2 0 1 6

(6th Semester)

CHEMISTRY

NINTH PAPER

Course No. : CHEM–361

(Organic Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks for the questions

1. *(a)* Explain Franck-Condon principle. 3

(b) Explain the following : 4

   (i) Fluorescence

   (ii) Phosphorescence

OR

2. *(a)* Discuss Jablonski diagram. 3

(b) Discuss the following with example : 2+2=4

   (i) Photoreduction

   (ii) Norrish type-I reaction

3. *(a)* Discuss the process of conrotatory ring closure for 1,6-disubstituted 1,3,5-hexatriene using FMO method. 3

(b) With the help of FMO, show that $[_s^4 \quad _s^2]$ cycloaddition reaction is thermally allowed process. 3

(c) What are dienophiles? 1

OR

4. *(a)* Discuss Woodward-Hofmann rule for electrocyclic reaction. 3

(b) Discuss the suprafacial and antarafacial mode of cycloaddition in pericyclic reaction using suitable example. 4

5. *(a)* Discuss with chemical reaction, the synthesis of—

   (i) thioether;

   (ii) sulphaguanidine. 4

(3)

(b) Discuss the 1,3-diaxial interaction in the case of—

(i) 1,3-dimethylcyclohexane;

(ii) 1,5-dimethylcyclohexane.   3

OR

6. (a) Complete the following reactions :   3

(i) Sulphonic acid + Br_2 /Fe

(ii) Sulphonic acid + HNO_3 H_2SO_4

(iii) Sulphonic acid + H_2SO_4 (oleum)

(b) Write all the possible isomers of 1,3-dimethylcyclohexane.   3

(c) Write one formation of thiol.   1

7. (a) Discuss with mechanism the reaction of—

(i) aldol condensation reaction;

(ii) Wittig reaction.   4

(b) Discuss the process of biochemical oxidation in organic synthesis.   3

OR

8. (a) Discuss the preparation of 2-chloro-N-aryl anthranilic acid from Green preparation process.   3

(4)

(b) Explain with mechanism Michael addition.   4

9. (a) Discuss the following in brief :   3

(i) Base peak in mass spectroscopy

(ii) Molecular ion peak

(iii) Metastable ion

(b) What do you understand by shielding and deshielding of protons in NMR?   2

(c) Define chemical shift.   2

OR

10. (a) Discuss the fragmentation pattern of 3,3-dimethylheptane.   3

(b) Predict the chemical shift for ethyl acetate and 1,1,2-tribromoethane.   2

(c) What do you understand by coupling constant?   2

★ ★ ★

Subject Code : CHEM/VI/09

Booklet No. A

Date Stamp ....

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INSTRUCTIONS TO CANDIDATES

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3. **While answering the questions of this booklet, any cutting, erasing, over-writing or furnishing more than one answer is prohibited. Any rough work, if required, should be done only on the main Answer Book. Instructions given in each question should be followed for answering that question only.**

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2 0 1 6

(6th Semester)

CHEMISTRY

NINTH PAPER

Course No. : CHEM–361

(Organic Chemistry—III)

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided for it :   1×5=5

1. Photosensitization is the process where

   (a) the photoexcited molecule expends its energy in exciting another molecule   (   )

   (b) the photoexcited molecule absorbs extra energy from another molecule   (   )

   (c) the   photoexcited   molecule decomposes   (   )

   (d) None of the above   (   )

(2)

2. Dienes have

(a) two π-electrons ( )

(b) four π-electrons ( )

(c) four π-bonds ( )

(d) two single bonds ( )

3. In disubstituted cyclohexane, most stable orientation is

(a) the substituants are in axial position ( )

(b) the substituants are in equatorial position ( )

(c) the substituants are in axial and equatorial position ( )

(d) All of the above ( )

4. Mannich reaction is an example of

(a) microwave assisted reaction ( )

(b) UV-assisted reaction ( )

(c) IR-assisted reaction ( )

(d) None of the above ( )

5. In NMR, we use

   (a)   tetramethylsilane (TMS) as reference   (   )

   (b) ^{13}C as reference   (   )

   (c) ^{1}H as reference   (   )

   (d)   methanol as reference   (   )

(4)

(*Marks* : 15)

Answer the following questions :   3×5=15

1. Explain Norrish type-II cleavage.

(5)

2. Define pericyclic reaction with suitable example.

(6)

3. Explain the advantage of organolithium in hindered carbonyl groups. Give one example.

4. Explain with example, the process of Diels-Alder reaction with mechanism.

(8)

5. Discuss the basic principle of mass spectroscopy.

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2 0 1 6

(6th Semester)

CHEMISTRY

TENTH PAPER

Course No. : CHEM–362

(Inorganic Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks
for the questions

1. *(a)* Describe the structure and bonding in $[Mn_2(CO)_{10}]$.   2

(b) What are -complexes? Explain the nature of bonding in organometallic compounds.   1+2=3

(c) How are organometallic compounds classified into two classes?   2

OR

2. *(a)* Discuss the structure and mode of hybridization in $Fe(CO)_5$.   2

(b) Write one method of preparation of $[Ni(CO)_4]$.   2

(c) What is Grignard reagent? How will you use it for preparation of alcohol from carbonyl compounds?   1+2=3

3. *(a)* Describe the separation of Lanthanides by ion-exchange method.   2

(b) What are transuranic elements? Give any common property among themselves.   1+1=2

(c) Contrast the similarities and dissimilarities between Lanthanides and Actinides.   2

(d) What is the most common oxidation state of Lanthanides?   1

OR

4. *(a)* What is Lanthanide contraction? Discuss its consequences.   1+2=3

(b) Write a note on 'colour of M^3 actinide ions'.   2

(3)

(c) Describe the ability of complex formation in Lanthanides. 2

5. (a) What is carbonic anhydrase? Discuss its function in biological system. 1+2=3

(b) Describe the role and mechanism of oxygen binding of haemoglobin. 3

(c) Name the element present in the active part of carboxypeptidase. 1

OR

6. (a) What are silicones? Discuss one method of preparation of linear silicones. 1+2=3

(b) How will you differentiate between organic polymers and inorganic polymers? 2

(c) Write some uses of phosphazenes. 2

7. (a) What do you understand by magnetic induction? 1½

(b) Compare the magnetic behaviours of $[Fe(CN)_6]^3$ and $[FeF_6]^3$. State the mode of hybridization of iron in the two coordinate compounds. 2+2=4

(c) Determine the magnetic moment of Cr^2 ion. 1½

(4)

OR

8. (a) What is Curie law? Why is it modified to give Curie-Weiss law? 1+1½=2½

(b) Discuss the variation of magnetic susceptibility with temperature for ferromagnetic and paramagnetic substances. 2½

(c) Write a note on 'orbital magnetic moment' for an atom having one electron. 2

9. (a) Compare the stretching frequencies for the given carbon-halogen bonds : 2½

C—F, C—Cl, C—Br

(b) Mention some applications of IR spectroscopy. 2

(c) Discuss the factors on which vibrational energy depends. 2½

OR

10. (a) Differentiate between 'Stokes lines' and 'anti-Stokes lines' in Raman spectra. 2

(b) Point out the differences between Raman spectroscopy and infrared spectroscopy. 2

(5)

(c) What do you understand by the term 'Raman shift'?   2

(d) Calculate the number of fundamental modes of vibration for CO_2.   1

★ ★ ★

Booklet No. A

To be filled in by the Candidate

DEGREE 6th Semester
(Arts / Science / Commerce /
......................) Exam., **2016**

Subject ....

Paper ....

INSTRUCTIONS TO CANDIDATES

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To be filled in by the Candidate

DEGREE 6th Semester
(Arts / Science / Commerce /
......................) Exam., **2016**

Roll No. ....

Regn. No. ....

Subject ....

Paper ....

Descriptive Type

Booklet No. B ....

2 0 1 6

(6th Semester)

CHEMISTRY

TENTH PAPER

Course No. : CHEM–362

(Inorganic Chemistry—III)

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided for it :   1×5=5

1. The properties of actinides are considerably different from each other due to the small difference between

(a) 3*d* and 4*d*   (   )

(b) 4*f* and 5*f*   (   )

(c) 5*f* and 6*d*   (   )

(d) None of the above   (   )

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2. The oxidation state of iron in deoxyhemoglobin is

(a) +2   ( )

(b) +3   ( )

(c) 0   ( )

(d) +4   ( )

3. The most convenient spectroscopic technique to establish the presence of intermolecular hydrogen bonding in hydroxy compounds is

(a) UV spectroscopy   ( )

(b) IR spectroscopy   ( )

(c) EPR spectroscopy   ( )

(d) mass spectroscopy   ( )

4. The general electronic configuration of Lanthanides is

(a) $4f^{1-14} 5d^{0-1} 6s^2$ ( )

(b) $5f^{1-14} 6d^{0-1} 7s^2$ ( )

(c) $7f^{1-14} 8d^{0-1} 9s^2$ ( )

(d) $6f^{1-14} 7d^{0-1} 8s^2$ ( )

5. For a non-linear molecule, the number of modes of vibration is given by

(a) $2n$ 4   (   )

(b) $3n$ 6   (   )

(c) $3n$ 5   (   )

(d) None of the above   (   )

(4)

(*Marks* : 15)

Answer the following questions :   3×5=15

1. Write a note on 'back bonding' in metal carbonyl compounds.

2. Discuss the magnetic property of Lanthanides having M^3 ions.

3. Explain, why $[Fe(CO)_5]$ is diamagnetic.

4. Discuss the structure and bonding in tricyclophosphazene, $[NPCl_2]_3$.

5. Give reasons why some vibrational modes of carbon dioxide (CO_2) are Raman active and IR inactive.

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2 0 1 6

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : CHEM–363

(Physical Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

*The figures in the margin indicate full marks
for the questions*

1. *(a)* State and explain Stark-Einstein law of photochemical equivalence.   1+2=3

(b) Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing 0·25 *M* solution.   2

(c) Write a short note on 'quenching'.   2

(2)

OR

2. *(a)* Discuss the photochemical reaction involving the decomposition of acetaldehyde.   3

(b) Explain the terms 'photosensitization' and 'chemiluminescence'.   2

(c) A certain system absorbs $3·25 \times 10^{18}$ quanta of light per second. On irradiation for 20 minutes, 0·0025 mole of the reactants was found to have reacted. Calculate the quantum yield for the process.
(Avogadro's number $= 6·02 \times 10^{23}$)   2

3. *(a)* Discuss Einstein theory of heat capacity of monatomic crystal and also comment on the results obtained on a plot.   4

(b) Light of wavelength 5500 Å falls on a sensitive plate with work function 1·7 eV. Find *(i)* energy of photon, *(ii)* energy of photoelectron and *(iii)* stopping potential.   3

(3)

OR

4. *(a)* Derive Schrödinger wave equation. 4

(b) An electron is confined to a molecule of length 1 nm (about 5 atoms long).

   (i) What is its minimum energy?

   (ii) What is the first (minimum) excitation from this state?

(Planck's constant = 6.26×10^{34} J-s,

     Mass of electron = 9.109×10^{31} kg) 3

5. *(a)* Derive an expression for the molecular translational partition function of an ideal diatomic gas. 5

(b) The first excited state of chlorine atom $^2P_{1/2}$, lies at 0.11 eV above the ground state, $^2P_{3/2}$. Calculate the electronic partition function of chlorine atom at 1000 K. 2

OR

6. *(a)* Derive an expression for the molecular vibrational partition function of an ideal diatomic gas. 4

(4)

(b) Calculate the characteristic rotational temperature and the rotational partition function for H_2 gas at 2727 °C, given that the moment of inertia of hydrogen gas molecule at this temperature is 4.6033×10^{48} kg-m^2. 3

7. *(a)* How many normal modes of vibrations are there in CO_2 and H_2O? 2

(b) Describe briefly the types of molecules exhibiting rotational spectra. 2

(c) The pure rotational spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20.80 cm^1. Calculate the *(i)* moment of inertia and *(ii)* internuclear distance. The atomic masses are ^1H 1.673×10^{27} kg, ^{35}Cl 58.06×10^{27} kg. 3

OR

8. *(a)* State mutual exclusion rule for vibrational translations. 1

(b) Discuss the basis of Raman spectroscopy. What are Rayleigh, Stokes and anti-Stokes lines? Explain with diagram. 3

(c) State and explain Franck-Condon principle. 3

(5)

9. *(a)* Differentiate between electrolytic and electrochemical (galvanic) cells. 4

(b) Write Nernst equation. 1

(c) What are concentration cells? 2

OR

10. *(a)* Differentiate between reversible and irreversible electrochemical cells with examples. 4

(b) Calculate the e.m.f. of the cell

$Cr|Cr^3$ $(0 1 M)||Fe^2$ $(0 01 M)|Fe$

Given, $E_{(Cr^3 |Cr)}$ 0·75 V

$E_{(Fe^2 |Fe)}$ 0 45 V 3

★ ★ ★

2 0 1 6

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : CHEM–363

(Physical Chemistry—III)

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided for it :   1×5=5

1. The free energy change (G) of a photochemical reaction

(a) is always positive   (   )

(b) is always negative   (   )

(c) can be both positive and negative   (   )

(d) is neither positive nor negative   (   )

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2. The system for which energy (E) increases quadratically with the quantum number (n) is

(a) particles in a one-dimensional box   (   )

(b) hydrogen atom   (   )

(c) one-dimensional harmonic oscillator   (   )

(d) rigid rotor   (   )

3. The unit of the molecular partition function is

(a) cm^{-1} (   )

(b) s^{-1} (   )

(c) $JK^{-1} mol^{-1}$ (   )

(d) dimensionless   (   )

4. Selection rules for vibrator transitions are

(a) $J \to 0,\ V \to 1,\ 2,\ 3\ldots$ (   )

(b) $J \to 1,\ V \to 1,\ 2,\ 3\ldots$ (   )

(c) $J \to 1,\ 2,\ 3,\ldots,\ V \to 1$ (   )

(d) $J \to 0,\ 1$ (   )

(3)

5. If the transference number of cation is greater than that of anion, i.e., $t_+ > t_-$, then liquid junction potential will be

(a) zero   (   )

(b) negative   (   )

(c) positive   (   )

(d) negligibly small   (   )

(4)

(*Marks* : 15)

Answer the following questions :   3×5=15

1. State and explain Grotthus-Draper law.

(**5**)

2. Describe Planck's quantum theory of radiation.

3. Write a short note on reference electrode (SHE).

4. What are radiative and non-radiative transitions?

5. Discuss the salient features of the Einstein theory of the heat capacity of monatomic crystals.

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2 0 1 6

(6th Semester)

CHEMISTRY

TWELFTH (B) PAPER

Course No. : CHEM–364

(**Natural Products**)

Full Marks : 75

Time : 3 hours

(PART : B—DESCRIPTIVE)

(*Marks* : 50)

*The figures in the margin indicate full marks
for the questions*

1. *(a)* Write the structure of atropine. 2

   (b) Draw the structures of the following compounds and indicate how many isoprene unit they contain : 1½+1½=3

   (i) Camphor

   (ii) -pinene

(**2**)

(c) What are terpenes? What are the acyclic and monocyclic monoterpenes? Give example of each. 2+3=5

OR

2. *(a)* Complete the following reaction : 3
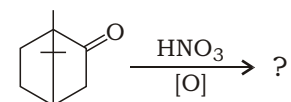
   (b) Describe the synthesis of nicotine starting with Claisen condensation of ethylnicotinate. 3

   (c) What is Hofmann degradation of alkaloids? What are its limitations? 2+2=4

3. *(a)* How many distinct absorptions will be observed in the ^{1}H-NMR spectrum of hex-1-ene? 2

   (b) The mass spectrum of 1-hexanol gives a base peak at $m/z = 56$. How will you account for this? 2

   (c) 2-Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies at $1692 \, cm^{-1}$ and $1658 \, cm^{-1}$. Explain. 3

(3)

(d) Using Woodward rules, calculate the expected position of $_{max}$ in the following compounds : 1½+1½=3

(i)

(ii)

CH_3O
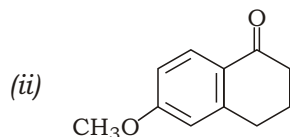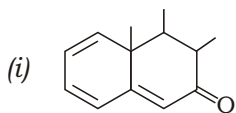
OR

4. (a) What do you understand by the term 'bathochromic shift'? 2

(b) What is the basic principle of mass spectrometry? 3

(c) Comment on the number of H^1-NMR signals and their splitting patterns (if any) in the following compounds : 2½+2½=5

(i) CH_3—⬡—OCH_3

(ii) H—⬡—H (with H atoms around ring)
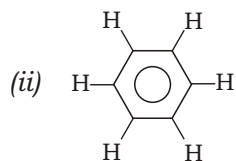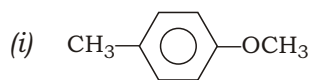
(4)

5. (a) Glucose reacts slowly with hemoglobin and other proteins to form covalent compounds. Why is glucose reactive? What is the nature of the product formed? 2

(b) What are polypeptides? 2

(c) Describe the synthesis of -amino acid starting with phthalimide potassium salt. 3

(d) What are glycosides? Comment on their biochemical effects. 1+2=3

OR

6. (a) Draw the Haworth projection formulae for -D-galactose and -D-galactose. 3

(b) What are the primary and secondary structures of protein? 3

(c) Explain the following terms : 2×2=4

(i) Isoelectric point

(ii) Denaturation of protein

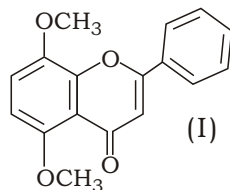7. (a) What are semiochemicals? Discuss their roles for the very survival of species possessing them. 3

(5)

(b) Complete the following reaction : 3
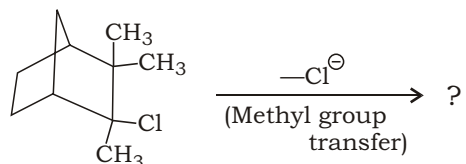
(c) Discuss the mechanism of Wesley-Moser rearrangement reaction involving demethylation of 5,8-dimethoxy flavone (I) to yield an isomeric product (dihydroxyflavone)

4

OR

8. (a) What are insect pheromones? How are they classified? 2

(b) Why molecular rearrangement of *N*-methyl papaverine chloride to *N*-methyl-pavine called a molecular yoga? Explain the mechanism. 3

(c) Comment on the statement, "chemical communication between plants and insects can be both mutually benign and antagonistic", using a suitable example. 5

(6)

9. (a) Give a brief account on mode of action of enzyme active site. 3

(b) Write a note on allosteric enzymes. 3

(c) Explain briefly the specificity of enzyme action. 4

OR

10. (a) What are the mechanisms that regulate the enzyme activity? 3

(b) Explain non-competitive enzyme inhibition, giving a suitable example. 3

(c) Discuss with a suitable example, the oxidoreductase enzyme synthesis. 4

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2 0 1 6

(6th Semester)

CHEMISTRY

TWELFTH (B) PAPER

Course No. : Chem–364

(Natural Products)

(PART : A—OBJECTIVE)

(*Marks* : 25)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 10)

Put a Tick (✓) mark against the correct answer in the brackets provided for it :   1×10=10

1. Which of the following compounds has a stimulant action on the central nervous system?

   (a) Nicotine   (   )

   (b) Atropine   (   )

   (c) Camphor   (   )

   (d) -pinene   (   )

2. One of the major constituents of turpentine oil is

(a) camphor-d   (   )

(b) citral   (   )

(c)   -pinene   (   )

(d) atropine   (   )

3. In IR spectrum of an alcohol, presence of —OH group is shown by broad but intense band centred at

(a) 3350 cm ^{1} (   )

(b) 1710 cm ^{1} (   )

(c) 2860 cm ^{1} (   )

(d) None of the above   (   )

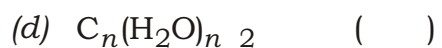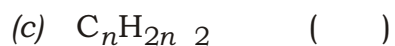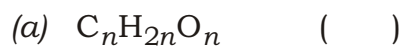**4.** Which of the following will not give signal in UV-vis spectrum?

(a) Ethene   (   )

(b) Benzene   (   )

(c) Acetone   (   )

(d) *n*-hexane   (   )

5. The general formula of monosaccharides is

(a) $C_nH_{2n}O_n$ ( )

(b) $C_nH_{2n\ 2}$ ( )

(c) $C_nH_{2n\ 2}$ ( )

(d) $C_n(H_2O)_{n\ 2}$ ( )

6. The principal linkage found in all proteins is

(a) —CO—ONO   ( )

(b) —CO—NH—   ( )

(c) —CN—CO—   ( )

(d) —CO—SH—   ( )

7. Which of the following is the product of acid-catalyzed rearrangement reaction of morphine?

(a) Amorphine   ( )

(b) Apomorphine   ( )

(c) Thebaine   ( )

(d) Neomorphine   ( )

8. Nametkin rearrangement is specifically confined to

(a) terpenoids   (   )

(b) alkaloids   (   )

(c) phenolic acids   (   )

(d) flavonoids   (   )

9. The optimum pH of enzyme activity lies in the range

(a) 5–9   (   )

(b) 3–7   (   )

(c) 10–14   (   )

(d) None of the above   (   )

10. Most of the enzyme-catalyzed reactions occur near the surface of protein at an area called

(a) -site   (   )

(b) aposite   (   )

(c) transition site   (   )

(d) active site   (   )

(5)

SECTION—B

(*Marks* : 15)

Answer the following questions :   3×5=15

1. Write the structure of menthol. Mention its medicinal properties.

2. What is a metastable ion in the mass spectra of an organic compound?

3. Write three biological roles of protein.

4. Write a brief note on defensive secretion of insects.

(9)

5. What are the main points of difference between enzymes and catalysts?

★★★