SEAT No._____ No. of Printed Pages: 02

[47] (87) SARDAR PATEL UNIVERSITY

M.Sc. (Analytical Chemistry) **Examination** (CBCS) **III**rd Semester

April-2017

Mon**day, Date:** 17.04.2017

Time: 2.00 p.m.to 5.00 p.m., **Paper :** PS03CANC03

Subject: Basic and thermal methods of analysis, **Total marks:** 70

N.B.: i) Figures to the right indicate marks.
ii) Assume the suitable data if necessary and indicate clearly.

Q.1. Answer by highlighting the correct choice [08]

i) Which among the following gives exothermic peak in DTA?
a) Melting **b)** Adsorption
c) Vaporization **d)** Sublimation

ii) Colloidal suspension is known to show_____
a) Scattering of light **b)** Tandyll effect
c) Both a) and b) **d)** None

iii) Adsorption of indicator ions is an endpoint detection in___
a) Mohr's method **b)** Volhard's method
c) FAJAN method **d)** Lie Big method

iv) For a very weak acid HA in water,$[OH^-]$ can be expressed as_
a) Kw[Ka+Kw] **b)** $Kw[KaF+Kw]^{1/2}$
c) $Kw[Ka+Kw]^{-1/2}$ **d)** $[KaF+Kw]^{1/2}$

v) The electric energy is consumed in____
a) Galvanic cell **b)** Electrolytic cell
c) Both a) and b) **d)** None

vi) At 10 pH, 26.37 mL of 0.0741M EDTA is equivalent to__
a) 1.96 mmol of Ca^{2+} **b)** 1.95 mmol of Mg^{2+}
c) a) or b) both **d)** 3.9 mmol of Cu^{2+}

vii) An example of complex is
a) $Ag(CN)_2^{1-}$ **b)** $Cu(NH_2COO)_2$
c) $Ag(NH_3)_2^{1+}$ **d)** All

viii) A titration '5.0 mL, 0.2M NaOH Vs 0.1M HCL' give equivalence point pH
a) 5 **b)** 6
c) 7 **d)** 8

Q.2. **a)** Attempt any ***Seven*** [14]

i) List thermal events taking place upon heating the substance
ii) State the 'buffer solution'. Calculate pH of the solution which is 0.1 F in HA and 0.1F in NaA, where Ka = $1.75X10^{-5}$
iii) Define hard acids and bases with suitable examples.
iv) Illustrate indicator error.
v) Give the working principle of Mohr's method.
vi) Distinguish between the terms 'iodimetry' and 'iodomery'.
vii) Illustrate effective stability constant for complex formation.
viii) Give importance of displacement strategy in EDTA titration.
ix) State the term 'homogeneous precipitation'.

Q.3. **a)** Draw various shapes of a characteristic TG curve, and name the phenomena associated to each of them. Discuss the TG curve of hydrated calcium oxalate in brief. [06]

b) Outline **(i)** Peptization, **(ii)** Co-precipitation, **(iii)** Occlusion [06]

OR

b) Define relative super saturation. Addition of 0.05 mL of 0.1M Ag^{1+} solution to 100 mL of 0.1M Cl^- solution was made to allow precipitation of AgCl(s). Calculate the degree of relative super saturation, where Ksp(AgCl) is equal to 1.0×10^{-10}.

Q.4 **a)** Attempt the following [06]

i) Reactions; $2H^+ + Cd \leftrightarrow H_2(g) + Cd^{2+}$, $2Ag^+ + H_2 \leftrightarrow 2Ag(s) + 2H^+$, and $Cd^{2+} + Zn(s) \leftrightarrow Cd(s) + Zn^{2+}$ are known to occur most to the right direction. Deduce the order of species H^+, Ag^+, Cd^{2+} and Zn^{2+} in terms of their oxidizing strengths.

ii) Define solubility. Calculate solubility of $Ba(IO_3)_2$ in a 0.02 F solution of KIO_3 [Ksp = 1.57×10^{-9}].

b) What is Nernst equation? State its importance, and comment whether half cell "Ni/Ni^{2+} (0.0943M)" acts as anode or cathode against SHE. Calculate the cell potential.[E° of the reaction $Ni^{2+} + 2e \rightarrow Ni$ is – 0.250 V]. [06]

OR

b) State the precipitation titrimetry. Calculate pCN value for titration of 50.0 mL, 0.2M of NaCN with 0.1M of $AgNO_3$ at equivalence and end points, both, where Ksp($Ag[Ag(CN)_2]$) and Kf($[Ag(CN)_2^-]$ are 2.0×10^{-12} and 7.1×10^{19} respectively.

Q.5. **a)** Derive the equation of pH for a weak acid (HA) in water. Show dissociation reaction of the same HA in pure ammonia, and hence expression for $p\{NH_4^+\}$. Comment on acidic strength of the acid achieved in this medium. [06]

b) State Lowry Brønsted concepts of acid and base. Identify the principal conjugate acid/base pair from the dissociation of H_2SO_3 in water. Calculate value of ratio [acid]/[base] at pH 6.0, where Ka_1 and Ka_2 have values 1.23×10^{-2} and 6.6×10^{-8} respectively. [06]

OR

b) A 50 mL, 0.05 M solution of formic acid was titrated against 0.1 M KOH solution, using indicator that has color shift pH range value 6.45–9.80. Comment on the feasibility of this titration [Ka of acid is 1.74×10^{-4}].

Q.6 **a)** Describe in brief complexometry. A 50.0 mL of 0.1M Ca^{2+} solution was titrated against 0.1M of EDTA solution using EBT as an indicator at 10 pH. Calculate pCa 0.1 mL before and after the equivalence point and at the equivalence point of the titration. [values of Kf(Ca-EDTA) and α_4 are 4.9×10^{-8} and 0.35 respectively] [06]

b) Outline: i) Types of EDTA titrations.
ii) Metallochriomic indicators. [06]

OR

b) Explain

i) Mg-EDTA titration is performed at pH 10!

ii) Pure ammonia is an excellent auxiliary agent for Zn–EDTA titrymetry!

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SEAT No._____

Total no of printed pages: 02

[117/118/A-60]

SARDAR PATEL UNIVERSITY

M.Sc. Chemistry Semester –III Examination
Spectroscopy-I (PS03CORC01/ PS03CANC01)

Date : 11/04/2017
Day : Tuesday
Time : 02:00 pm to 05:00 pm
Total Marks : 70

N.B. 1) Figures to right indicate full marks.
2) Attempt all questions.

Q. 1 : Select the correct answer from each of the following. **[08]**

1) The continuous source which emits radiations over wide range of wavelength in AAS is --------- .
   a) Laser b) Hg vapour lamp c) Xe-lamp d) HCL
2) When alkali metals introduced into the flame, it emits radiations in ------ range.
   a) UV b) infra red c) radiofrequency d) visible
3) -------- is used as a fluorescent indicator.
   a) Methyl orange b) Phenolphthalein c) Eosin d) crystal violet
4) Bioluminescence is caused by enzyme -------- .
   a) Brease b) Luciferase c) Lipase d) Invertase
5) In ESCA, peak formed due to simultaneous ionization of valance shell electron is known as --------- .
   a) Shake off b) shake up c) valance peak d) none of these
6) The probability of emission of auger electron decreases as atomic number of emitting element ---------- .
   a) decreases b) increases c) both a and b d) none of these
7) -------- measures the electrical conductance between probe tip and the surface.
   a) TEM b) AFM c) AES d) STM
8) -------- is a analytical technique that relies upon the use of electron microprobe.
   a) EPXMA b) XMA c) PXMA d) EMA

Q. 2 : Answer the following (Any Seven) **[14]**

i) Write any two applications of scanning electron microscope (SEM).
ii) Discuss the 'Resonance fluorescence'.
iii) Explain the term work function in electron spectroscopy.
iv) Draw neat and labelled schematic diagram of SEM.
v) Define Plasma and Nebulization.
vi) Give the difference between premixed burner and total consumption burner.
vii) Explain intersystem crossing in photoluminescence.
viii) Write the principle of UPS.
ix) Draw neat and labelled schematic diagram of atomic absorption spectrometer (AAS).

Q. 3 : A) Discuss in detail on atomizers used in atomic absorption spectroscopy. [06]

B) Discuss briefly the simultaneous and sequential multielement spectrometer used in ICP instrument. [06]

OR

B) Name different sources of radiation used in atomic spectroscopy. Explain any one line source with labelled diagram. [06]

Q. 4 : A) Draw neat and labelled schematic diagram of spectroflurometer and explain in brief about function of each component . Also describe the advantages of spectroflurometer. [06]

B) Write a note on [06]

i) Chemiluminescence

ii) Quenching in photoluminescence

OR

B) Discuss in detail on various applications of fluorometric analysis. [06]

Q. 5 : A) Give an account on instrumentation and applications of auger electron spectroscopy. [06]

B) Answer the following. [06]

i) Describe various applications of XPS.

ii) Differentiate between ESCA and auger electron spectroscopy.

OR

B) Answer the following. [06]

i) Name the various detectors used in electron spectrophotometer and explain any one of them briefly.

ii) Explain the chemical shift in ESCA.

Q. 6 : A) What is tunneling current? Write a note on scanning tunneling microscope along with its applications. [06]

B) Give an account in detail on atomic force microscope (AFM). [06]

OR

B) Answer the following. [06]

i) Discuss the instrumentation of electron microprobe with neat and clean diagram. [06]

ii) Explain elastic and inelastic scattering events in SEM.

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SEAT No._____

No of pages: 04

[116/A-66]

SARDAR PATEL UNIVERSITY

M.Sc. Semester-III (Organic Chemistry) Examination

Thursday, 13th April 2017

PS03CORCO2: Organic Synthesis – A Disconnection Approach

Time: 2:00pm to 05:00pm **Total Marks: 70**

Q.1 Select the Correct answer in the following. **8**

1 The synthetic equivalent for the illogical synthon $^{-}COOH$ is _____.
(a) Oxalic acid (b) Benzoic acid
(c) H_2/Pd (d) KCN

2 An analytical operation which breaks a bond and converts a molecules in to a possible starting material is known as _____.
(a)Target Molecule (b) Leaving group
(c) Protecting groups (d) Disconnection

3 Whenever there is at list one double bond is present in the six member cyclic compound & any electron withdrawing group present at 3rd Position from the double bond, then _____ reaction is applicable.
(a) Aldol (b) Diel's Alder
(c) wittig (d) None of these

4 An umpolung of aldehyde carbonyl group can be carried out by converting into_____.
(a) Hydrazone derivative (b) 1,3- dithiane derivative
(c) Amine derivative (d) Acetal derivative

5 In a disconnection, the Reconnection Concept is possible in _____.
(a) 1,2-dicarbonil Compound (b) 1,6-dicarbonil Compound
(c)1,4-dicarbonil Compound (d) 1,5-dicarbonil Compound

6 The THP derivative is used for the protection of _____.
(a) Phenol (b) Amine
(c) Ketone (d) Alcohol

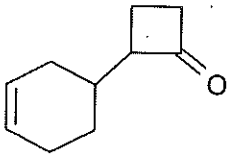
7 α-Hydroxy ketone can be prepared by _____
(a) Acyloin reaction (b) Pinacol reduction
(c) Darzan reaction (d) Dieckmann reaction

8 The Olefin's hydroxylation can be carried out by _____
(a) H_2O_2 (b) OsO_4
(c) $KMno_4$ (d) SeO_2

Q.2 Answer the following (**Any Seven**). 14

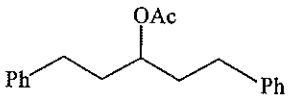
1 Define the term Synthetic Equivalent with suitable example.
2 Define the term function group interconversion with example.
3 Give the mechanism of Benzoin condensation with suitable example.
4 Define the term Illogical Electophiles.
5 Write the pinacol reduction reaction
6 Write about the protection of ketone
7 What is the importance of enamine in organic synthesis
8 Using umpolung approach, plan the synthesis for the following molecule.

9 Do the disconnection and plan the synthesis for the following compound.



Q.3 A. Do the disconnection and plan the synthesis for the following molecules. 06

(i)



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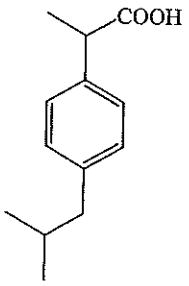
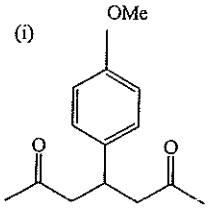


B. Do the disconnection and plan the synthesis for the following molecules. 06

(i)



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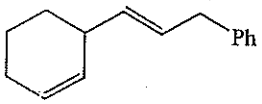
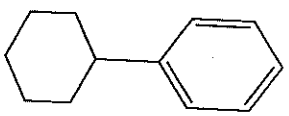


OR

B. (i) Do the disconnection and plan the synthesis for the following compound. 06

1.



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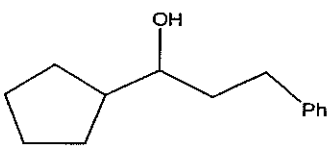
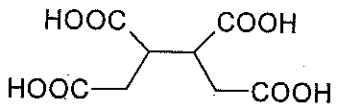
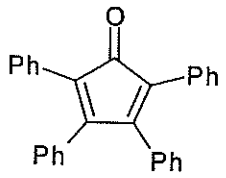


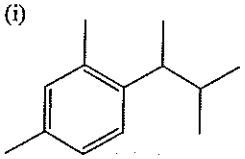
Q.4 A. Do the disconnection and plan the synthesis for the following molecules. 06



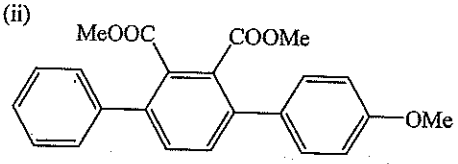


B. Do the disconnection and plan the synthesis for the following molecules. 06

(i)



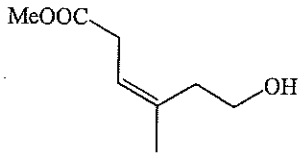
(ii)



OR

B. Do the disconnection and plan the synthesis for the following molecules. 06

(1)



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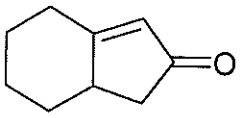
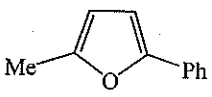


Q.5 A. Do the disconnection and plan the synthesis for the following molecules. 06

(1)



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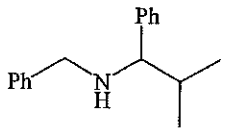
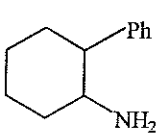


B. Do the disconnection and plan the synthesis for the following molecules. 06

(1)



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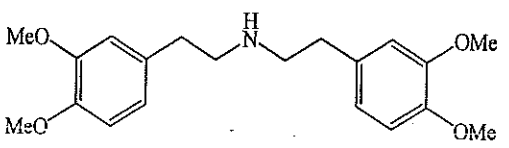
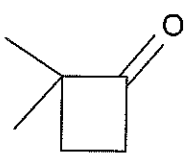


OR

B. Do the disconnection and plan the synthesis for the following molecules. 06

(1)



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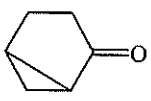
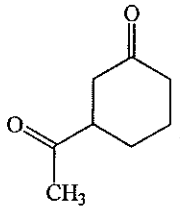


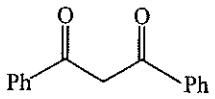
Q.6 A. Answer the followings.

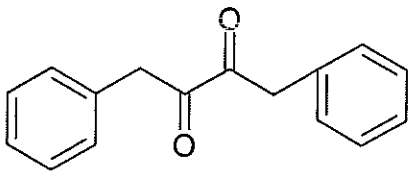
(i) Discuss the protection and deprotection of aldehydes and amines. 03

(ii) Give the synthesis of following molecule.(Starting material is acetaldehyde) 03



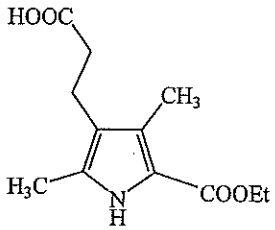
B. Do the disconnection and plan the synthesis for the following molecules. 06



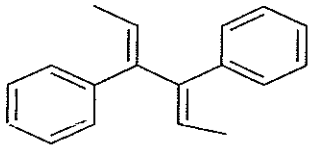


OR

B. (I)Give the synthesis of following pyrrole derivative used as intermediate in the synthesis of Mesoporphyrin IX. 03



(ii) Do the disconnection and plan the synthesis for the following molecules 03



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SEAT No._____

[88/A·54]

No. of Printed Pages : 3

SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-III) EXAMINATION
Monday, 17th April 2017
TIME: 02.00 A.M. to 05.00 P.M.
HETEROCYCLIC CHEMISTRY: PS03CORC03

Note: Figure to the right indicate full marks. **Total marks: 70**

Q.1 Choose the correct answers from the options given below. **[08]**

(1) Condensation of urea with diethyl melonate gives_____.
(a) uracil (b) barbituric acid (c) flavone (d) pyridazine

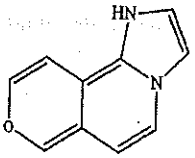
(2) Pyridine derivatives can be synthesized by_____.
a) Hantzch synthesis b) Gaurechi-Thorpe synthesis c) Both d) None

(3) What is the correct order of reactivity (most reactive first) of pyrrole, furan and thiophene towards electrophiles?
a) furan > pyrrole > thiophene b) thiophene > pyrrole > furan
c) pyrrole > furan > thiophene d) furan > thiophene > pyrrole

(4) 2,3,8-trimethylquinoline $\xrightarrow[\text{EtOH / Reflux}]{SeO_2}$?
a) 2,8-dimethylquinoline-3-carbaldehyde b) 3,8-dimethylquinoline-2-carbaldehyde
c) 2,3-dimethylquinoline-8-carbaldehyde d) None of the above

(5) Which of the following solvents is a heterocyclic compound?
a) DMSO b) THF
c) DMF d) Diglyme

(6) Give the correct name of the following compound,



a) 1*H*-imidazo[1,2-*a*]pyrano[4,3-*c*]pyridine b) 1*H*-pyrano[3,2-*a*]pyrido[2,3-*c*]imidazole
c) 1*H*-pyrolo[1,2-*c*]pyri lo[2,3-*c*]imidazole d) 1*H*- pyrano[1,2-*a*] imidazo[4,3-*c*]pyridine

(7) Which reagent would you use to convert 2-pyridone to 2-chloropyridine?
a) HCl b) $POCl_3$
c) PCl_3 d) CCl_4

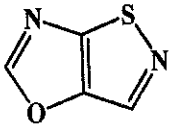
(8) Reaction of s-triazine with alkyne gives _____.
a) pyridine b) pyrimidine c) pyrazine d) piperazine

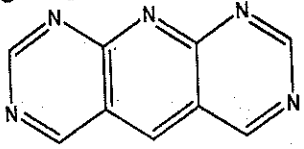
Q.2 Answer the following. [Any seven] **[14]**

1. "Pyridine is weak base than methyl amine" Justify
2. Draw the structure of the following.
   (i) [1,4]benzothiazino[2,3-b]phenoxazine
   (ii) [1,2]oxazino[6,5-b]indole
3. Suggest the product and mechanism of the following.

Uracil $\xrightarrow{MeNHNHMe}$?

4. Give the synthesis of 7-methoxy 2-methyl quinoxaline.
5. Write the mechanism for the conversion of 4-pyrone into 1-phenyl-4-pyridone by reaction with aniline.
6. Give complete name of the following compound by an accepted method.

i) 

ii) 

7. Suggest the mechanism for the following:

2-acetyl furan $\xrightarrow{NH_3}$ 2-methyl,3-hydroxypyridine

8. "Boiling point of imidazole is higher than compare to other azoles" Explain
9. Give the synthesis of 1,2-diazine.

Q.3 A. "Synthesis of benzo[b]furan involves intramolecular cyclization of ortho-substituted phenol" Justify by giving at least two suitable examples. Describe its electrophillic substitution reaction. **[06]**

B. Answer the following.

i) Give the Bischler and Reissert synthesis for Indole preparation. **[03]**

ii) Write the electrophilic substitution reaction of benzo[b]thiophenes. **[03]**

OR

B. Give the mechanistic interpretation describing the product from the following: **[06]**

i) 1,3-dimethyl indole + $Me_2C = CHCOMe \xrightarrow{H_2SO_4 / aq.EtOH}$?

ii) Phenyl hydrazine + OHCH2-CH_2-CH_2-CH_2-Cl $\xrightarrow{aq.\ EtOH}$ **?**

Q.4 A. Complete the following reaction scheme and suggest the mechanism for last step. **[06]**

Aniline + Ethylacetoacetate $\xrightarrow{200^\circ C}$ ——— $\xrightarrow{250^\circ C}$ ———

$\xrightarrow[(ii)\ H_2/Pd]{(i)\ POCl_3}$ ——— $\xrightarrow[HOAc]{H_2O_2}$ ———

$\xrightarrow[Bf3\ /\ HCONMe2,\ reflux\ 2.5\ Hr]{p\text{-toluene sulphonyl chloride}}$ ———

B. i) Explain briefly on 1,3,5,8-tetrazo naphthalene. **[03]**

ii) Discuss the cyanine dye of quinoline. **[03]**

OR

B. Explain the formation of isomeric quinolones by Conrad-Limpach-Knorr method. Describe briefly on electrophilic and nucleophilic reactions of quinoline. **[06]**

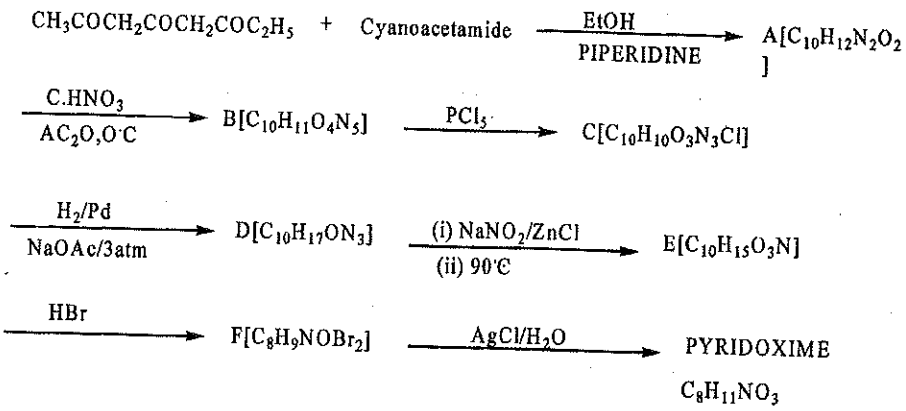
Q.5 A. i) Discuss at least two methods for synthesis of pyrimidine and describe any one ring transformation reaction of pyrimidine. **[03]**

ii) Explain the reaction of s-triazine with N_2H_4, NH_2OH and R-NH_2. **[03]**

B. Electrophilic substitution reaction in substituted pyridine N-oxide **[06]**

OR

B. Complete the following reaction scheme. **[06]**



Q.6 **A.** Write the synthesis of pyrylium salt and its reaction with NH_2NH_2, Ph-CH_2MgBr, wittig reagent and H_2O_2. **[06]**

B. Give any one synthesis of each (i) α-pyrone (ii) ν-pyrone. Briefly mention their reaction with CH_3MgCl and NaCN. **[06]**

OR

B. Write the synthesis of coumarin and chromone; also write their reaction with electrophilic reagents. **[06]**

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SEAT No._____ No of Printed Pages: 02

[57/A-38]

SARDAR PATEL UNIVERSITY
M.Sc. CHEMISTRY
Semester – III, External Examination
April 19, 2017 (Wednesday)
Time: 2:00 pm - 05:00 pm
Synthetic Dyes and Pigments [PS03ECHE01]

N.B. Figures to the right indicate full marks **[Total Marks – 70]**

Q.1 Answer the following multiple choice questions. **[08]**

1 Dye forming process is a process used in .....
(a) Electronic dyes (c)Biological dyes
(b)Color photography (d)Electrical dyes

2 From the following _____ is independent chromophore.
(a) carbonyl (b) azoxy (c) Ethylenic (d) thiocarbonyl

3 _____ Dyes are used to overcome poor photo stability of liquid crystal dyes.
(a) Azo (b) Azoic (c) Indigo (d) Anthraquinone

4 _____ is used as a food colour from the following.
(a) Indigo (b) Saframine T (c) Amaranth (d) NIR

5 According to Dewar's theory any electron accepting group at stared position should cause _____shift.
(a) hypochromic (b) bathochromic (c) hypsochromic (d) hyperchromic

6 Security marks and features that are not visible under normal light are made with____.
(a) Fluorescein (b) Luminescent pigments (c) Special dyes (d) All of above

7 _____ is the complimentary color of green color.
(a)Blue (b) yellow (c) orange (d) gray

8 Natural leather can be dyed with ..... dye.
(a) Mordant dyes (b) yellow dyes (c) acid dyes (d) basic dyes

Q.2 Answer the following questions. **(ANY SEVEN)** **[14]**

1 Explain Red and Violet shift.
2 Explain Leather dye.
3 Write a note on type of fibers used for dying.
4 Explain methods of Textile Printing in short.
5 Write a short note on azoacetoacetanilide pigment.
6 Write characteristics of functional dyes.
7 Give structure of any two Novel Chromophore.
8 Write structure of any two metal free pigment.
9 Give the difference between dye and pigment.

Q.3

[A] Write a note on VB Theory. [06]

[B] **Write Synthesis of ANY THREE from the following** [06]

1 Malachite green
2 Stilbene azo.
3 Crystal Violet.
4 Alizarine.
5 Fluorescein.

Q.4

[A] Explain the pretreatment of textile fibers and dyeing mechanism. [06]

[B] **Write a Brief Note on ANY TWO of the following.** [06]

1 Color photography
2 Non textile dyes
3 Food Dyes
4 Explain Ionic and covalent Interaction between dye and fiber.

Q.5

[A] Give synthesis, discuss construction and applications of indigo dye. [06]

[B] **Explain the following:** [06]

(I) Liquid crystal dye (II) Near infrared absorption (NIR) dyes

OR

[B] **Answer the following** [06]

1 What is Donor-Acceptor Chromophore? Write approach to achieve bathochromic shift in Donor-Acceptor Chromophore.
2 Explain Medicinal and Security application of colorants.

Q.6

[A] What is FBA? Write its characteristics and give synthesis of any two fluorescent brightening agent. [06]

[B] **Answer the following questions.** [06]

Enlist the type of pigments and explain inorganic pigments.

OR

[B] **Answer the following questions.**

I Explain applications of organic pigments.
II Explain the lake of acids.

BEST OF LUCK