

First Year M.Sc.(Chemistry) Degree Examination

August / September 2009

Directorate of Distance Education

(Freshers)

Analytical Chemistry - I

Time : 3 Hours

Max. Marks : 85

Note : Answer question 1 (any eleven subdivisions) any three questions each from Part B and Part C.

Part - A

1. a. What is R_f value? Write its importance in chromatography. (2x11=22)
- b. What are CFCs? Why they have been banned in developed countries?
- c. Name the threshold limits of water quality parameters.
- d. List the ideal characteristics of a mobile phase in HPLC.
- e. Write the principle of affinity chromatography?
- f. An iron- thiocyanate complex gave an absorbance value of 0.362 at 545 nm. If the solution contains 3.2×10^{-4} g of Iron in 250 ml of solution, calculate the molar absorptivity value (path length = 10mm)
- g. What is Q test? Write its importance in the statistical evaluation of analytical data.
- h. What are metal in indicators? Give any two examples.
- i. Mention the factors influencing the solubility of precipitates in gravimetry.
- j. Define sample mean and population mean. Write its significance in analytical measurement.
- k. What are the ideal characteristics of wash liquids used in gravimetry?
- l. Write the expression between the plate height and number of plates in chromatography.
- m. Why GCMS technique is widely used on the analysis of gaseous pollutants?
- n. Mention the factors affecting the separations of components in TLC.
- o. Liquid SO_2 is a better non aqueous solvent than an unhydrous H_2SO_4 why?

Part - B

(8x3=24)

2. a. Explain the mechanism of a redox indicator i.e. diphenylamine in the titration of iron (II) with $\text{K}_2\text{Cr}_2\text{O}_7$.
- b. Discuss the gaussian error distribution curve with an example. (4+4)
3. a. Describe the requisites for an ideal precipitation in gravimetric analysis.
- b. Derive Nernst distribution law in solvent extraction. (4+4)

4. a. Explain the chemical reactions in liquid ammonia.
- b. Describe pararosaniline method of atmospheric sulphur dioxide estimation. (4+4)
5. a. Explain the principle of column chromatography. How do you improve the column efficiency?
- b. Describe the working principle of electron capture detector in gas chromatography with a neat diagram. (4+4)

Part - C**(13x3=39)**

6. a. Explain the various approaches used to develop plates for analyte spot identification in TLC.
- b. What is ion exchange capacity? Explain the mechanism of ion exchange in cation exchange resin with an example.
- c. Calculate the carrier gas velocity and the minimum plate height if He is the carrier gas with $A = 0.01\text{cm}$ $B = 0.30\text{ cm sec}$ $C = 0.05$ in van Deemeter's equation. (5+5+3)
7. a. Discuss the sources of the following metal ions i) As ii) pb
- b. Explain the toxic effects of heavy metals and CFCs on biological systems.
- c. Calculate the concentration of NO_2 in ambient air when 60 litres of air was sampled through FIA which gave 0.362 absorbance value in 50ml solution. (path length = 10mm) (5+5+3)
8. a. Explain the theory of acid - base indicator with an example.
- b. Describe the mechanism of precipitation from homogeneous solution.
- c. Calculate the pH of the following solutions with $[\text{H}^+]$ ion concentration
i) $2.4 \times 10^{-3}\text{ M HCl}$ ii) $3.2 \times 10^{-2}\text{ M HNO}_3$ (4+5+4)
9. a. Write the applications of gel permeation chromatography in polymers.
- b. Discuss the applications of affinity chromatography.
- c. What was the retention volume (V_r) if external solution (V_o) is 16ml and internal solution is 5 ml and fraction of internal solution (V_i) acceptable to solute (K) is 12ml? (4+5+4)
10. Write short notes on the following
 - a. acid base concept in non- aqueous media.
 - b. photochemical smog
 - c. thermal conductivity detector. (5+4+4)

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First Year M.Sc.(Chemistry) Degree Examination

August / September 2009

Directorate of Distance Education

(Freshers)

DECHEM : 1.02 : Chemistry - II

Inorganic Chemistry

Time : 3 Hours

Max. Marks : 85

- Note : 1) Answer Part- A (any Eleven subdivisions) any Three questions from Part - B and Part- C
- 2) Figures to right

Part - A

(11x2=22)

1. a. What are the σ and π bonds? Why σ bond is stronger than π bond?
- b. $AlCl_3$ is covalent, where as AlF_3 is ionic. Give reasons.
- c. Explain the term lattice energy.
- d. What is spectrochemical series?
- e. $[Co(NH_3)_6]^{3+}$ is diamagnetic where as $[CoF_6]^{3-}$ is paramagnetic. Give reasons.
- f. What are the limitations of VBT?
- g. Which is more polar: H_2S or H_2O ? Why?
- h. Why bond angles in NH_3 and PH_3 are different although N and P belongs to the same group?
- i. What is meant by siloxane bond?
- j. What is a three centred bond? Give an example.
- k. Why borazole is called 'inorganic benzene'?
- l. Many noble gases generally form compounds with fluorine. Why?
- m. What are pseudohalogens? Give two examples.
- n. What are crystal defects?
- o. What do you understand by colour centre ?

Part - B

2. a. Calculate the bond order for CO. Comment on its magnetic property.
- b. Describe Born - Haber cycle and its applications. (5+3)
3. a. Sketch and explain the molecular orbital energy level diagram of $[Co(NH_3)_6]^{3+}$ complex.
- b. Give the energy level diagram of 3- centred molecular orbital of borane. (5+3)

4. a. How are the borazine and S_4N_4 prepared? Give their structure and important uses.
b. Sketch and explain salient features of perovskite. (5+3)
5. a. Give a note on branched chain and cyclic silicone polymers.
b. Suggest probable structure for IF_7 . (5+3)

Part - C

6. a. Mention the salient features of VSEPR theory. Draw the structures of XeF_4 and SF_4 .
b. What is radius- ratio rule? How it is useful in predicting the structures of ionic compounds? (8+5)
7. a. Describe the principles of VBT and CFT. Account for their relative merits and demerits.
b. What is Jahn- Teller effect? How does it affect the stability of the metal complexes? (8+5)
8. a. Give the synthesis and structure of sulphur nitrogen polymer systems.
b. Iodine monochloride and bromine trifluoride behave as ionizing solvents. Explain. (8+5)
9. a. Briefly discuss above various types of defects encountered in solids.
b. What is Keto-enol tautomerism? Discuss the factors influencing the same. (8+5)
10. a. Indicate the bond order and number of unpaired electrons in the following:
 NO^+ , O_2 , O_2^+ and CN^+
b. Explain with examples the effect of ligands on the magnitude of Δ . (8+5)

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First Year M.Sc.(Previous) Chemistry Degree Examination

August / September 2009

Directorate of Correspondence Course

(Freshers)

DECHEM : 103 : Chemistry - I

Organic Chemistry

Time : 3 Hours

Max. Marks : 85

Note : Answer Part A (any Eleven questions) THREE questions from Part B and Part - C

Part - A

(2x11=22)

1. a. How free radicals are generated? Give example.
- b. How do you explain the stability of benzyl cation?
- c. What are electrophiles and nucleophiles? Give one example to each.
- d. What is mutarotation?
- e. Complete the following reaction.



- f. State Huckel Rule of aromaticity.
- g. Write the structure of R and S for 2- butanol.
- h. State Markownikov's rule ?
- i. What are enantiomers? Give examples.
- j. Illustrate with an example the Hoffman's rule
- k. Write the ring structure for sucrose
- l. Calculate the number of optical isomers for a compound containing four chiral centres.
- m. Give any one example of molecular rearrangement involving carbocations.
- n. What is an aldol condensation? Explain with example.
- o. Why pyridine is more basic than pyrrole?

Part - B

(8x3=24)

2. a. With a suitable example discuss the stereo chemistry of SN1 mechanism.
- b. Discuss the aromaticity of cyclopentadienyl anion. (4+4)

3. a. Describe the factors influencing the stability of carbo cations.
b. Describe the relation between elements of symmetry and optical activity. (4+4)
4. a. Write the mechanism of aromatic sulphonation by taking a suitable examples.
b. Discuss the mechanism of Fisher Indole synthesis. (4+4)
5. a. How amino acids are classified? Give the use of melonic ester synthesis for amino acids.
b. Write a note on blocking agents in the synthesis of peptides. (4+4)

Part - C**(13x3=39)**

6. a. Describe the mechanism of free radicles addition which leads to polymerisation.
b. What are DL and RS nomenclature? Discuss with an example.
c. Write any two methods of synthesis of quinolines. (4+4+5)
7. a. Elucidate the structure of sucrose.
b. Define saytzeff's rule. Explain with an example.
c. Write a note on cope eliminations. (4+4+5)
8. a. State the requisite conditions for an organic molecule to exhibit aromaticity.
b. How carbo anions are generated? Give any two methods of their synthesis.
c. Discuss secondary structure of proteins. (4+4+5)
9. a. Out line the synthesis of amino acids by Azolactone and Hydention approaches.
b. Write a note on structure of proteins.
c. List out the applications of [18] crown in organic synthesis. (5+4+4)
10. a. Describe a reaction where it does not follow Markovnikov's Rule.
b. Give the generation and application of carbenes in organic synthesis.
c. Write a note on comparative aromaticity of furan, pyrrole and thiophene. (4+4+5)

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First Year M.Sc. Chemistry Degree Examination
August / September 2009
Directorate of Correspondence Course
(Freshers)
Physical Chemistry
DECHEM : 104 : Chemistry - IV

Time : 3 Hours

Max. Marks : 85

Note : Answerer Part A (any Eleven questions), any THREE questions each from Part- B and Part C.

Part - A

1. a. What is a perfect differential? (2x11=22)
- b. Under what conditions does the isothermal expansion of a gas become a free expansion process?
- c. What are the limitations of the First law of thermodynamics? Justify the need for the Second law.
- d. Define space wave function.
- e. Give any two postulates of Bohr's theory.
- f. What are the characteristics of an activated complex?
- g. State the differences between order and molecularity.
- h. What are the successes of homogeneous catalysis?
- i. Explain the ionizations of phosphoric acid and their dissociation constants.
- j. What is buffer capacity?
- k. Explain activity and mean ionic activity.
- l. What are the defects in standard hydrogen electrode?
- m. Explain the types of concentration cell.
- n. Name the factors which affect the limiting current .
- o. What are the disadvantages of amperometric titrations?

Part - B

2. Derive the Schrodinger's wave equation. (8)
3. What is meant by Joule- Thomson effect? How do you account for it? (8)
4. Derive Nernst equation giving the effect of concentration of the surrounding electrolytes on the potential of an electrode. (8)
5. Discuss the dropping mercury electrode with a neat sketch of the electrode assembly. (8)

Part - C

6. a. Derive rate expressions for second - order reactions for a= b condition. (8)
 b. For the second - order reaction

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
 at 25°C, $k_2 = 6.21 \times 10^{-3}$ litre/mole/sec. Calculate the time required for the hydrolysis of 90% ester if the initial concentration of the reaction in the reaction mixture are:
 a. 0.05M ester + 0.1M NaOH
 b. 0.05M ester + 0.5M NaOH (5)
7. a. Explain the mechanism and kinetics of enzyme catalyzed reaction. (8)
 b. State and explain the Zeroeth law of thermodynamics. (5)
8. a. Discuss proton transfer theory of acids and bases. Explain the effect of solvent on the strength of acids and bases. (8)
 b. Using the Lewis acid - base concept, determine the trend in the acid strength in the series.
 a. HClO_4 , HClO_3 , HClO_2 and
 b. H_3PO_4 , H_3PO_3 , H_3PO_2 (5)
9. a. What is meant by hydrolysis constant and degree of hydrolysis. Explain the relation between K_h , K_a and K_w . (8)
 b. Calculate the hydrolysis of 0.1 M solution of sodium acetate at 25 °C, $K_a = 1.7 \times 10^{-5}$ and $K_w = 1 \times 10^{-14}$. (5)
10. a. Explain the basic principles of cyclic voltammetry and its application. (8)
 b. Write a note on Compton effect. (5)

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