

Q.P. Code – 56761

Previous M.Sc. Degree Examination

OCTOBER/NOVEMBER 2014

(Directorate of Distance Education)

CHEMISTRY

(DPA 510) Paper DECHEM 1.01 – ANALYTICAL CHEMISTRY - I

Time : 3 Hours]

[Max. Marks : 75/85

Instructions to Candidates :

- 1) *Scheme : 75 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**.*
- 2) *Scheme : 85 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**; and any **ONE** question from Part **D**.*

PART – A

- I. Answer any **TEN** of the following : **10 × 2 = 20**
1. (a) The determination of iron in an ore sample gave the following results (%) : 31.31, 31.07, 31.92 and 31.72. Calculate the standard deviation for the data set.
 - (b) What are acid base indicators? Give two examples. What is the minimum change in pH required to cause a colour change of an acid-base indicator?
 - (c) Phenol is titratable in ethylene diamine but not in aqueous medium. Explain.
 - (d) What is meant by gravimetric analysis? What two requirements a reaction must satisfy before it can be used as basis for gravimetric analysis?
 - (e) The calcium in a 0.8432 g sample is precipitated as CaC_2O_4 . The precipitate is washed, ignited to CaCO_3 and found to weigh 0.3462 g. Calculate the percentage of CaO in the sample.
 - (f) In the extraction of cerium (IV), with oxine in chloroform, the volumes of the aqueous and organic phases were 25 ml each with a percent extraction of 99.8. What is the distribution ratio?
 - (g) What are the advantages and disadvantages of liquid ammonia as a solvent?

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- (h) How do chemical process industries contribute to air pollution? Name the major industrial sources of atmospheric pollution.
- (i) Distinguish between BOD and COD of a waste water sample.
- (j) With the help of a chromatogram, write the meaning of retention time, void time, retention volume and void volume.
- (k) Define : retardation factor as used in TLC. Indicate its significance. Mention the factors which influence its magnitude.
- (l) Distinguish between a cation exchanger and anion exchanger with one example for each.
- (m) What are bonded phase packings used in HPLC? List out their advantages and limitations.
- (n) Write the characteristics of an ideal matrix for affinity chromatography. Name any four common matrix materials used in affinity chromatography.
- (o) Give the meaning of size exclusion chromatography. Make a clear distinction between gel filtration chromatography (GFC) and gel permeation chromatography (GPC).

PART – B

- II. Answer any **TWO** questions : **2 × 8 = 16**
- 2. (a) What are the sources of instrumental determinate errors? Suggest ways to reduce their impact on analytical results.
 - (b) Give an account of solutions of alkali metals in liquid ammonia and their properties. **4 + 4 = 8**
 - 3. (a) Describe the principles upon which the flame ionization detector is based. What are its advantages and limitations?
 - (b) The distribution coefficient for x between chloroform and water is 9.6. Calculate the concentration of x remaining in aqueous phase after 50 ml of 0.15 M x is treated by extraction with one 40 ml portion and two 20 ml portions of chloroform. **4 + 4 = 8**
 - 4. (a) Discuss the theory of acid-base indicators. Why is methyl orange not a suitable indicator for the titration of acetic acid with NaOH?
 - (b) A chemist obtained the following results for replicate determinations of calcium in limestone : 14.35, 14.41, 14.40, 14.32 and 14.37%. What is the confidence interval at the 95% confidence level? (Given : $t = 2.776$) **4 + 4 = 8**

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PART – C

- III. Answer any **THREE** questions : **3 × 13 = 39**
5. (a) Explain the terms : eddy diffusion and longitudinal diffusion. How do they affect the height of theoretical plate (H) in column chromatography?
(b) What is the basis of separation by size exclusion chromatography? How is this technique useful in the separation of polymers?
(c) Write the schematic of a modern HPLC instrument and label the components. Give an account of stationary phases used in HPLC. **4 + 4 + 5 = 13**
6. (a) What is meant by capacity factor? How can it be determined from a chromatogram?
(b) Draw the schematic of a dust fall jar for collecting particulates and explain its salient features. Mention its limitations.
(c) Discuss the following reactions in liquid SO₂ : acid-base, solvation and complex formation, giving suitable examples. List out the advantages and limitations of liquid SO₂ as a solvent. **4 + 4 + 5 = 13**
7. (a) Describe the principles of separation by GC. Illustrate the application of the technique for the determination of gaseous air pollutants and petrochemicals.
(b) Write the indicator action of :
(i) phenolphthalein in the titration of acetic acid with NaOH.
(ii) potassium chromate in the titration of chloride with Ag⁺.
(c) Explain the following observations :
(i) occluded impurities are not removed by washing
(ii) Fe(OH)₃ is usually precipitated from acidic solutions
(iii) AgCl is never filtered on paper **4 + 4 + 5 = 13**
8. (a) What is paper chromatography? Describe its methodology with respect to choice of mobile phase and techniques of development.
(b) A 6.5 ml of sewage was diluted to 650 ml and the diluted sample was distributed to two BOD bottles. One bottle was incubated at 25°C for 5 days and in the other DO was determined immediately (blank). In the Winkler method for DO, 200 ml of the blank required 4.2 ml of 0.025 N thiosulfate where as 200 ml of the sample after incubation required 3.1 ml of the same thiosulfate. Calculate the BOD of the sample
(c) With one example for each, discuss the extraction of ion association complexes of the type : non-chelated and oxonium systems. What is the role of salting out agents in such extractions. **4 + 4 + 5 = 13**

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9. (a) List out the requirements of an useful resin. Write the steps involved in the synthesis of a strongly acidic cationic and a strongly basic anionic exchange resins.
- (b) Describe the mechanism of separation by affinity chromatography with the help of a schematic.
- (c) Methylcyclohexane and methylcyclohexene have retention times of 10.0 and 10.9 min. respectively. An unretained species passes through the column in 1.9 min. The peak widths (at base) were 0.76 and 0.82 min, respectively.

Calculate :

- (i) The column resolution
- (ii) The average number of plates
- (iii) The plate height
- (iv) The length of the column required to achieve a resolution of 1.5 and
- (v) The time required to elute methylcyclohexene on the column that gives a resolution of 1.5. **4 + 4 + 5 = 13**

PART – D

IV. Answer any **ONE** question : **1 × 10 = 10**

10. (a) Describe statistical tests to compare
- (i) the experimental mean value with the true value and
- (ii) two means obtained from two different methods
- (b) Solve the following :
- (i) A 0.5 g bronze containing zinc is dissolved in 100 ml of acid. If an aliquot of 25 ml of 0.01 M EDTA is required for titration, calculate the percentage of zinc in the bronze sample.
- (ii) A 2.165 g sample of copper ore is dissolved and excess KI is added to liberate iodine. The iodine requires 31.43 ml of 0.0978 M thiosulfate solution for titration. Calculate the % copper in the sample. **5 + 5 = 10**
11. (a) Discuss the realization of PFHS, with appropriate examples, by
- (i) pH change (ii) ion-release and (iii) change in oxidation state methods.
- (b) Answer the following :
- (i) salts as a whole are less soluble in liquid SO₂ than in water
- (ii) strong oxidizing agents do not exist in liquid NH₃
- (iii) liquid ammonia is a better solvent for organic compounds than water. **5 + 5 = 10**

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Previous M.Sc. Degree Examination

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(Directorate of Distance Education)

CHEMISTRY

(DPA 520) Paper DECHEM 1.02 – INORGANIC CHEMISTRY - II

Time : 3 Hours]

[Max. Marks : 75/85

Instructions to Candidates :

- 1) *Scheme : 75 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**.*
- 2) *Scheme : 85 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**; and any **ONE** question from Part **D**.*

PART – A

- I. Answer any **TEN** of the following : **10 × 2 = 20**
1. (a) What is radius ratio? Mention its significance.
 - (b) Explain why in general polar solids will dissolve in polar solvents and organic compounds will dissolve in non polar solvents.
 - (c) The conductivity of semiconductor increases with temperature - why?
 - (d) Differentiate cubic close packing from hexagonal close packing.
 - (e) What is inductive effect? Explain with examples.
 - (f) “Octahedral field splitting energy, Δ_0 is always higher than that of tetrahedral splitting energy, Δ_t ”. Justify.
 - (g) What is Styx number? Explain with examples.
 - (h) MgC_2 , CaC_2 are considered as acetalides where as Cu_2C_2 , Ag_2C_2 are not. Why?
 - (i) The Δ_0 value for $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$ is greater than $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion eventhough both contain tripositive metal ion, same ligand and same geometry. Explain.
 - (j) Eventhough diamond and graphite are the allotropic modifications of carbon, former is insulator and later is semiconductor in nature.

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- (k) What are Zeolites? Give their industrial application.
- (l) Explain : resins and elastomers.
- (m) Borazine is known as inorganic benzene. Why?
- (n) Cyanogen is called as pseudo halogen. Why?
- (o) Predict the oxidation states of Xe in the following :
 - (i) XeF_6 (ii) XeO_3 (iii) XeOF_4 (iv) XeO_2F_2

PART – B

II. Answer any **TWO** questions : **2 × 8 = 16**

- 2. (a) Sketch the MO diagram for O_2 molecule and predict the bond orders for O_2 , O_2^+ , O_2^- and O_2^{2-} .
(b) Explain how Fajan's rule helps in predicting the percentage covalent character in ionic bonds. **4 + 4 = 8**
- 3. (a) Discuss the merits and demerits of valence band theory.
(b) With a suitable diagram, discuss the splitting pattern of d-orbitals in octahedral and tetrahedral field. **4 + 4 = 8**
- 4. (a) What are intercalation compounds? Discuss the intercalation compounds of graphite.
(b) Explain the causes and consequences of Jahn Teller distortion. Give examples. **4 + 4 = 8**

PART – C

III. Answer any **THREE** questions : **3 × 13 = 39**

- 5. (a) Construct the Born Haber cycle for the formation of NaCl from metallic sodium and chlorine gas.
(b) Sketch and comment on the crystal structures of NaCl and TiO_2 .
(c) The internuclear distance in HF is 0.92 Å and the dipole moment when electron is completely transferred from H to F is 4.42 D. If the actual dipole moment of HF is 1.98 D, calculate the percentage of ionic character. **5 + 5 + 3 = 13**
- 6. (a) Explain resonance with suitable structure. Discuss the concept of resonance in CO_3^{2-} .
(b) Write notes on (i) Template effect (ii) Wader rules.
(c) Explain : (i) p-n junctions (ii) hyper conjugation. **5 + 5 + 3 = 13**

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7. (a) Discuss the spectroscopic evidences for the presence of M-L covalent bonding in metal complexes.
- (b) With examples, explain the classification of boranes and carboranes on the basis of their skeletal structures.
- (c) Enumerate and explain the shortcomings of CFT. **5 + 5 + 3 = 13**
8. (a) Discuss the classification of silicon. Give examples.
- (b) Explain preparation, properties and applications of $(\text{SN})_4$ compounds.
- (c) Give the preparation and reaction of thio-cyanogen. **5 + 5 + 3 = 13**
9. (a) Discuss the preparation, properties and structures of XeF_4 , XeOF_4 and XeO_2F_2 .
- (b) Explain the properties and structures of BrCl , BrF_3 and IF_5 .
- (c) Write notes on borophosphate glasses.

PART – D

- IV. Answer any **ONE** question : **1 × 10 = 10**
10. (a) Explain the causes and consequences of Schotky and Frankel defects.
- (b) Describe the band theory of solids and classification of solids in metals, semiconductors and insulators. **5 + 5 = 10**
11. What are the postulates of VSEPR theory? Sketch and explain the structure of AB_2E_2 and AB_4E type compounds. **5 + 5 = 10**
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**Previous M.Sc. Degree Examination
OCTOBER/NOVEMBER 2014
(Directorate of Distance Education)
CHEMISTRY**

(DPA 530) Paper DECHEM 1.03 – ORGANIC CHEMISTRY - III

Time : 3 Hours]

[Max. Marks : 75/85

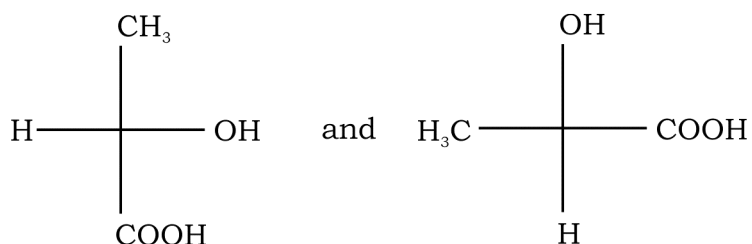
Instructions to Candidates :

- 1) Scheme : 75 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**.
- 2) Scheme : 85 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**; and any **ONE** question from Part **D**.

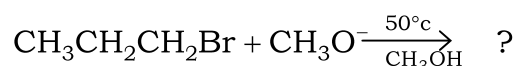
PART – A

I. Answer any **TEN** of the following : **10 × 2 = 20**

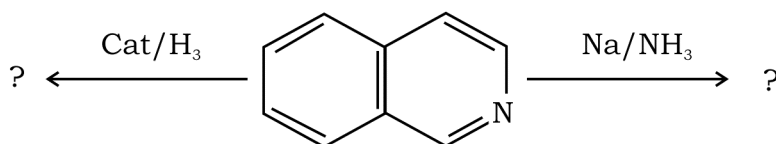
1. (a) How are singlet and triplet carbenes generated?
(b) Tropyllium cation shows a single peak in its PMR spectrum. Explain.
(c) Explain the mechanism of cope elimination with an example.
(d) Mention the steric relation between the following pairs :



- (e) Define the terms enantiomers and diastereomers.
(f) Write the product(s) in the following and justify :



- (g) Formulate the products in the following :



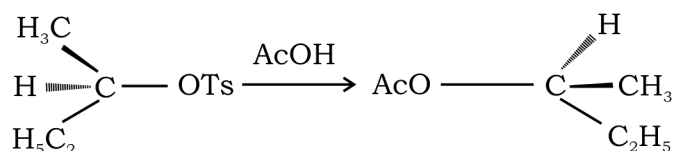
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- (h) Write the structures of any two drugs containing quinoline nucleus.
- (i) Why does S_N1 reaction yields always a racemic product? Explain.
- (j) Furan undergoes Diel's-Alder addition whereas pyrrole and thiophene does not. Give reason.
- (k) What are α – and β – glucosidic linkages? Explain.
- (l) Mention the reagents used to block the aminogroups of amino acids in peptide synthesis.
- (m) Why does t-butyliodide undergoes solvolysis by S_N1 mechanism and not by S_N2 mechanism?
- (n) Why does butane exists in staggered conformation?
- (o) Explain the difference between configuration and conformation.

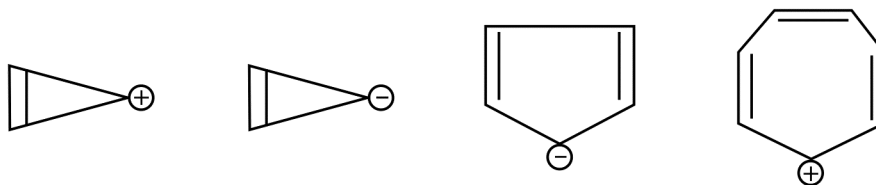
PART – B

II. Answer any **TWO** questions : **2 × 8 = 16**

- 2. (a) Describe any two rearrangements involving nitrene as an intermediate.
- (b) Write an account of determination of configuration of geometrical isomers. **4 + 4**
- 3. (a) Comment on the mechanism of the following reaction. Write its rate equation and energy profile diagram.



- (b) Write an account on secondary structure of proteins. **4 + 4**
- 4. (a) Indicate which of the following are aromatic and non-aromatic stating reasons.



- (b) Describe the insertion reactions of carbenes. **4 + 4**

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PART – C

- III. Answer any **THREE** questions : **3 × 13 = 39**
5. (a) Describe the mechanism of Fischer indole synthesis.
- (b) Write an account of generation stability and reactions of carbocations.
- (c) Explain the stereospecific addition of carbene to olefins with suitable examples. **4 + 5 + 4**
6. (a) Discuss the aromaticity of benzenoid and non-benzenoid compounds by taking suitable examples.
- (b) Describe with suitable example, the various steps involved in the assignment of R and S configuration of an asymmetric centre.
- (c) Explain the reaction of HBr with 1, 3 - butadiene in absence of air with a energy profile diagram. **4 + 5 + 4**
7. (a) How the ring structure of fructose is determined?
- (b) Give suitable reason for the slow reactivity of neopentyl halide in S_N2 reaction.
- (c) With the help of resonance structures show the most reactive position towards electrophilic substitution in furan. **4 + 5 + 4**
8. (a) Formulate a method for the synthesis of 18-crown-6. Give its synthetic utility.
- (b) Describe the mechanism of Skraup synthesis of quinoline.
- (c) Give the electrophilic substitution reactions of pyrimidine. **4 + 5 + 4**
9. (a) Outline any two methods of synthesis of pyrazoles.
- (b) Explain the basic principle involved in solid phase peptide synthesis.
- (c) Discuss the use of HIO_4 in the determination of size of the ring in glucose. **4 + 5 + 4**

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PART – D

IV. Answer any **ONE** question : **1 × 10 = 10**

10. (a) Give any two methods of synthesis and reactions of thiophene.
(b) Write an account of Gabriel phthalimide synthesis. **5 + 5**
11. (a) Describe the chemical reactions to establish the structure of cellulose.
(b) Write note on :
(i) Neighbouring group participation
(ii) Hudson's rule. **5 + 5**
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Previous M.Sc. Degree Examination

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CHEMISTRY

(DPA 540) Paper DECHEM 1.04 – PHYSICAL CHEMISTRY - IV

Time : 3 Hours]

[Max. Marks : 75/85

Instructions to Candidates :

- 1) *Scheme : 75 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**.*
- 2) *Scheme : 85 marks - Answer Part **A** (any **TEN** subdivisions), any **TWO** questions from Part **B** and any **THREE** questions from Part **C**; and any **ONE** question from Part **D**.*

PART – A

- I. Answer any **TEN** of the following : **10 × 2 = 20**
1. (a) What is meant by atomic model?
 - (b) List out the objections of Bohr's atomic model.
 - (c) What are the outcome of Davission and Germer experiment?
 - (d) Explain the terminologies of Thermodynamics.
 - (e) What is meant by internal energy change in thermodynamics?
 - (f) What is rate constant?
 - (g) What are catalysts? Give examples.
 - (h) Explain buffer index.
 - (i) What are reversible electrodes? Give examples.
 - (j) Calculate free energy change for an electrochemical reaction involving three electrons with emf of 1.5 V. Given $F = 96500$ coulombs.
 - (k) Calculate the over voltage for an electrochemical process having extra potential of 0.3 volt over its initial value of 1.2 volt.
 - (l) What are the characteristics of Dropping mercury electrode?

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- (m) How to check the completeness of deposit in electrogravimetry?
- (n) Define standard electrode potential.
- (o) Give the significance of wave equation employed in quantum mechanics.

PART – B

- II. Answer any **TWO** questions : **2 × 8 = 16**
2. Explain particles, wave nature and angular momentum quantisation of electron. Calculate the deBroglie wavelength of an electron moving with velocity $5.93 \times 10^6 \text{ ms}^{-1}$ and mass = $9.11 \times 10^{-31} \text{ kg}$, $h = 6.626 \times 10^{-34} \text{ JS}$. **8**
3. (a) Explain the terms : State variables and thermodynamic equilibrium.
(b) What is Zeroth law of thermodynamics? Explain. **4 + 4 = 8**
4. (a) With equation explain order and molecularity of complex reactions.
(b) Discuss the general characteristics of catalyst. **4 + 4 = 8**

PART – C

- III. Answer any **THREE** questions : **3 × 13 = 39**
5. (a) Discuss different concepts of Acids and Bases.
(b) Explain the terms pH scale and Dissociation of weak acid.
(c) Explain degree of hydrolysis and acid-base hydrolysis. **5 + 4 + 4 = 13**
6. (a) What is glass membrane electrode and how it is used to measure pH of a solution?
(b) Define Faraday's laws and explain decomposition potential.
(c) What are the advantages of ion selective electrodes. **6 + 4 + 3 = 13**
7. (a) What are the advantages of pt electrode in electrogravimetric analysis? Explain the determination of copper under constant current method.
(b) Explain different types of currents of a polarogram.
(c) What is polarographic maxima? How is it eliminated in the analysis? **5 + 4 + 4**

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8. (a) Explain any two postulates of quantum mechanics. What are the advantages of Rutherford's atomic model? 5 + 5 + 3
- (b) Describe Bohr's theory of hydrogen atom and justify its use in explaining hydrogen spectra.
- (c) What are exact and inexact differentials? 5 + 5 + 3
9. (a) Explain the comparison of isothermal and adiabatic reversible expansions.
- (b) What is Joule-Thomson effect? Explain.
- (c) Sixteen moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm³ to a volume of 10 dm³ at 27°C. What is the maximum work done in Joules (R = 8.314). 5 + 5 + 3

PART – D

- IV. Answer any **ONE** question : 1 × 10 = 10
10. (a) Obtain the rate expression for second order reaction, when $a = b$.
- (b) Explain the terms : Rate, Rate equation, Order and Molecularity of a reaction. 5 + 5
11. (a) Explain free energy, enthalpy and EMF of an electrochemical cell.
- (b) What is electrochemical series? Explain activity and mean ionic activity of electrolytes. 5 + 5
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