

Time: 3 Hours

#### VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST

(Autonomous & Residential) [Affiliated to Madurai Kamaraj University] **M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Core Subject : Second Semester : Paper – I

#### **ORGANIC CHEMISTRY – II**

Under CBCS – Credit 4

Max. Marks: 75

### $\underline{SECTION-A}$

#### **Answer ALL Questions :**

 $(10 \times 2 = 20)$ 

- 1. What are ambident nucleophiles? How will you prove that DMSO is an ambident nucleophile?
- 2. Allychloride reacts faster than n-propylchloride in  $S_N1$  reaction. Explain.
- 3. Why neomenthyl chloride undergoes rapid E2 elimination while in menthyl chloride this elimination is much slower?
- 4. What is Bredt's rule? Explain with an example.
- 5. What are ylides? How ylides are used in Wittig reaction?
- 6. Alkylation of enamine is carried out using tertiary alkyl halide. Why?
- 7. Illustrate the term Robinson annulation with an example.
- 8. Explain Ene reaction with a suitable example.
- 9. Sodium borohydride is mild reducing agent than lithium aluminium hydride. Comment on it.
- 10. Predict the product in the following



#### <u>SECTION – B</u>

#### **Answer ALL Questions :**

 $(5 \times 5 = 25)$ 

11. a) Narrate the effect of leaving group and solvent on nucleophilic substitution reactions.

#### (**OR**)

- b) How does nucleophilic substitution take place at vinylic carbon?Illustrate with examples.
- 12. a) Explain the  $E1_{C}B$  mechanism with evidences to support it.

## (**OR**)

b) Illustrate Hofmann and Saytzeff rules with suitable example.

13. a) Explain the mechanism of acid catalysed Mannich reaction.

#### (**OR**)

b) What is Wittig reaction? Discuss its mechanism.

14. a) Explain the mechanism of Birch reduction with suitable example.

#### (OR)

b) Discuss the mechanism of Stobbe condensation.

15.a) Write short notes on significance of Merrifield resin.

### (OR)

b) Give an account of Woodward and Prevost hydroxylation.

#### <u>SECTION – C</u>

## **Answer any THREE Questions :** $(3 \times 10 = 30)$ 16. a) Illustrate neighbouring group participation with any two examples. (6 + 4)b) Write briefly on substitution nucleophilic internal reactions. 17. a) Discuss in detail $S_E1$ and $S_E2$ mechanisms. (6 + 4)b) Write short notes on pyrolytic cis-elimination. 18. a) What is hydroboration? Give any two synthetic applications of the same with mechanism. (6 + 4)b) Write short notes on Reformatsky reaction. 19. Illustrate the following reactions with suitable mechanism. a) Shapiro reaction b) Wolf-Kishner reduction c) Dieckman condensation $(3 + 3\frac{1}{2} + 3\frac{1}{2})$ 20. Illustrate the applications of the following reagents involved in a) Lithiumdimethylcuprate (3) organic synthesis

organic synthesis.	a) Liununununneuryicupiate	(3)
b) Osmium tetroxide	c) Wilkinson's catalyst	$(3^{1/2} + 3^{1/2})$

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(Autonomous & Residential) [Affiliated to Madurai Kamaraj University] **M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Core Subject : Second Semester : Paper – II

**INORGANIC CHEMISTRY – II** 

Under CBCS – Credit 4 Time: **3** Hours

Max. Marks: 75

### <u>SECTION – A</u>

#### **Answer ALL Questions :**

 $(10 \times 2 = 20)$ 

- 1. Give the definition of electronic spectrum.
- 2. What is meant by term symbol?
- 3. Explain the classical magnetism.
- 4. State the Marcus theory.
- 5. Write a brief note on Wilkinson catalyst.
- 6. Illustrate the Wacker process.
- 7. What are metal carbonyls?
- 8. Write any one preparation of the metal nitrosyl.
- 9. What is meant by Q value?
- 10. Define the artificial radioactivity.

# <u>SECTION – B</u>

### **Answer ALL Questions :**

 $(5 \times 5 = 25)$ 

11.a) Briefly describe the charge transfer spectra.

### (**OR**)

b) Write about the nephelauxetic ratio and series.

12. a) Compare the dia, para, ferro and antiferromagnetism.

# (OR)

- b) Discuss in briefly the substitution reactions in octahedral complexes.
- 13.a) Write the sixteen and eighteen rule with examples.

### (**OR**)

b) Explain in briefly the metal carbyne complexes.

14.a) Discuss the structure and important reactions of metal nitrosyl.

## (OR)

- b) Write the preparation, bonding and structure of dioxygen complexes.
- 15.a) Distinguish between the nuclear fission and nuclear fusion reactions.

### (**OR**)

b) Give a brief account of synchrocyclotron.

# <u>SECTION – C</u>

### **Answer any THREE Questions :**

 $(3 \times 10 = 30)$ 

- 16. Draw and explain Tanabe-Suguno diagram of d<sup>6</sup> configuration with examples.
- 17. Discuss in detail the outer and inner sphere electron transfer reaction mechanisms with examples.
- 18. Describe about the synthesis, structure, bonding and reactivity of metallocene.
- 19. Write any five important reactions of metal carbonyls.
- 20. Explain the followingb) isotope dilution techniquec) radiometric titration

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### VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST

(Autonomous & Residential) [Affiliated to Madurai Kamaraj University] **M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Core Subject : Second Semester : Paper – III

PHYSICAL CHEMISTRY - II

Under CBCS – Credit 4

Max. Marks: 75

# <u>SECTION – A</u>

**Answer ALL Questions :** 

Time: 3 Hours

 $(10 \times 2 = 20)$ 

- 1. How can you apply variation method to hydrogen atom?
- 2. State and explain \Pauli exclusion principle.
- 3. What is force constant?
- 4. Define the term 'overtones'.
- 5. Write any two advantages of Raman spectroscopy over IR Spectroscopy.
- 6. What is the basic principle of photo acoustic spectroscopy (PAS).
- 7. Write any two differences between physisorption and chmisorption.
- 8. What is zeta potential?
- 9. Define i) IC ii) ISC
- 10. What is delayed fluorescence?

# <u>SECTION – B</u>

# Answer ALL Questions :

 $(5 \times 5 = 25)$ 

11.a) Explain LCAO and MO approximation of hydrogen molecule.

(OR)

b) Evaluate the charge density and bond order of butadiene molecule using HMO theory.

- 12. a) How will you determine the bond strength of the molecule using IR spectroscopy? (OR)
  - b) Draw and explain Fortrat diagram.
- 13.a) Explain the classical theory of Raman Spectroscopy. **(OR)** 
  - b) Explain the following i) Koopmans theoremii) Photo electric effect
- 14.a) Derive Langmuir adsorption isotherm and give the importance.

(**OR**)

- b) Write notes on  $T-jump \mbox{ and } P-jump \mbox{ methods}.$
- 15. a) Discuss the photochemical process in 'Photosynthesis'. (OR)
  - b) Explain radiative and non radiative transitions in photochemical Process.

## **SECTION – C**

## Answer any THREE Questions :

 $(3 \times 10 = 30)$ 

- 16. Explain the Huckel pi-electron theory of ethylene and benzene.
- 17. Explain the following i) Stark effect ii) Born – Oppenheimer approximation
- 18. Raman spectra and IR spectra complementary to each other. Substantiate with suitable examples.
- 19. What is enzyme catalysis? Explain Michaelis Menton kinetics and its significance.
- 20. Derive Stern Volmer equation and give on account an its application.





#### VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST (Autonomous & Residential) [Affiliated to Madurai Kamaraj University]

### M.Sc. Chemistry Degree (Semester) Examinations, April 2015

Part - III : Core Subject : Fourth Semester : Paper - I

#### **ORGANIC CHEMISTRY – IV**

Under CBCS – Credit 4

Time: 3 HoursMax. Marks: 75

## $\underline{SECTION-A}$

#### **<u>Answer ALL Questions</u>** :

 $(10 \times 2 = 20)$ 

- 1. Discuss a method to generate free radicals.
- 2. Explain Sandmeyer reaction with example.
- 3. What do you mean by a peptide bond?
- 4. Draw the structures of Vitamin  $A_1$  and thiamine.
- 5. What will happen when a steroid is heated with selenium at  $360^{\circ}$  C?
- 6. Give the conversion of cholestanylacetate to androsterone and epiandrosterone.
- 7. How enzymes are differ from catalysts?
- 8. What is Host-Guest Chemistry? Give example.
- 9. What is the need for electroorganic synthesis?
- 10. What are cyclodextrins? Mention its uses.

#### <u>SECTION – B</u>

#### **Answer ALL Questions :**

 $(5 \times 5 = 25)$ 

11.a) How will you prepare N-Bromo succinimide?Discuss the synthetic utility of it.

#### (**OR**)

- b) What is diazotization? Briefly mention the applications of diazonium salts.
- 12. a) Give the synthesis of chloramphenicol.

## (OR)

- b) Discuss the various chemical bonds involved in the protein structure.
- 13.a) Discuss the synthesis of testosterone from cholesterol.

#### (**OR**)

- b) Give the synthesis of progesterone from cholesterol.
- 14. a) Explain the role of cyclodextrins based enzyme modules.

## (**OR**)

- b) Write a short note on enzymatic isomerisation and rearrangement reactions.
- 15. a) Describe briefly the orientation effects in electro organic synthesis.

#### (**OR**)

b) Explain the nature of substrate and nature of solvent in electro organic synthesis.

#### SECTION – C

Answer any THREE Questions :	$(3 \times 10 = 30)$		
16. Explain the following reactions with mechanisms	: (4 + 3 + 3)		
i) Hofmann rearrangement.			
ii) Bayer-Villiger rearrangement.			
iii) Curtius rearrangement.			
17. Describe the synthesis of Vitamin C and Vitamin	n E. ( <b>5</b> + <b>5</b> )		
18. How will you prove	(5 + 5)		
i) the OH group in cholesterol is attached to the terminal			
6-membered ring.			
ii) the OH group and double bond in cholesterol are present in			
two different rings.			
19. i) Discuss Michaelis-Menton hypothesis.	(7 + 3)		
ii) Describe Fischer's lock and key model of en	zymes.		
20. Discuss in detail about	(5 + 5)		
i) Anodic conversions.			
ii) Cathodic conversions.			

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### VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST

(Autonomous & Residential) [Affiliated to Madurai Kamaraj University] **M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Core Subject : Fourth Semester : Paper – II

**INORGANIC CHEMISTRY – IV** 

Under CBCS – Credit 4 Time: **3** Hours

Max. Marks: 75

## $\underline{SECTION} - \underline{A}$

### **Answer ALL Questions :**

 $(10 \times 2 = 20)$ 

- 1. Write the significance of Stern Volmer plot.
- 2. Mention the role of Ru (II) polypyridine complexes in the study of quenching reactions.
- 3. What is Wilkinson's catalyst?
- 4. Write the principle involved in DTA technique.
- 5. Write the preparation and any two properties of thiocyanogen.
- 6. Name any four pseudohalogens.
- 7. What are the advantages of directional bond approach?
- 8. Give the uses of Pt based molecular squares.
- 9. Write the difference between fluorescence and phosphorescence.
- 10. What do you mean the term FRET?

# <u>SECTION – B</u>

# Answer ALL Questions :

 $(5 \times 5 = 25)$ 

11.a) Define and explain photophysical and photochemical reactions.

### (**OR**)

b) Write a short note on photosubstitution and LF photochemistry.

- 12. a) Explain paper chromatographic technique. (OR)b) Write a note on hydroformylation.
- 13.a) Write the preparation, properties of Caro's and Marshall's acid.

## (OR)

- b) Describe the structure and synthesis of Xenon fluorides.
- 14.a) What do you know about molecular triangles? (**OR**)
  - b) What are dinuclear macrocycles? Explain with an example.
- 15.a) Write a note on fluorescence quenching and enhancement.

# (OR)

b) Explain energy transfer and electron transfer involved in fluorescent chemical sensors.

# <u>SECTION – C</u>

# **Answer any THREE Questions :**

 $(3 \times 10 = 30)$ 

- 16. Explain the following: a) Reinecks salt actinometer
  b) Photoisomerisation
  c) Adamson's rule (3 + 3 + 4)
- 17. a) Explain Fischer-Tropsch process for the synthesis of gasolines.b) Write a note on nephelometry. (5 + 5)
- 18. a) Compare phosphorous and sulphur in terms of structure and reactivity. (5 + 5)
  - b) Write a method of preparation and two properties of peroxoborates and percarbonic acid.
- 19. Write a note on i) molecular cages ii) anion sensing
- 20. Name two amino acids which are fluoroscent in nature. Explain the metal containing fluorosensors for amino acids.





### VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST

(Autonomous & Residential) [Affiliated to Madurai Kamaraj University] **M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Core Subject : Fourth Semester : Paper – III

**PHYSICAL CHEMISTRY – IV** 

Under CBCS – Credit 4 Time: **3** Hours

Max. Marks: 75

# <u>SECTION – A</u>

<u>Answer ALL Questions</u> :

 $(10 \times 2 = 20)$ 

- 1. Explain the term interphase region.
- 2. What is a non-polarizable interface? Give an example.
- 3. Define over voltage.
- 4. What are the advantages of a dropping mercury electrode?
- 5. Define ensembles and micro-ensembles.
- 6. What is meant by population inversion? How is it achieved?
- 7. Differentiate between Fermions and Bosons.
- 8. What is photon gas?

**Answer ALL Questions :** 

- 9. What is condensation polymerization? Give an example.
- 10. Mention any two differences between emulsion and suspension polymerization.

# <u>SECTION – B</u>

 $(5 \times 5 = 25)$ 

11.a) Derive the Butler-Volmer relation and give its approximations.

(OR)

- b) Explain the following
- i) Tafel relation
- ii) Charge transfer resistance

- 12. a) Discuss the principle and applications of polorography. (OR)
  b) What are fuel cells? Explain the construction and working of H<sub>2</sub>-O<sub>2</sub> fuel cell.
- 13.a) Derive Boltzmann distribution law. (OR)
  - b) Write short notes on i) Micro-canonical and Canonical ensemble ii) Absolute negative kelvin temperature
- 14. a) Derive an expression for Fermi-Dirac statistics. (OR)
  - b) Describe the heat capacity of diatomic gases.
- 15.a) Explain the kinetics and mechanisms of free radical polymerization.

## (OR)

b) Write a note on Zeigler-Natta catalysis.

# **SECTION – C**

### **Answer any THREE Questions :**

 $(3 \times 10 = 30)$ 

- 16. Give an account of the Helmholtz, Guoy-Chapman and Stern models of electrical double layer.
- 17. Discuss the principle and instrumentation of cyclicvoltammetry.
- 18. Describe the thermodynamic properties from partition function and equilibrium constant.
- 19. Give an account of Einstein and Debye theories of heat capacities of solids.
- 20. a) Describe the viscosity method of determination of molecular weight of polymers.
  - b) Write a note on conducting polymers.



**33EP2A** 

# **VIVEKANANDA COLLEGE, TIRUVEDAKAM WEST** (Autonomous & Residential) [Affiliated to Madurai Kamaraj University] M.Sc. Chemistry Degree (Semester) Examinations, April 2015 Part – III : Elective Subject : Second Semester : Paper – I MEDICINAL AND PHARMACEUTICAL CHEMISTRY Under CBCS - Credit 5 Time: **3** Hours Max. Marks: 75 **SECTION – A Answer ALL Questions :** $(10 \times 2 = 20)$ 1. Define pharmacology. 2. What is meant by assay of drugs? 3. Write the uses of neem and tulsi. 4. Give one example for action of drug at extracellular site? 5. How chemotherapy helps in treating diseases? 6. Draw the structure of tetracyclins and its use as antibiotics. 7. What do you meant by normal blood pressure? 8. Account the HDL and LDL in blood. 9. In what ways iodine is used as therapeutic agent. 10. Why vitamins are essentials for human body? How are they classified? **SECTION – B Answer ALL Questions :** $(5 \times 5 = 25)$

11.a) Enumerate with examples the common air borne diseases, their control and treatment.

(**OR**)

b) Discuss the various routes for administration of drugs.

12.a) What are drug receptors and explain their biological responses?

## (OR)

- b) How drugs are classified?
- 13.a) Briefly discuss on narcotic analgesics.

### (**OR**)

b) Write the structural activity relationship of chloramphenicol.

14. a) Discuss antiarrhythmic agents.

#### (OR)

- b) Write a note on LSD.
- 15. a) How aluminium can be used as drug. Explain.

### (**OR**)

b) Discuss i) Metyrapone ii) Sulpho bromo phthalein sodium?

## **SECTION – C**

### **Answer any THREE Questions :**

16. Define the following term

- $(3 \times 10 = 30)$
- a) Pharmacognesy
  - b) Pharmacokinetics
  - c) Pharmacodynamics
- d) Antimetabolites
- 17. Bring out the importance of various plants and trees as medicine in India.
- 18. Compare local and general anaesthetic. Discuss with examples.
- 19. Explain the mechanism of barbiturates.
- 20. Write a note on organic pharmaceutical bases.



- 31. What happens to the oxidizing agent in an oxidation-reduction reaction?
  - a) It is oxidized as it gains electrons
  - b) It is oxidized as it loses electrons
  - c) It is reduced as it gains electrons
  - d) It is reduced as it loses electrons
- 32. In which substance does bromine have an oxidation number of +1?

a)  $Br_2$  b) HBr c)  $HBrO_2$  d)  $HBrO_2$ 

- 33. Which statement is true for an electrochemical cell?
  - a) Oxidation occurs at the anode only
  - b) Reduction occurs at the anode only
  - c) Oxidation occurs at both the anode and cathode
  - d) Reduction occurs at both the anode and cathode
- 34. A cycloaddition reaction occurs when
  - a) the number of rings in a compound increases
  - b) two different pi-bond-containing molecules react to form a cyclic compound
  - c) two cyclic products react d) the size of a ring increases
- 35. A symmetry-allowed pathway
  - a) leads to overlap of out-of-phase orbitals
  - b) leads to overlap of in-phase orbitals
  - c) allows only even-numbered orbitals
  - d) allows only odd-numbered orbitals

#### 36. Suprafacial bond formation is one in which

a) two pi bonds form from the same side of a pi systemb) two pi bonds form from opposite sides of a pi systemc) two sigma bonds form from opposite sides of a pi systemd) two sigma bonds form from the same side of a pi system

37. What are the units of the rate constant for a reaction in solution that has an overall reaction order of Two?

a)  $M^{-1}s^{-1}$  b)  $M^{-1}$  c)  $s^{-1}$  d)  $M s^{-1}$ 



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**M.Sc. Chemistry** Degree (Semester) Examinations, April 2015 Part – III : Elective Subject : Fourth Semester : Paper – II

#### CHEMISTRY FOR NATIONAL ELIGIBILITY TEST

Under CBCS – Credit 5 Time: **3** Hours

Max. Marks: **75** 

#### <u>SECTION – A</u>

### Answer ALL Questions :

 $(50 \times \frac{1}{2} = 25)$ 

- 1. Which of the following is smallest in size?a) F<sup>-</sup>b) Cl<sup>-</sup>c) Br<sup>-</sup>d) I<sup>-</sup>
- 2. An Element with high electronegativity has
  a) High IE and high EA
  b) High IE and low EA
  c) Low IE and high EA
  d) Low IE and low EA
- 3. Which of the following compounds will be optically active?
  a) propanoic acid
  b) 3-chloropropanoic acid
  c) 2-chloropropanoic acid
  d) 3-chloropropene
- 4. Optical isomers that are not mirror images are called
  a) diastereomers
  b) enantiomers
  c) metamers
  d) mesocompounds
- 5. Which one of the following priority is correct in the assigning of absolute configuration?
  - a) Br < Cl < COOH < Hc) COOH > Br > Cl > Hd) Br > Cl > COOH > H
- 6. Which of the following correctly lists the conformations of cyclohexane in order of increasing energy?
  a) chair < boat < twist < half-chair</li>
  b) half-chair < boat < twist < chair</li>
  c) chair < twist < half-chair < boat</li>
  d) chair < twist < boat < half-chair</li>

- 7. The hybridization of PCl<sub>5</sub> is a)  $sp^3$  b)  $sp^3d$  c)  $sp^2$  d) sp
- 8. The term symbol for  $d^3$  state is a)  ${}^{3}F$  b)  ${}^{4}F$  c)  ${}^{2}D$  d)  ${}^{3}D$
- 9. Schordinger wave equation applicable only \_\_\_\_\_\_ electron system.

a) one b) many c) two d) not applicable for electrons

- 10. The IUPAC Name of this compound is
  - a) 2-Bromo-4-methylpentaneb) 2-Methyl-4-bromopentane
  - c) 2-Methyl-2-bromopentane





- 11. Which of the following is called as Caro's acid?a) H<sub>2</sub>SO<sub>4</sub>b) H<sub>2</sub>SO<sub>3</sub>c) H<sub>2</sub>SO<sub>5</sub>d) H<sub>2</sub>SO<sub>2</sub>
- 12. Which of the following symmetry element is associated with? a) C b) C<sub>2</sub> c) S<sub>n</sub> d)  $\sigma_n$
- 13. The reference point of delta scale of PMR spectrum is based ona) TMSb) CCl<sub>4</sub>c) CSd) cyclohexane
- 14. In a potentiometric titration accurate end point determination is possible by pointing volume of titrant against a) Electrode potential b) E/V c)  $\Delta E /\Delta V$  d)  $\Delta^2 e /\Delta V^2$
- 15. The STYX code for diborane a) 2020 b) 2200 c) 2002 d) 0220
- 16. One of the modern methods of studying free radical isa) IR spectrab) UV spectrac) CIDNPd) Microwave spectra
- 17. Which is an indicator of air quality?a) Lichens b) Moss c) Rhizopus d) Virus
- 18. The result of electrophilic addition to enones appears to be a/an \_\_\_\_\_\_ to C=C.
  - a) Markownikoff additionb) Anti-Markownikoff additionc) Clemmensen reductiond) Wolff Kishner reduction

- 19. The molecules of  $H_2O$  belongs to the point group of a) D<sub>4</sub> b)  $C_2V$ c)  $C_3V$ d)  $C_3$ 20. Which of the following is a hard acid? b)  $Cu^+$ a) Li<sup>+</sup> c)  $Ag^+$ d) Au<sup>+</sup> 21. Lanthanide are separated by \_\_\_\_\_ technique. b) HPLC a) Ion exchange c) Flash Chromatography d) TLC 22. Which one of the following obey 18 electron rule a) FeCO<sub>5</sub> b) CrCO<sub>5</sub> c) VCO<sub>6</sub> d) FeCO<sub>4</sub> 23. Wilkinson's catalysed reaction. a) Reduction b) Oxidation c) Hydrolysis d) Elimination 24. The entropy of pure crystalline is a) 3 b) 0 c) 1 d) 2 25. Thermal flask is an example for a) Isolated system b) open system c) closed system d) none of these 26. In the Kinetic theory gases, the molecular collision is c) both a and bd) none of these b) Non elastic a) Elastic 27. Cis-2-amino cyclohexanol reacts with nitrous acid gives \_\_\_\_\_ product a) Aldehyde b) ketone c) alcohol d) ester 28. Which one of the following act as protecting group a) Umpolung b) LDA c) SeO2 d) DDO 29. Which one of the following reagents exhibit selective reduction of aldehyde and ketone a) Sodium borohydride b) sodium cyano borohydride c)  $Pd/H_2$ d) SnBu<sub>3</sub>H
- 30. Pick out the reagent for cis-hydroxylation of olefinsa) OSO4b) DCCc) LDAd) AlCl3

- 38. As the temperature of a reaction is increased, the rate of the reaction increases because the a) reactant molecules collide with greater energy b) reactant molecules collide less frequently c) reactant molecules collide less frequently and with greater d) activation energy is lowered energy 39. The cell potential,  $E^{\circ}$ , for an oxidation-reduction reaction was found to equal 1. What can be said b) endothermic a) equilibrium d) spontaneous c) nonspontaneous. 40. Consider the reaction in which nitric oxide is oxidized to nitrogen dioxide  $((2NO_2(g)+O_2(g)))$  2NO<sub>2</sub>(g)), for which the rate law is =  $[NO]^2[O_2]$ .if this reaction takes place in a sealed vessel and the partial pressure of nitric oxide is doubled, what effect would this have on the rate of the reaction? a) The reaction rate would triple b) The reaction rate would double c) The reaction rate would quadruple d) there would be no effect on the reaction rate 41. <sup>1</sup>H NMR spectrum of H-D (I for  ${}^{2}D = 1$ ) is, a) Singlet b) doublet d) quartet c) triplet 42. The more intensed IR absorption band will arise for the bond c) C-Br a) C-F b) C-Cl d) C-I 43. In the broad decoupled <sup>13</sup>C NMR spectrum, the number of signals appearing for the following pyrenoid (A) is, a) eight d) five b) sixteen c) ten 44. The molar absorptivity at  $\lambda_{max}$  is maximum for
  - a)  $[Mn(H_2O)_6]^{2+}$  b)  $[MnO_4]^-$  c)  $[Co(H_2O)_6]^{2+}$  d)  $[CoCl_4]^{2-}$

- 45. <sup>31</sup>P NMR of P<sub>4</sub>S<sub>3</sub> shows (I for <sup>31</sup>P =1/2), a) one signal b) two signals c) three signals d) zero
- 46. Of the following ions, which will show highest LMCT absorption maximum (λ<sub>max</sub>)?
  a) VO4<sup>3-</sup> b) CrO4<sup>3-</sup> c) MnO4<sup>-</sup> d) All show same LMCT band
- 47. Which among the following gases will be EPR active? a) O<sub>2</sub> b) N<sub>2</sub> c) CO d) F<sub>2</sub>
- 48. Fe<sub>2</sub>(CO)<sub>9</sub> obeys EAN rule and it shows howmany v<sub>CO</sub> IR peak(s)?a) Oneb) twoc) threed) nine
- 49. <sup>1</sup>H NMR of 2-butyne gives,a) one signal b) two signals c) three signals d) four signals
- 50. <sup>19</sup>F nmr of ClF<sub>3</sub> will show
  a) a doublet and a triplet
  b) singlet
  c) quartet
  d) two doublets

### <u>SECTION – B</u>

**Answer ALL Questions :** 

 $(10 \times 5 = 50)$ 

51. a) Write the various postulates of quantum mechanics.

#### (**OR**)

- b) An electron is confined in 1-D box of length 1A°. Calculate its ground state energy in electron volts.
- 52. a) With the help of MO diagram explain why
  - i) the bond order in  $N_2^+$  ion less than that in  $N_2$  molecule whereas the bond order in  $O_2^+$  is greater than that in  $O_2$ molecule.
  - ii) the bond length of  $CO^+$  is larger than that of CO.

#### (**OR**)

- b) i) Draw the most stable conformation of trans-1,2-dimethylcyclohexane.
  - ii) Draw the most stable conformation of cis-1,2-dimethylcyclohexane.

53. a) Give the product of each of the following reactions.



- b) Compare Raman and IR spectroscopy.
- 54. a) Name the following reaction and explain the mechanism.



#### (OR)

- b) Derive expressions for moment of inertia and bond length of a diatomic molecule.
- 55. a) Write the Products of reaction of cis and Trans amino cyclohexanol with nitrous Acid. Are products same or different explain?

#### (**OR**)

- b) Explain the synthetic applications of LiAH<sub>4</sub>.
- 56. a) Write short notes on Le Chatelier Principle.

#### (**OR**)

b) Discuss the features of Kinetic theory of Gases.

- 57. a) Iron rust more in the presence of water. Explain by writing redox equations and discuss the mechanism of rusting of iron how it is related with oxidation and reduction.
  - b) Discuss in detail about the experimental setup and applications of cyclic voltammetric technique.
- 58. a) Explain electrocyclization reactions with example.

(**OR**)

- b) Briefly state the meaning of each of the following terms, giving an example for each.
  - i) [4 + 2] cycloaddition

ii) [3,3] sigmatropic rearrangement

- iii) ene reaction.
- 59. a) Discuss the Mössbauer spectra of  $K_4[Fe(CN)_6]$ .3H<sub>2</sub>O and  $K_3[Fe(CN)_6]$ .

(**OR**)

b)  $Rh_4(CO)_{12}$  obeys EAN rule and shows two  $v_{CO}$  IR peaks, one in the range of 2044-2074 cm<sup>-1</sup> and another at 1886 cm<sup>-1</sup> with the intensity ratio of 3:1. Predict the structure of the compound.

60. a) Arrange the following metal carbonyls in their increasing order of

carbonyl stretching frequency ( $v_{CO}$ ) and give justification.

 $[Mn(CO)_6]^+, [V(CO)_6]^-, Ti(CO)_6]^{2-}, [Co(CO)_6]$ 

(**OR**)

b) Prove the fluxional behaviour of PF<sub>5</sub> molecule by using <sup>19</sup>F NMR.

