of vaporization of benzene at its normal boiling point (80.09°C) is 30.72 kJ. mol<sup>-1</sup>. Assuming that  $\Delta_{\text{vap}}\bar{H}$  and  $\Delta_{\text{vap}}\bar{S}$  stay constant at their values at 80.09°C, calculate the value of  $\Delta_{\text{vap}}\bar{G}$  at 75.0°C, 80.09°C and 85.0°C. Interpret these results physically. [7]
4. (a) Discuss changes in the thermodynamical parameters such as chemical potential, enthalpy, entropy and heat capacity with Temperature in first order phase transitions. [5]
- (b) An ideal gas subjected to Joule-Thomson cooling. What will be the outcome, Explain? [3]

- (c) Calculate the residual entropy of carbon monoxide and nitrogen monoxide at near absolute temperatures? Explain the differences observed in both the systems. [4]
- (d) The enthalpy of vaporization of a liquid at its boiling point ( $T_b = 200\text{ K}$ ) is  $15.3\text{ kJ mol}^{-1}$ . If the molar volumes of the liquid and the vapor at  $200\text{ K}$  are  $110$  and  $12000\text{ cm}^3\text{ mol}^{-1}$  respectively, then calculate the slope of the liquid-vapor boundary up to two decimal places. (Note:  $1\text{ Pa} = 1\text{ Jm}^{-3}$ ) [3]

Model Question Papers  
Department of Chemistry