

(76)

This question paper contains 4 printed pages]

09/5/17

Roll No.

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S. No. of Question Paper : 761

Unique Paper Code : 217401

Name of the Paper : Inorganic Chemistry—III
(Paper—CHHT 408)



Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt any five questions.

All questions carry equal marks.

1. Explain any five of the following, giving suitable reasons :
- Borazine readily undergoes addition reactions, but benzene does not.
 - Substitution method is adopted for the determination of Ca^{2+} ion in complexometric titration.
 - Unlike carbon, nitrogen has little tendency for catenation.

P.T.O.

- (d) White phosphorus is highly reactive while red phosphorus is not.
- (e) Interhalogen compounds are more reactive than halogens.
- (f) Perchloric acid is a stronger acid than other oxoacids of chlorine.
- (g) He does not form clathrate compounds. 3×5
2. (a) What are silicates ? How are they classified ? Draw the structures of the basic unit of each class of silicates. 1,1,3
- (b) Arrange H_3PO_2 , H_3PO_3 and H_3PO_4 in increasing order of :
- (i) Acid strength and
- (ii) Reducing power.
- Explain the order giving suitable reasons. 2½,2½
- (c) What are hydrides ? What type of hydrides are formed by s-block elements ? Give a brief account of covalent hydrides. 1,1,3
3. (a) How does diborane react with ammonia under different conditions ? Explain the structure and bonding of diborane. 3,2

- (b) Draw the structures of the following :
- (i) XeF_2 , 2SbF_5
- (ii) Basic beryllium acetate.
- (iii) IF_5 . 2,2,1
- (c) What are phosphonitrilic compounds ? Give the structures of two cyclic phosphonitrilic compounds. State the potential uses of these compounds. 1,2,2
4. (a) Explain giving relevant chemical equations, what happens when :
- (i) Conc. nitric acid reacts with copper metal
- (ii) Phosphorus pentoxide reacts with water
- (iii) Boric acid is heated strongly
- (iv) Chlorine trifluoride reacts with platinum pentafluoride
- (v) Nitrous oxide reacts with sodium amide. 5×1
- (b) What are carboranes ? How are they classified ? Draw the structures of three isomers of $\text{C}_2\text{B}_{10}\text{H}_{12}$. 1,1,3
- (c) What are polyhalides ? How are they prepared ? Discuss the structures of :
- (i) ICl_4^- , and
- (ii) ICl_2^- on the basis of VSEPR theory. 1,1,3

5. (a) How is peroxodisulphuric acid prepared by electrolysis ? Draw its structure. How does it react with :
- (i) Fe^{2+} , and 2,1,2
- (ii) I^- . 2,3
- (b) What is allotropy ? Explain the change in viscosity with the increase of temperature on the allotropic forms of sulphur. 2,3
- (c) How are the fluorides of xenon prepared ? Explain the structure of XeF_2 on the basis of molecular orbital theory. 3,2
6. Write short notes on any *three* of the following : 3×5
- (a) Silicones
- (b) Inert pair effect
- (c) Complexometric titration
- (d) Basic properties of halogens.

This question paper contains 7 printed pages]

Roll No.

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S. No. of Question Paper : 762

Unique Paper Code : 217403

Name of the Paper : Organic Chemistry-III (CHHT-409)

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt six questions in all.

Question No. 1 is compulsory and carries 15 marks.

All other questions are of 12 marks each.

1. (a) Piperidine on exhaustive methylation followed by heating with AgOH gives a compound A which on repeating the same process gives a compound B (C_5H_8) which isomerises into another compound C. Identify A, B, C and write the reaction involved. 6

P.T.O.

(b) Give a suitable explanation for the following (any three) :

(i) Anthracene undergoes electrophilic substitution as well as addition reaction at 9, 10 positions.

(ii) Acylation of aniline deactivates it towards electrophilic aromatic substitution.

(iii) Furan-2-aldehyde gives Tollen's test but pyrrole-2-aldehyde does not.

(iv) Sulphonation of naphthalene with conc. H_2SO_4 at 40°C yields mainly the naphthalene-1-sulphonic acid and at 160°C , the main product is the naphthalene-2-sulphonic acid.

3×3=9

2. (a) Explain with the help of mechanism why nitration of naphthalene occurs at 1-position and not a 2-position.

4

(b) Describe the Haworth synthesis of phenanthrene.

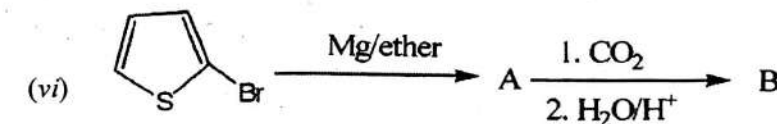
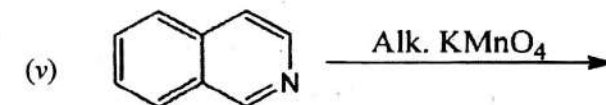
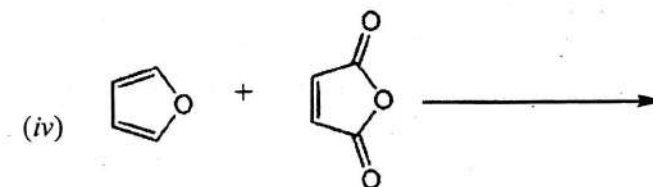
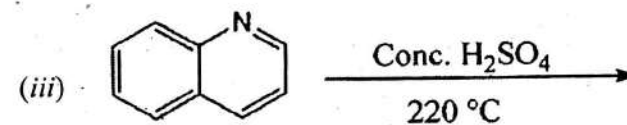
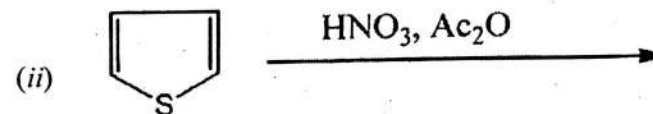
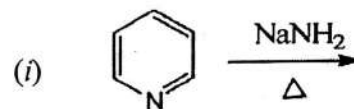
4

(c) Synthesise 2, 9-dimethyl anthracene starting from compound containing one benzene ring.

4

3. Complete the following reactions (any six) :

6×2=12



4. (a) Why electrophilic substitution in pyridine occurs at 3-position while nucleophilic substitution is favoured at position-2 ? 2

(b) Compare the basicities of pyridine and piperidine. 2

(c) How will you carry out the following conversions (any four) :

(i) Furan to furoic acid

(ii) *o*-acetamidotoluene to indole

(iii) Benzaldehyde into isoquinoline

(iv) Pyridine to 4-amino pyridine

(v) 2-phenyl ethylamine to 1-methyl isoquinoline. $2 \times 4 = 8$

5. (a) How was the presence of pyrrolidine ring in nicotine proved by Karrer ? Write *two* important medicinal uses each of morphine and quinine. 6

(b) How will you distinguish between 1°, 2° and 3° amines ? 3

(c) Write the steps for the synthesis of propane-1-amine : 3

(i) Using Gabriel phthalimide process

(ii) From suitable cyanide.

6. Write short notes on any *three* of the following : $4 \times 3 = 12$

(a) Fischer indole synthesis

(b) Skraup synthesis of quinoline

(c) Hantzsch synthesis of substituted pyridine

(d) Bischler-Napieralski synthesis for isoquinoline.

7. (a) Write the mechanism to synthesise 3-chloropyridine from pyrrole.

(b) Write the product when ethanenitrile is treated with methyl magnesium bromide followed by hydrolysis.

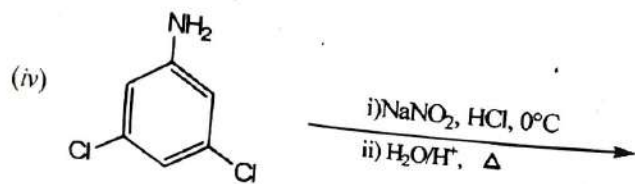
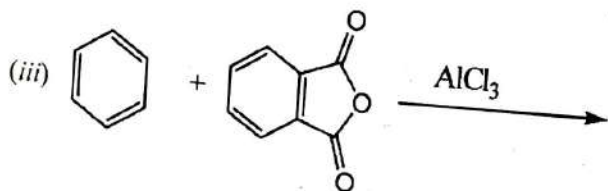
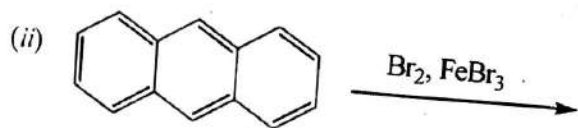
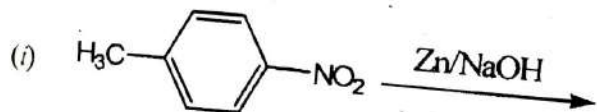
(c) Why coupling reactions with diazonium salts are generally not carried out in a solution less than pH 4 or more than pH 10.

(d) How will you convert naphthalene into : $3 \times 4 = 12$

(i) 1-Naphthylamine

(ii) 2-Naphthol.

8. (a) Complete the following reactions (any three) : $3 \times 1 = 3$



(b) Give reasons for the following : $3 \times 3 = 9$

(i) Furan is least aromatic of the five member ring compounds.

(ii) Pyridine-N-oxide readily undergoes electrophilic and nucleophilic substitution at 4-position.

(iii) Phenanthrene and anthracene both have three fused nucleus but phenanthrene has more resonance energy than anthracene.

This question paper contains 8 printed pages]

Roll No.

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S. No. of Question Paper : 763

Unique Paper Code : 217405

Name of the Paper : Physical Chemistry-III (CHHT-410)

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Physical Constants :

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$F = 96500 \text{ C mol}^{-1}$$

Attempt *six* questions in all, selecting at least *two* questions

from each Section. Question No. 1 is compulsory.

Use of Scientific calculator is permitted.

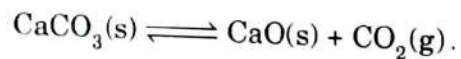
Graph sheet is provided.

1. Attempt any *five* questions given below :

(a) Addition of naphthalene increases the CST of the phenol-water system at constant pressure. Explain.

P.T.O.

- (b) The slope of the sublimation curve of any substance is greater than that of its vapour pressure curve. Explain.
- (c) Azeotropic mixtures have definite composition and definite boiling points yet they are not compounds. Explain.
- (d) Give the number of components in the following system and justify :



- (e) The e.m.f. of the hydrogen electrode is linearly dependent only on the pH of the solution. Explain.
- (f) Explain the role of salt bridge in electrochemical cells.
- (g) Why is a voltmeter not used for determination of the e.m.f. of a galvanic cell ?

5×3

Section A

2. (a) Differentiate between congruent and incongruent melting point systems with an example.

- (b) Construct the properly labelled phase diagram for zinc and magnesium system using the following data :
- (i) Melting point of magnesium, 655°C
- (ii) melting point of zinc, 500°C
- (iii) One eutectic point at 350°C with 20 mole per cent of zinc and another at 430°C with 92 mole per cent of zinc.
- (iv) A solid compound of MgZn_2 is formed which melts at 540°C. The maxima is not very sharp. Comment on the stability of the compound.
- (c) Draw the cooling curves for melts containing 40 mole percent zinc and 95 mole per cent zinc. Describe the cooling curves. 4,4,4
3. (a) The mean enthalpy of vaporization of water in the temperature range between 363.15 K and 373.15 K is 2268 J g^{-1} . Calculate the vapour pressure of water at 363.15 K, given that its value of 373.15 K is 76.0 cm Hg.

- (b) (i) Write the Gibbs-Duhem equation. Use this equation to derive the relationship :

$$\frac{d \ln p_A}{d \ln x_A} = \frac{d \ln p_B}{d \ln x_B}$$

- (ii) Use the above expression to show that in a binary miscible solution if one component shows ideal behaviour, the other also does so.
- (c) Draw and discuss the phase diagram for the three component system $\text{CH}_3\text{COOH}-\text{CHCl}_3-\text{H}_2\text{O}$. 4,4,4
4. (a) Derive the relation between the number of phases (P), components (C) and degrees of freedom (F) for a non-reactive system in which one component is present in all but one phase, and another one is present in only two phases. Rest of the components are present in all the phases.
- (b) The vapour pressures of two pure liquids A and B, which form an ideal solution, are 300 and 800 torr, respectively, at temperature T. A liquid solution of A and B for which the mole fraction of A is 0.60 is contained in a cylinder closed by a piston on which the pressure can be varied. The solution is slowly

vaporized at temperature T by decreasing the applied pressure, starting with a pressure of about 1 atm. Calculate (a) the pressure at which the first bubble of vapour is formed, (b) the composition of the vapour in this bubble (c) the composition of the last droplet, (d) the pressure when only this last droplet of liquid remains.

- (c) What is the basic principle underlying steam distillation ? A substance immiscible with water is distilled using this method. Derive an expression to calculate the relative mass of substances in the vapour phase in terms of their molar mass and vapour pressure. 4,4,4
5. (a) State and explain Nernst Distribution law. Discuss its limitations.
- (b) In a distribution experiment the following procedure is followed : An aqueous solution containing 0.2 g aspirin (as) in 50 ml solution is mixed with 30 ml ether. The bottle is shaken and allowed to come to equilibrium at

298 K. The distribution coefficient is determined as 4.7

$[C_{as}(\text{ether})/C_{as}(\text{water})]$:

- (i) Calculate how much aspirin is left in the aqueous phase.
- (ii) What amount of aspirin would remain unextracted in the aqueous phase if the extraction is done with three successive 10 ml portion of ether.
- (c) With the help of a suitable diagram, discuss the fractional distillation process of a two component system which forms an azeotropic mixture. 4,4,4

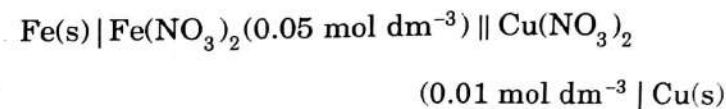
Section B

6. (a) Describe briefly the potentiometric method for determination of emf of a cell.
- (b) What are thermodynamic criteria for spontaneity of a cell ? Will Fe^{3+} ions be reduced to Fe^{2+} by Sn^{2+} ions ? Write cell reactions and formulate the cell involved.

$$E_{\text{Sn}^{4+}, \text{Sn}^{2+}|\text{Pt}}^{\circ} = 0.150 \text{ V and } E_{\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}}^{\circ} = 0.771 \text{ V.}$$

- (c) Describe the calomel half cell and derive its Nernst equation. 4,4,4

7. (a) Write the cell reaction and determine E_{cell} for the given cell at 25°C.



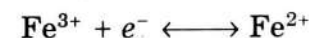
$$E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} = -0.441 \text{ V and } E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} = -0.337 \text{ V.}$$

- (b) Starting from Gibbs-Helmholtz equation and the relation $\Delta G = -nFE$, derive the following expression of ΔH and ΔS .

$$\Delta H = -nF \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right]$$

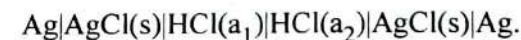
$$\Delta S = -nF \left(\frac{\partial E}{\partial T} \right)_P$$

- (c) Compute E° for the reaction :



$$\text{Given } E_{\text{Fe}^{3+}|\text{Fe}}^{\circ} = -0.336 \text{ V and } E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} = -0.441 \text{ V.}$$

8. (a) Derive the expression to calculate the liquid junction potential for the following cell with :



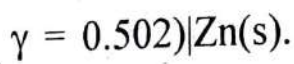
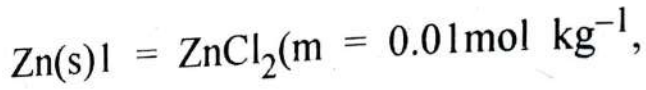
- (b) Determine the standard equilibrium constant for the following reaction at 298 K.



Given :

$$E_{\text{Sn}^{4+}, \text{Sn}^{2+}|\text{Pt}}^{\circ} = 0.150 \text{ V and } E_{\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}}^{\circ} = 0.771 \text{ V.}$$

- (c) Find the cell reaction and calculate the potential of the following cell at 298 K.



4,4,4

9. Write short notes on (any *three*) :

- (a) Reference electrode
- (b) Glass electrode
- (c) Potentiometric titration
- (d) Redox indicator.

4,4,4

This question paper contains 4 printed pages]

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28/5/17

Roll No.

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S. No. of Question Paper : 764

Unique Paper Code : 222453

Name of the Paper : Physics-II

Name of the Course : B.Sc. (Hons.) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt five questions in total.

Use of non-programmable calculator is allowed.

1. (a) State and prove Gauss's law in electrostatics. Give its differential form. 1,5,2
- (b) What are polar and non-polar dielectric materials ? Give one example of each. 2,1
- (c) If the electric field near the earth's surface be 310 N/C directed downwards, what is the surface charge density of earth. (Assume earth to be conducting sphere, Permittivity of free space $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) 4

P.T.O.

2. (a) Derive the relation for magnetic field due to a current-carrying straight conductor of finite length at some distance away from it using Biot-Savart law. 6
- (b) State Lenz's law of electromagnetic induction. What is its physical significance in electromagnetic induction process ? 2,3
- (c) An air core solenoid of length 1.2 m having 2500 turns draws a current of 1.2 mA. Find the magnetic field at the center of the solenoid. (Permeability of free space is $4\pi \times 10^{-7}$ Tm/A) 4
3. (a) What is displacement current ? Give expression of modified Ampere's law. 3,2
- (b) Using Maxwell's equations obtain the solution of plane electromagnetic wave propagating through uniform dielectric material. Show that em wave is a transverse in nature. Obtain the expression for velocity of this wave in terms of its dielectric constant and relative permeability. 5,3,2
4. (a) Define electric potential. How is it related to electric field ? 2,2

- (b) Derive expression for electric potential due a uniformly charged hollow sphere at a point :
 (i) inside it and
 (ii) outside it. 4,4
- (c) Show that electric field is a conservative field. 3
5. (a) Draw the circuit diagram of full wave bridge rectifier. Obtain the expression for ripple factor of rectified output. 2,7
- (b) What is zener diode ? Explain the working of zener diode as a voltage regulator. 2,4
6. (a) Draw the circuit diagram of common emitter small signal amplifier. Obtain the expression for its voltage amplification. 4,4
- (b) What is fixed biasing of a transistor ? Obtain the expression of stability factor. 2,5
7. (a) What are positive and negative feedback mechanisms in amplifiers ? Give comparative analysis of both. Obtain the expressions of effective gain in both cases. 2,2,4
- (b) What is Barkhausen's criterion for self-sustaining oscillations ? Give in short working of LC oscillator. 3,4

8. (a) What are 2's complements ? Subtract (1010) from (1101) using 2's complement. 3,2
- (b) Give symbol, truth table and Boolean expression for the following gates :
- (i) NAND 3,3
- (ii) XOR 3,3
- (c) How can a half adder be made using basic logic gates ? Give its truth table. 2,2

SET-A

20

11/5/17

100

S. No. of question paper: 1545

Unique Paper Code: 2171402

Name of the Course: B.Sc. (H) CHEMISTRY

Name of the Paper: Inorganic Chemistry of p - Block Elements

Semester: IV

Duration : 3 Hours.

Your roll no.:



Maximum Marks. : 75

Instructions for Candidates:

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any five questions.
3. All questions carry equal marks.

1. Explain any five of the following:

- (a) While nitrogen exists as N_2 , phosphorus exists as P_4 .
- (b) Iodine has low solubility in water but more in KI solution.
- (c) He and Ne do not form clathrate compounds.
- (d) Trimethylamine is a stronger base than trisilylamine.
- (e) N_3^- is a pseudohalide.
- (f) Oxygen is a gas while sulphur is a solid.
- (g) Borazine undergoes addition reaction but benzene does not. (5x3)

2. (a) How are peroxomonosulphuric acid and peroxodisulphuric acid prepared? Give their structures and any two properties.

(b) Write balanced equations for the preparation of XeF_4 and XeF_6 . Give their reactions with water.

(c) How does H_3BO_3 ionise in water? In aqueous solution H_3BO_3 is a weak acid but in the presence of polyhydroxy alcohols it behaves as a strong acid. Explain. (5,5,5)

3. (i) Draw the structures of the following (any five):

(a) $XeOF_4$ (b) $[Mg EDTA]^{2-}$ (c) BrF_5

(d) Basic Beryllium acetate (e) N_2O_5 (f) $[Si O_4]^{4-}$ (5x2)

(ii) What are silicones? What are the chain stopping and chain propagating units used in the preparation of silicones? Give important uses of silicones. (5)

4. (a) What is inert pair effect? Explain with suitable examples. Tl forms monovalent compounds, explain.

(b) Discuss the allotropes of phosphorus with respect to their structures, stabilities and reactivities.

(c) What are interhalogens? Explain why all interhalogens are diamagnetic. Give the reaction for hydrolysis of BrF_3 . (5,5,5)

5. Write short notes on any three of the following:

- (i) Silicates
- (ii) Phosphazenes
- (iii) Intercalation compounds of graphite
- (iv) Allotropes of sulphur

(5x3)

6. (a) Giving suitable reasons briefly comment on the comparative behaviour of any five of the following:

- (i) Acid strength of HClO_3 and HClO_4
- (ii) Bond angles of NH_3 and PH_3
- (iii) Catenation tendencies of carbon and silicon
- (iv) Densities of Graphite and Diamond
- (v) Reactivities of Cl_2 and ICl
- (vi) P-O bond lengths in P_4O_6 and P_4O_{10}
- (vii) Thermal stabilities of HBr and HI
- (viii) Solubilities of Kr and Xe in water

(5x2)

(b) Explain the structure of B_2H_6 and give at least two experimental evidences supporting the presence of two different types of hydrogen atoms in B_2H_6 . (5)

Sl - No. of Q.P. : 1546

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Unique Paper Code: 2171401

(21)

18/5/17

Name of the Paper: Organic Chemistry (Paper-10)

Name of the Course: B.Sc(H) Chemistry (~~EX-UP~~)

Semester: IV

Duration: 3 hrs

Maximum Marks: 75



F-8

Instructions for Candidates

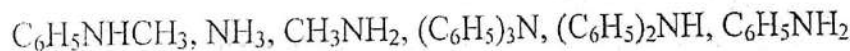
1. Write your Roll No. on the top immediately on receipt of this paper
2. Attempt **ANY SIX** questions in all
3. Question No. 1 carries 15 marks
4. All other questions are of 12 marks each

Q1. a.) Account for the fact that the substitution of the nitro group at *p*-position makes aromatic amine a weaker base but makes phenol a stronger acid.

b.) Explain why electrophilic substitution in Indole takes place at C-3 position?

c.) How will you synthesise crotonic acid from diethyl malonate?

d.) Arrange the following compounds in decreasing order of their basic strength:



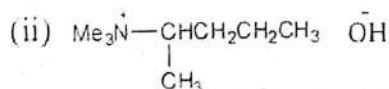
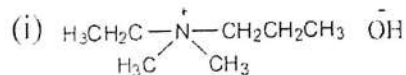
e.) An aromatic amine **A** (C_6H_7N) on acetylation gives compound **B** (C_8H_9NO).

Compound **B** on bromination followed by hydrolysis gives compound **C** (C_6H_6NBr).

Write the reaction sequence and identify compounds **A**, **B** and **C**.

(3, 3, 3, 3, 3)

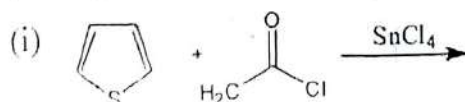
Q2. a.) Give the alkenes formed upon heating the following compounds:

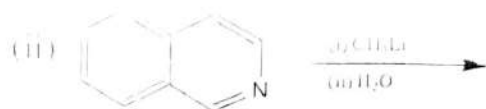


b.) Explain why pyridine and pyrrole are aromatic in nature?

c.) $H_3\overset{\cdot}{N}CH_2COO^-$ exists as a dipolar ion where as *p*- $NH_2-C_6H_4-COOH$ does not. Explain.

d.) Complete the following reactions:



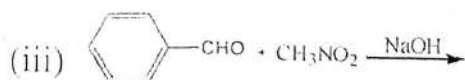
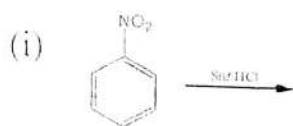


(1.5×2=3, 3, 3, 1×3=3)

Q3. a.) How will you prepare Chloropicrin from nitromethane?

b.) Coupling reactions of diazonium salts are generally not carried out in a solution of pH < 4 and pH > 10. Explain.

c.) Complete the following reactions:



d.) Condensation of $C_6H_5NH_2$ with C_6H_5CHO yields **A**, which is hydrogenated to give compound **B**. Identify the compounds **A** and **B**.

(3, 3, 1×3=3, 3)

Q4. a.) Explain keto-enol tautomerism in diethyl malonate and also explain why is it called an active methylene compound?

b.) Synthesise **ANY THREE** of the following compounds from ethyl acetoacetate:

(i) 4-Methyl uracil

(ii) 2-Butanone

(iii) Propanoic acid

(iv) Succinic acid

(3, 3×3=9)

Q5. a.) Give reasons for **ANY TWO** of the following:

(i) Pyridine undergoes electrophilic substitution reaction at 3-position.

(ii) Nitration in naphthalene occurs at 1-position.

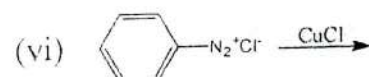
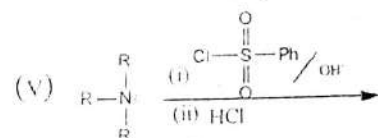
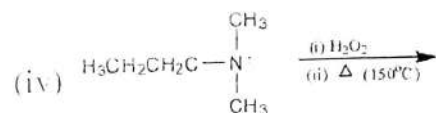
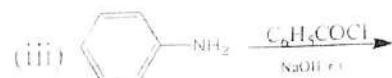
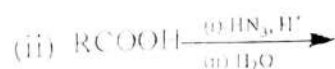
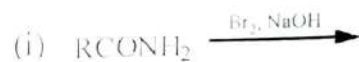
(iii) Phenanthrene undergoes oxidation at 9, 10-position.

b.) Deduce the structure of naphthalene.

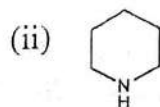
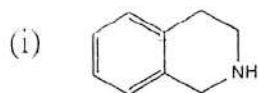
c.) Give the Haworth synthesis of anthracene.

(2×2=4, 4, 4)

Q6. a.) Name the reaction and give the product of the following reactions (ANY FIVE):



b.) Give the Hofmann exhaustive methylation products of ANY ONE of the following:



(2×5=10, 2)

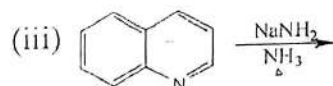
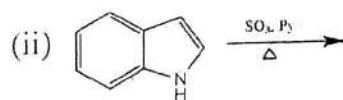
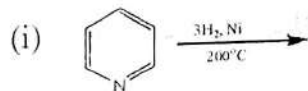
Q7. a.) Describe ANY TWO synthesis mentioned below:

(i) Knorr Pyrrole synthesis

(ii) Friedlander synthesis of quinoline

(iii) Haworth synthesis of phenanthrene

b.) Complete the following reactions (ANY TWO):



(4×2=8, 2×2=4)

Q8. Write short notes on ANY THREE of the following:

(i) Lossen rearrangement

(ii) Gabriel phthalimide synthesis

(iii) Mannich reaction

(iv) Pictet-Spengler synthesis of isoquinoline

(4, 4, 4)

5070 Q.P. 1547
Unique Paper Code : 2171403

(22)

Name of the Paper : Physical Chemistry (Electrochemistry & Conductance) Paper 1 I

Name of the Course : B.Sc. (II) Chemistry (~~First~~ ~~Year~~ ~~UP~~)

Semester : IV

Duration : 3 hours

Maximum Marks : 75



Instructions for candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **five** questions in all selecting any **two** questions from each Section.
3. Q. No. 1 is **compulsory**.
4. Attempt all parts of a question together.
5. Use of scientific calculator and logarithmic table is allowed.

1. Answer any **five** of the following: (5 x 3 = 15)
 - a. The role of a salt bridge is to reduce the liquid junction potential to zero. Explain.
 - b. The mobility of alkali metal ions in aqueous solution follows the order: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$. Explain why.
 - c. Write the half-cell for a glass electrode. A glass electrode is not suitable for determining pH of solutions greater than 9. Explain why.
 - d. Write the expression of Walden's rule. Explain why only large ions like picrate or quaternary ammonium salts obey the Walden's rule?
 - e. What are the advantages of conductometric titrations over volumetric titrations?
 - f. Define ionic velocity and ionic mobility. Give their SI units. Also give mathematical relationship between mobility and transport number.
 - g. The H^+ ion is the smallest known ion. Yet its conductance is appreciably high in aqueous solution. Why?

Section A

2.
 - a. Explain the asymmetry and electrophoretic effect observed in strong electrolytes like KCl.
 - b. What are the criteria for choosing the indicator electrolyte in the moving boundary method? Using the moving boundary method, calculate the transport number of H^+ ion from the following data
(Given equivalent mass of Ag = 108 g).
Concentration of HCl solution = 0.1 N
Mass of Ag deposited = 0.1209 g
Movement of boundary = 7.5 cm
Cross-section of the tube = 1.24 cm²

- c. Conductance of a saturated solution of CaF_2 at 27°C was found out to be $7.26 \times 10^{-5} \text{ S}$ when it was placed between a cell where the electrodes are 2.2 cm apart and have an area of 3.8 cm^2 . The molar ionic conductivities at infinite dilution of Ca^{2+} and F^- are 104 and $48 \text{ S cm}^2 \text{ mol}^{-1}$. The conductivity of water used for making the solution was $2 \times 10^{-6} \text{ S cm}^{-1}$. Calculate
- Cell Constant
 - Specific Conductance of the solution.
 - Molar Conductance of CaF_2 at infinite dilution
 - Solubility (S)
 - Solubility product (K_{sp}) of the salt

(5, 5, 5)

3.

- How does the Kohlrausch's law help in determining the equivalent conductance of a weak electrolyte at infinite dilution? The molar conductance of CH_3COONa , HCl and NaCl at infinite dilution are 91.0×10^{-4} , 426.16×10^{-4} and $126.45 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ respectively at 25°C . Calculate molar conductance at infinite dilution (λ_m°) for acetic acid.
- Write the Debye-Hückel Onsager equation for strong electrolytes explaining the significance of each term. Show using this equation that under conditions of infinite dilution (conc ≈ 0), the molar conductance reaches its limiting value. On the basis of the equation, explain the effect of dielectric constant, viscosity and temperature on the conductance of a solution.
- At 25°C , the specific conductance of 0.01 M aqueous solution of a weak acid is $1.63 \times 10^{-2} \text{ S m}^{-1}$ and its molar conductance at infinite dilution is $390.7 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation and the dissociation constant of the acid.

(5, 5, 5)

4. Write short notes on any **three** of the following ($3 \times 5 = 15$)

- Debye-Falkenhagen Effect & Wien Effect
- Kohlrausch's Law of Independent Migration of Ions
- Hittorf's method for determining the transport number of ions
- Types of Conductometric Titrations

Section B

5.

- Derive the expression for determining the pH of a solution using quinhydrone electrode. List a limitation of the quinhydrone electrode.
- Calculate the standard electrode potential for the reaction
 $\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cr}(\text{s})$
 Given $E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^\circ = 0.74 \text{ V}$; $E_{\text{Cr}^{3+}/\text{Cr}^{2+}/\text{Pt}}^\circ = 0.40 \text{ V}$
- The emf of the cell :
 $\text{AgCl}(\text{s}) / \text{Ag}(\text{s}) / \text{KCl}(\text{aq}) / \text{Hg}_2\text{Cl}_2(\text{s}) / \text{Hg}(\text{l})$
 is 0.0455 V at 298 K and the temperature coefficient is $3.38 \times 10^{-4} \text{ VK}^{-1}$. Write the cell reaction and calculate ΔG , ΔH and ΔS of the cell.

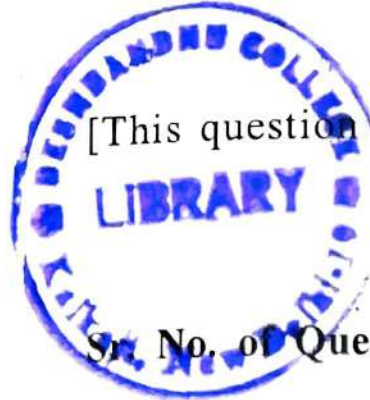
(5, 5, 5)

- 6.
- It is possible to determine the accurately the ionic product of water with the help of an electrochemical cell. Explain.
 - The standard equilibrium constant for the reaction $2\text{Cu}^+ (\text{aq}) \rightleftharpoons \text{Cu}^{2+} (\text{aq}) + \text{Cu} (\text{s})$ at 298 K is 1.646×10^6 .
 - Write down the half-cell reactions and construct the cell having the above cell reaction.
 - Calculate the standard potential of the cell.
 - The potential of the cell $\text{Zn} / \text{ZnCl}_2 (0.01021 \text{ mol kg}^{-1}) / \text{AgCl}(\text{s}) / \text{Ag} (\text{s})$ is found to be 1.1566 V. What is the mean ionic activity coefficient of ZnCl_2 in the solution at 298 K?

Given $E_{\text{Cl}^- / \text{AgCl} / \text{Ag}}^\circ = 0.2221 \text{ V}$; $E_{\text{Zn}^{2+} / \text{Zn}}^\circ = -0.7628 \text{ V}$

(5, 5, 5)

7. Write short notes on any **three** of the following: ($3 \times 5 = 15$)
- Determination of solubility product of a sparingly soluble salt using electrochemical cell
 - Classification of Concentration cells
 - Potentiometric Titrations – Principle, Types
 - Standard Calomel Electrode



[This question paper contains 8 printed pages.]

115119
Your Roll No.....

Sr. No. of Question Paper : 2793

GC-4

Unique Paper Code : 32171401

Name of the Paper : Inorganic Chemistry – III. Coordination Chemistry

Name of the Course : **B.Sc. (H) Chemistry**

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

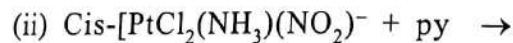
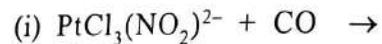
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **FIVE** questions in all.
3. Question No. 1 is compulsory.

1. (a) Give the oxidation state of the central metal ion in the following complexes :

- (i) Co in $\text{Na}[\text{Co}(\text{CO})_4]$,
- (ii) Tc in TcO_4^- ,
- (iii) Cr in $[\text{CrO}_2\text{Cl}_2]$,
- (iv) Hg in $\text{Na}_3[\text{Hg}(\text{S}_2\text{O}_3)_2]$

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(b) Predict the geometry of the product formed in the following reaction.

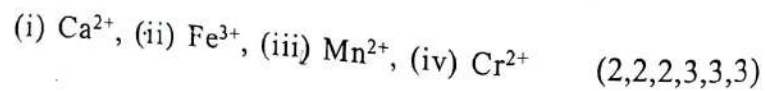


(c) Give the complete electronic configuration of terbium (Atm. No. 65) and the number of unpaired electrons in Tb^{3+} ion.

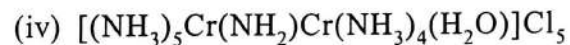
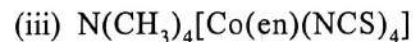
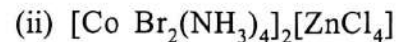
(d) 4d and 5d elements usually form low spin complexes. Justify.

(e) When acidified (with conc. H_2SO_4) H_2O_2 is added slowly with continuous stirring to a beaker containing orange aqueous solution of compound A and benzene, a dark blue layer of compound B appears and separates in the benzene layer. Identify A and B. Give the structure of B.

(f) In a plot of lattice energies of divalent transition metal ions against atomic number, a smooth curve is not obtained. Which of the following ion(s) will have lattice energy value higher than expected in an octahedral complex with a weak field ligand and why?



2. (a) Give the IUPAC names of the following:



(b) Write the formulae of the following:

(i) Barium tetranitratoborate(III)

(ii) Sodium triiodidomethylplatinate(II)

(iii) Caesium dodecachloridotrirhenate(III)

(c) How will you distinguish between the cis and trans isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ using trans effect? Explain.

(d) Give the structure of the first totally inorganic optically active compound resolved by Werner. What evidence does it provide in the study of coordination compounds?

(6,3,3,3)

3. (a) (i) The order of stability of $\text{Hg}(\text{II})$ and $\text{Cd}(\text{II})$ compounds has been found to be: $\text{I}^- > \text{Br}^- > \text{Cl}^-$. Assign the reason.

(ii) Higher oxidation states of transition elements are stabilized by small anions like oxide or fluoride. Explain.

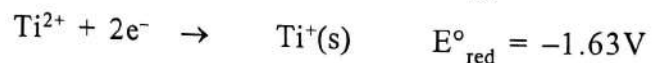
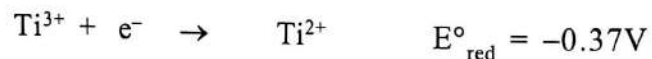
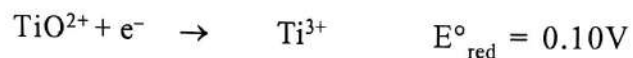
(b) Give all possible geometrical isomers of (i) Square planar $[\text{Pt}(\text{gly})(\text{OH}_2)_2]^+$ (ii) Octahedral $[\text{CrBr}_2\text{Cl}_2(\text{en})]^-$. Indicate which isomers in each compound will show optical activity.

(c) Which one of following transition metal complex ions would be more stable according to the electroneutrality principle ?



Give reasons to support your answer. (6,5,4)

4. (a) Based on the given standard reduction potentials in volts at 25°C in acidic medium draw the Latimer diagram for Titanium.



Based on the Latimer diagram, answer the following :

(i) Will Ti^{2+} change to Ti under normal conditions in acidic solution ?

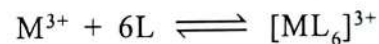
(ii) Which is the most stable species ?

(iii) Calculate $E^\circ \text{TiO}^{2+}/\text{Ti}^{2+}$ in acidic medium.

(iv) Is there any species likely to undergo disproportionation ? Why/Why not ?

(b) For Cr^{2+} octahedral complexes in strong and weak field, determine the (i) configuration in terms of $t_{2g}^m e_g^n$, (ii) number of unpaired electrons, and (iii) crystal field stabilization energy. Show the distribution of electron in respective d-orbitals in the crystal field splitting diagram.

(c) Write all the stepwise stability constants (K's) and overall stability constant (β) for the following reaction :



where L is a monodentate ligand. Give the relationship between the stepwise and overall stability constants. Predict which of all the stepwise constants will be the greatest and the smallest. (6,5,4)

5. (a) (i) Define Jahn-Teller theorem.

(ii) Which of the ligand; F^- or CN^- will form octahedral complex with nickel (III) ion with significant Jahn-Teller effects and Why ?

(iii) Give the crystal field splitting diagram of the distorted complex and explain.

(b) (i) The CFSE is highly useful to determine whether a spinel structure would be normal or inverse. What is the arrangement of M^{2+} and M^{3+} ions in both? If M^{3+} ion has a higher CFSE in an octahedral field compared to M^{2+} ion, which spinel will result?

(ii) Match the energy of the electronic spectral band with the appropriate complex and explain your answer.

$\bar{\nu}$	20,100 cm^{-1}	22,300 cm^{-1}
Complex	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Ti}(\text{CN})_6]^{3-}$

(c) Which of the following complexes has a greater stability? Explain giving reasons:

$[\text{Co}(\text{pn})_3]^{3+}$ or $[\text{Co}(\text{tn})_3]^{3+}$ where pn is 1,2-diaminopropane and tn is 1,3-diaminopropane. (6,5,4)

6. (a) (i) Give the balanced chemical equation to show the use of potassium ferrocyanide as analytical reagent to identify Fe^{3+} ions.

(ii) Calculate spin only magnetic moment of the complex ion. Is there any possibility of quenching the magnetic moment?

(iii) Predict and explain whether potassium ferrocyanide would have spin forbidden or spin allowed transitions.

(iv) Predict whether potassium ferrocyanide would be labile or inert.

(b) The magnetic moment for $[\text{MnBr}_4]^{2-}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are 5.9 and 2.8 B.M. respectively. Give the hybridization, geometry of each complex on the basis of Valence Bond theory.

(c) Compare the molecular orbital diagram for a π -donor ligand with respect to a pure σ -donor ligand and explain the effect on the Δ_0 . (6,5,4)

7. Attempt any FIVE of the following:

(a) Explain the principle and method behind the separation of Ln^{3+} ions from their aqueous solution by ion exchange method.

(b) Discuss the magnetic behaviour in lanthanides and actinides as compared to transition elements/ions.

(c) "Actinides exhibit other than +3 oxidation states." Comment.

- (d) Though transition elements possess high electrode potential yet they are not good reducing agents.
- (e) In case of lanthanides, the bonding on coordination is mainly ionic in character. Why is the bonding so ionic ?
- (f) Account for the colour in $[\text{CrO}_4]^{2-}$ ion. (5×3)

[This question paper contains 8 printed pages.]

2

15/5/17

Your Roll No.....

Sr. No. of Question Paper : 2794

GC-4

Unique Paper Code : 32171402

Name of the Paper : Organic Chemistry – III, Heterocyclic
Chemistry

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **Six** questions in all.
3. Question No. 1 carries **15** marks.
4. All other questions are of **12** marks each.

1. (a) A resolvable amine (A) is subjected to exhaustive methylation with MeI to give (B). (B), when subjected to Hofmann Elimination gives an alkene, (C). On reductive ozonolysis the isolated alkene (C) yields an

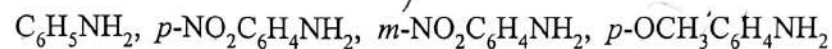
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equimolar mixture of methanal and butanal. Deduce the structures of A, B and C. Write all the involved reactions and products and also justify your choice of A.

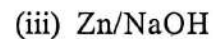
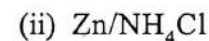
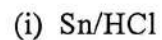
- (b) How will you distinguish between nitriles and isonitriles? Explain giving involved reactions.
- (c) Discuss the advantage of Emde's modification over Exhaustive methylation using suitable examples.
- (d) How will you convert pyrrole to 3-chloropyridine? Give the mechanism involved. (6,3,3,3)

2. (a) How will you show that naphthalene consists of 2-benzene rings fused together? Explain giving suitable reactions.
- (b) Anthracene undergoes electrophilic substitution at 9, 10 position. Explain.
- (c) Sulphonation of naphthalene gives different products at low and high temperature. Give the reactions and explain, giving suitable reason.
- (d) Resonance energy of phenanthrene is higher than that of anthracene. Explain with the help of suitable structures. (3,3,3,3)

3. (a) Arrange the following in the increasing order of basicity, giving reasons.



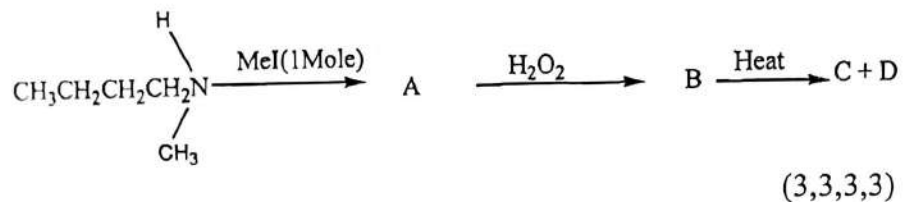
- (b) Coupling reactions of diazonium salts occur in mildly acidic or mildly alkaline conditions only. Explain giving all the involved structures.
- (c) Write the final product formed in reaction of nitrobenzene with the following reagents :



(4,4,4)

4. (a) How will you distinguish between ethylamine, diethylamine and triethyl amine using nitrous acid? Give the involved reactions.
- (b) How will you prepare n-propylamine by Gabriel-phthalimide synthesis? Give the involved mechanism.
- (c) N-ethyl-N-methyl amine is chiral but non resolvable. However, $C_6H_5N^+(CH_3)(C_2H_5)(C_3H_7)Cl^-$ is resolvable. Explain with the help of suitable structures.

(d) Complete the following reaction and also name the reaction involved in conversion of B to C & D :



5. (a) How will you carry out the following conversions ?

(Any three)

(i) Naphthalene to 1-fluoronaphthalene

(ii) Benzene to 1,3-dichlorobenzene

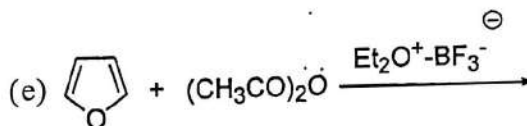
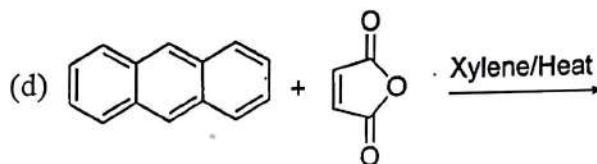
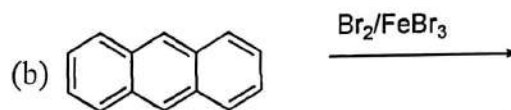
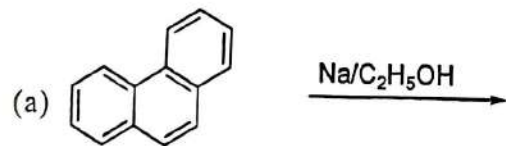
(iii) Thiophene to thiophene-2-carboxylic acid

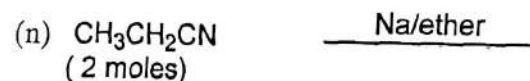
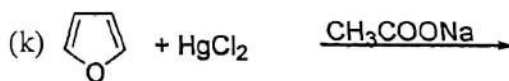
(iv) Indole to 2-aminoquinoline (3×3=9)

(b) Pyridine primarily undergoes nucleophilic substitution at 2, 6 position. Explain. (3)

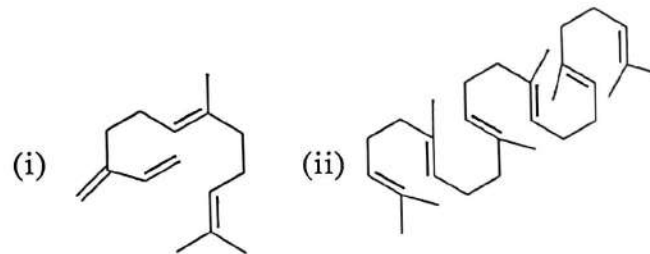
6. Complete the following reactions : (Any twelve)

(1×12=12)





7. (a) Mark out isoprene units in the following with dotted lines and name the class of terpenes to which each one of the following belongs :



- (b) How will you convert acetone to Citral? Give all the involved reactions.

- (c) How will you show the presence of the following in an alkaloid?

(i) O-methylgroup

(ii) Alcoholic group

- (d) How was the presence of pyrrolidine ring in nicotine proved by Karrer? (3,3,3,3)

8. (a) Write short notes on the following (Any two):

(i) Fischer- Indole synthesis

(ii) Skraup synthesis of Quinoline

(iii) Pomeranz-Fritsch synthesis (4×2=8)

(b) Give reasons for the following :

- (i) Nitration and sulphonation reactions of furan are carried out under mild conditions. Also give the relevant structures.
- (ii) Pyridine is less basic than piperidine. (2,2)

[This question paper contains 8 printed pages.]

2017

Your Roll No.....

Sr. No. of Question Paper : 2795

GC-4

Unique Paper Code : 32171403

Name of the Paper : C X : Physical Chemistry IV

Name of the Course : B.Sc. (H) Chemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. Question No. **1** is compulsory.
4. Attempt at least **one** question from each section.
5. Use of scientific calculator and graph is permitted.

1. Explain any **five** of the following : (5×3)

(a) First order reactions never go to completion.

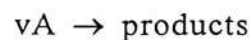
(b) Difference between stationary and non-stationary chain reactions.

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- (c) Beer's law fails in case of aqueous solution of potassium dichromate.
- (d) Walden's rule is not applicable to cations of small size.
- (e) Metallic conductance decreases while electrolytic conductance increases with temperature.
- (f) The transference number of an ion can be positive, negative or zero.

SECTION A

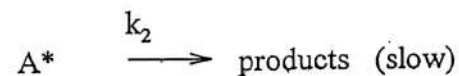
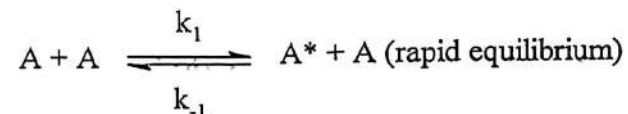
2. (a) The reaction (4)



is a first order reaction with respect to A.

- (i) Write down the differential rate law and deduce from it, the integrated rate law.
- (ii) Show that the half-life of such a reaction is independent of the initial concentration of the reactant.
- (b) For the decomposition of acetone di-carboxylic acid, the rate constants are $2.46 \times 10^{-5} \text{ s}^{-1}$ at 273 K and $1.63 \times 10^{-3} \text{ s}^{-1}$ at 303 K. Calculate the activation energy of the reaction. (4)

- (a) Lindemann mechanism for the first order reaction is given as follows :

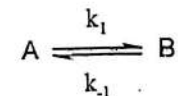


Show that

$$\frac{d[\text{product}]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2}$$

Under what condition will the order of the reaction be equal to 1? (4)

3. (a) For a first order opposed by first order reaction

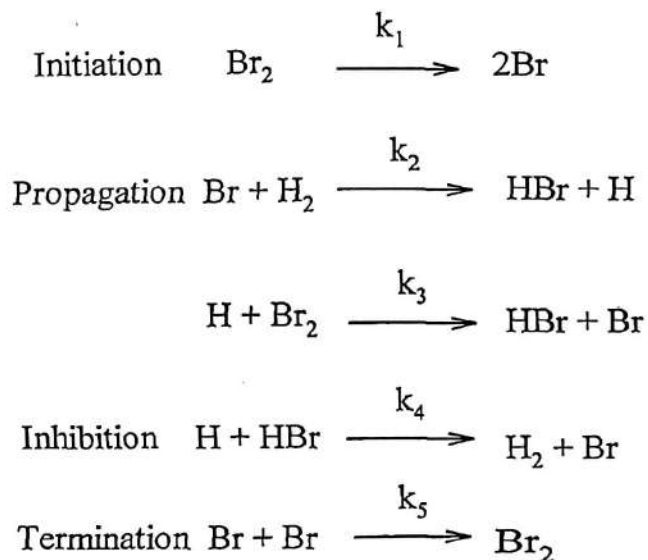


with the initial concentration of A and B as $[A]_0$ and zero respectively, show that the integrated rate expression is given by

$$\ln \frac{x_{eq}}{x_{eq} - x} = (k_1 + k_{-1})t$$

where x is the concentration of B at time t and x_{eq} is the concentration at equilibrium. (6)

- (b) The following mechanism was proposed for the reaction between H_2 and Br_2 at 300 K.



Using the steady state approximation, show that

$$\frac{d[HBr]}{dt} = \frac{2k_2 (k_1/k_5)^{1/2} [Br_2]^{1/2} [H_2]}{1 + (k_4/k_3) \frac{[HBr]}{[Br_2]}} \quad (6)$$

4. (a) Describe the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

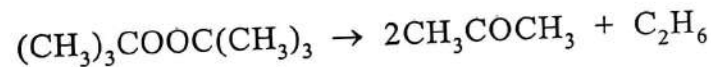
$$r = p \left\{ \pi \sigma_{AB}^2 \left(\frac{8kT}{\pi \mu} \right)^{1/2} N_A^* N_B^* \right\} \exp(-E_0/RT)$$

Explain the significance of the term p in the above expression. (6)

- (b) The following data were obtained at a constant volume for the decomposition of di-tertiarybutyl peroxide in the gas phase at 427.7 K

t/min	0	3	6	9	12	15	18	21
p/torr	169.3	189.2	207.1	224.4	240.2	255.0	269.7	282.6

The reaction is



Show that the reaction is of first order and calculate its rate constant. (6)

SECTION B

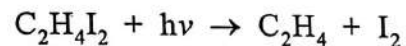
5. (a) Describe the moving boundary method for determining the transport number of ions. (4)
- (b) At 25°C, the specific conductance of 0.01 M aqueous solution of a weak acid is $1.63 \times 10^{-2} \text{ S m}^{-1}$ and its molar conductance at infinite dilution is $390.7 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation (α) and the dissociation constant (K_a) of the acid. (4)
- (c) During the electrolysis of a solution of potassium chloride, 0.0137 g of chloride was lost from the cathodic compartment and 0.0857 g of silver was deposited in a silver coulometer connected in series with the cell. Find out the transport number of K^+ and Cl^- ions. (4)

6. (a) Explain the main features of Debye-Hückel-Onsager theory for strong electrolytes. (6)
- (b) Specific conductance of water is $7.6 \times 10^{-3} \text{ S dm}^{-1}$ at 300 K and that of a 0.1 mol dm^{-1} aq. KCl solution is $1.1639 \times 10^{-1} \text{ S dm}^{-1}$. A cell had a resistance of 33.21Ω when filled with 0.1 mol dm^{-3} KCl solution and 300Ω when filled with 0.1 mol dm^{-3} acetic acid solution. Calculate
- Cell constant
 - Specific conductance of 0.1 mol dm^{-3} acetic acid
 - Molar conductance of 0.1 mol dm^{-3} solution of acetic acid. (6)
7. Write short notes on any **three** of the following: (3×4)
- Conductometric titrations
 - Wien effect and Debye-Falkenhagen effect
 - Kohlrausch's law of Independent Migration of Ions
 - Determination of hydrolysis constant of salts from conductometric measurements

SECTION C

8. (a) State and derive the Lambert-Beer's law for light absorption by solutions. Also, plot the graph for (i) Absorbance vs Concentration and (ii) Transmittance vs Concentration. (6)

- (b) In the photochemical decomposition of ethylene iodide



with radiation of 424 nm, the iodine formed after 20 minutes required 41.14 cm^3 of $0.0025 \text{ mol dm}^{-3}$ solution of $\text{Na}_2\text{S}_2\text{O}_3$. The intensity of the light source was $9.15 \times 10^{-4} \text{ J s}^{-1}$. Calculate the quantum yield assuming absorption of the energy was complete. (6)

9. (a) Kinetics of enzyme catalyzed reactions are studied with Michaelis-Menten mechanism. Using the steady state approximation, relate enzyme and substrate concentration to reaction rate. Discuss also how the rate of the reaction changes when Michaelis Constant > Substrate concentration. (6)
- (b) Using the Michaelis-Menten equation for an enzyme catalysed reaction, determine the value of Michaelis constant from the following data. (6)

[S]	r_0
Substrate Concentration mol/dm ³	(initial rate) mol dm ⁻³ s ⁻¹
0.4	2.40
1.0	4.80
2.0	7.40
3.0	8.70
4.0	9.50
5.0	10.50