2010

CHEMISTRY (Honours)

FIFTH PAPER

(Revised New Syllabus)

Time : 4 hours   Full Marks : 60

The figures in the margin indicate full marks

Answer Question No. 1 and only **five** from the rest

1. Answer any **five** questions :   2×5=10

   (a) Chemical equilibrium is dynamic in nature. How?

   (b) A solution of NaCl in water has nearly double the osmotic pressure expected. Why?

   (c) Quinhydrone electrode is not suitable for pH measurement in strongly alkaline solution. Explain.

   (d) What do you mean by Ampholyte?

   (e) What do you mean by 'Reynolds number'?

MRD—300/82   (Turn Over)

1. (i) Which gas and solid has surface tension or not ? Comment.

   (ii) Transport number of an ion sometimes gives a negative value. Explain.

2. (a) What is meant by reaction isotherm? Deduce an expression for the reaction isotherm. What is the importance of this isotherm? 1

   (b) What is reversible and irreversible reaction? Give examples. 3

   (c) Assuming that the degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.3, calculate the pressure at which this substance will be half dissociated at the same temperature. 3

3. (a) What will be the pH of 10^{-7} (M) HCl? 2

   (b) What is meant by buffer capacity? Show that the buffer capacity of a solution of weak acid and its salt is maximum when their concentrations are equal. 1

   (c) Calculate the pH of (i) a decinormal solution of ammonium acetate, and (ii) a decinormal solution of ammonium cyanide in water at 298.15 K. 4
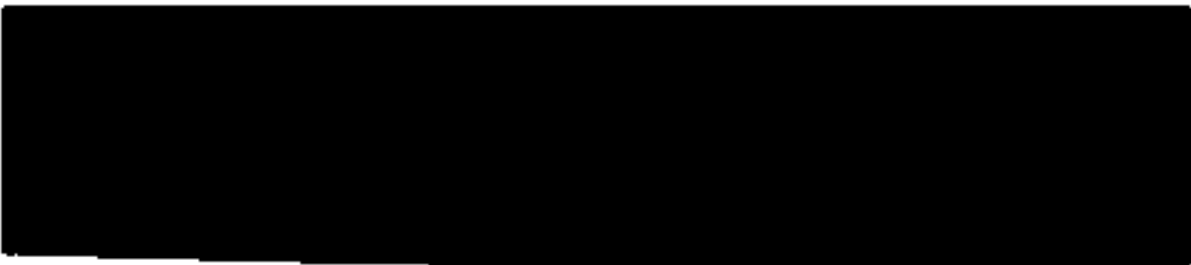
   Given $K_{NH_4OH} = 1.8 \times 10^{-5}$

(Continued)

4. (a) Define 'transference number'. How one determines transference number by Moving Boundary method?

   (b) Write down 'Kohlrausch's law of independent migration'. How can one determine the equivalent conductance of acetic acid on infinite dilution using this law ? 2

   (c) At 18 °C, the resistance of 0.1(N) KCl in a conductivity cell is 86.8 ohm and that of 0.05(N) NaCl is 263 ohm. What is the specific conductance and equivalent conductance of 0.05(N) NaCl? (Specific conductance of 0.1(M) KCl is 0.01192 mho cm^{-1}) 3

5. (a) Define coefficient of surface tension and viscosity of a liquid with units. 3

   (b) At 20 °C, toluene rises 1.93 cm in a capillary tube of radius 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20 °C is 0.866 gm/cc. 4

   (c) Explain why viscosity of a gas increases with temperature. 2

6. (a) Explain the terms phase, component and degree of freedom of a system. 2

(Turn Over)

(b) Discuss the application of phase rule to water system with phase diagram.

(c) Derive the phase rule introduced by Gibbs. 3

7. (a) What are colligative properties? 2

(b) Derive an expression for the molal freezing point depression constant of the solution in terms of enthalpy of fusion. 4

(c) A solution of 4×10^{-3} kg of camphor in 25.3×10^{-3} kg of chloroform boils at 334.3 K. Boiling point of chloroform is 334 K. Calculate ΔH_{vap} and K_b for chloroform. 2

8. (a) What is the basic difference between electrochemical potential and chemical potential? 2

(b) Construct a cell where the following reaction takes place : 3

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 5H_2O + 5O_2$$

(c) Calculate the e.m.f. of the following cell at 298 K :

Pt | H2 | HCl ...

9. (a) State and explain why DC can not be used in the measurement of conductance of electrolytic solution. 2

(b) Derive an expression of pH of an aqueous solution of CH_3COONa. 2

(c) Explain the nature of conductometric titration curve for KCl vs $AgNO_3$ taken in the burette.

(d) NaCl and LiCl have abnormal equivalent conductance in water. Explain.

10. Write short notes on any four of the following : 2.5×4=10

(a) Ionic product of water

(b) Dipole moment

(c) Fractional distillation

(d) Reference electrode

(e) Concentration cell

(f) Temperature dependence of equilibrium constant

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CHEMISTRY (Honours)

SEVENTH PAPER

[Revised New Syllabus]

Time : ? hours   Full Marks : ?5

The figures in the margin indicate full marks

Answer Question No. 1 and any **five** from the rest
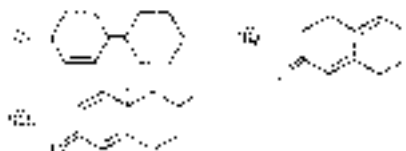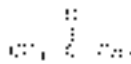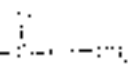
1. Explain the following facts :

    (a) The $n \to \pi^*$ transition of acetone occurs at higher wavelength than that of $\pi \to \pi^*$ transition but absorption band due to $n \to \pi^*$ transition has less intensity.   3

    (b) Electrophilic substitution of pyridine occurs chiefly at 3 position.   2

    (c) The cis- and trans-isomers of stilbene have λ_{max} of 343 nm and 295 nm respectively in ethanol.   2

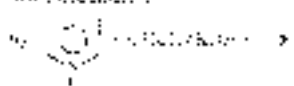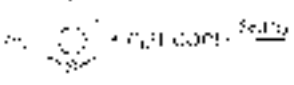   (d) Dilution has no effect on O–H stretching frequency of o-nitrophenol.   2

1.

b. There is of one bond as a part of conjugated system. Yet Maleic acid which is cis is not able to exhibit single enol tautomer.

c. Cyclohexadiene undergoes Diels Alder reaction more readily than butadiene.

2. a. Draw using relative energy levels representing the bonding molecular orbitals of benzene.

b. Using the orbital overlap, explain why Diels-Alder reaction between butadiene and ethylene is thermally allowed but is not catalyzed by light.

c. Trace the route 2,4,6 with addition on photochemical irradiation to give from butadiene cyclohexa 3,5 dien-1-ol. Reaction

3. a. Explain the effect of polar solvent on n-π^* and π-π^* transition.

b. Calculate the λ_{max} of the following compounds:

i.
ii.
iii.

4.

b. The carbonyl stretching frequency of cyclopropanone is greater than that of cyclohexanone. Explain.

d. How will you distinguish the following pair of compound in IR spectroscopy?

CH_3—C—CH_3 and —CH=CH—

4 a. Define chemical shift.

b. A given sample compound is shown exhibit a signal at 200 Hz using a 60 MHz NMR spectrometer. What would be its equivalent position using 90 MHz spectrometer?

c. How will you differentiate iodopropane and n-chloropropane in NMR spectroscopy?

d. A compound with molecular formula C_3H_7O gives the following PMR data:
i. Multiplet at 3.7 δed δr
ii. Doublet at 12.4 2 Hz
iii. Triplet at 43.78 6 H

5. a. Draw the energy profile diagram along transition state reactions by thermally.

(b) Cyclohexane is flexible whereas trans-decalin is rigid. Explain. 2

(c) Give the structures of preferred conformations of the following compounds: 3

  i) Cis-1,3 Dimethyl cyclohexane

  ii) Trans-1,2-dimethyl cyclohexane

(d) Indanones have unique conformations in seven-membered system, whereas in six-membered system there present a good degree of flexibility. Explain. 3

5. (a) Pyrrole is weaker base than pyridine. Explain. 2

(b) Predict the products with plausible mechanism: (5×4=8)

(c) Pyridine-1-oxide is more suitable for preparation of pyridine derivatives than pyridine itself. Explain.

7. (a) Explain why furan is less aromatic than...

(b) Give evidences on which the structure of D-glucose is based.

(c) An aldopentose on oxidation with nitric acid gave optically inactive dicarboxylic glutaric acid. The osazone formation on similar oxidation gave mesotartaric acid. Deduce the configuration of the... form of the pentose.

8. (a) Outline the synthesis of the following dyes: 2×2

  i. Methyl orange

  ii. Congo red

(b) How is the structure of indigo established?

(c) 9-Position of anthracene is more reactive than any other position. Explain.

9. (a) Discuss about the dipolar structure of amino acids.

(b) Give the name and structure of an acid of amino acids:

  i. have a secondary amino group

  ii. having a hydroxyl moiety

(g) How can Curtius reaction be utilised for the synthesis of amino acids? 2

(h) When sodium trichloroacetate is heated in diglyme solution with a ketone, there are formed 2,2-dichlorooxiranes. How do you account for this? 3

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CHEMISTRY (Honours)

EIGHTH PAPER

[Revised New Syllabus]

Time — 4 hours *Full Marks : 60*

The figures in the margin indicate full marks

Answer Question No. 1 and any **five** from the rest.

1. (a) Square planar d^8 paramagnetic complexes are rare. Explain why. 2

   (b) CrO_4^{2-} is a d^0 compound and yet it is coloured. Explain why.

   (c) Calculate the bond order of N_2.

   (d) Find out the value of x in $Zn_x(CO)$

   (e) The magnetic moment of $Mn(H_2O)_6^{2+}$ is 5·9 BM. Calculate the number of unpaired electrons. 1

   (f) Explain why N_2 is less than N_2^-.

(2)

(d) A pink cobaltous chloride solution turns blue on addition of excess KCl. Explain why. 2

(e) Give an example of an optically active purely inorganic complex. 1

2. (a) Draw the plot of ψ vs r and ψ^2 vs r for 1s, 2s and 2p orbitals. Discuss briefly the different plots. 4

(b) Write briefly on the success of MO theory over VB theory. 3

(c) Write down the Schrödinger wave equation for hydrogen atom and briefly explained all the terms associated with it. 3

3. (a) State and explain Hume-Rothery rule. 3

(b) Discuss the allotropy of tin. 3

(c) The ground state of zinc has no unpaired electron. Yet it shows metallic character. Explain this in the light of Pauling's theory. 3

(d) Calculate the EAN for the complex $K_4[Fe(CN)_6]$. 1

[3]

4. (a) Give examples of Ambidentate, hexadentate ligands and inner metallic complex. 1

(b) Discuss the splitting of d orbitals in an octahedral field with proper diagrams.

(c) What is trans-effect? 1

(d) Discuss the following types of isomerism using suitable examples

A. Coordination isomerism

B. Ionisation isomerism

5. (a) What is CFSE?

(b) Discuss the factors on which Δ depends.

(c) $[Ni(CN)_4]^{2-}$ is diamagnetic whereas $[NiCl_4]^{2-}$ is paramagnetic. Explain.

(d) Explain the ability of CO and CN ligands in stabilizing the low oxidation states of metals.

(e) Give an example of tetragonal distorted octahedral complex.

6. (a) Describe the structure of Na_2KIO_6. 3

(b) Write a short account on the bonding and structure of ferrocene.

(c) Draw the structure of Zeise's salt and state the importance of Zeise's salt. 2

7. (a) What is the basic difference between Haemoglobin and Myoglobin? 2

(b) The ability of a heme-group to bind O_2 is nullified if the iron atom becomes oxidised to Fe(III) state. Explain. 3

(c) What is cooperative interaction? 3

(d) How is pH measurement used to detect complex formation? Give an example to explain this. 3

8. (a) Why does lanthanides exhibit common oxidation state of +3? 2

(b) What is lanthanide contraction? 2

(c) Name one important ore of titanium. Briefly explain how titanium is extracted from its ore with relevant reactions. 5

9. (a) A liquid NH_3 solution of phenolphthalein is colourless but becomes red on adding of KNH_2. Explain the observation. 3

(b) What happens when

(i) $AgNO_3$ is added to KNH_2.

(ii) PCl_5 is soluble in liq. SO_2?

(c) Arrange the following in the increasing order of bond length O—O and explain why you have arranged it in that order :

$$O_2, O_2^-, O_2^+, O_2$$

(d) Give an example with relevant explanation of compound in which EAN rule is violated.

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CHEMISTRY (Honours)

NINTH PAPER

[Revised New Syllabus]

Time — 4 hours   Full Marks : 65

The figures in the margin indicate full marks.

Answer Question No. 1 and any five from the rest.

1. Account for the following (any five) :   3×5=15

    (a) Reactions of the higher orders are rare.

    (b) Solids break into pieces of characteristic angles.

    (c) Ducks cannot float in water containing too much detergent.

    (d) Monodispersity and polydispersity in macromolecules.

    (e) Micelles are association colloids.

    (f) Energy of a free particle is not quantized.

    (g) Thermodynamic probability (p) is a measure of disorder of a system.

MRC—1200/164   (Turn Over)

2. (a) Mention the salient main points of a simple harmonic oscillator. Derive an expression for the vibrational energies of a diatomic molecule. 2+4

(b) What is Raman spectroscopy? How is it helpful in determining the structure of molecules? 1+3

3. (a) What are consecutive reactions? Discuss the kinetics of the first order consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Depict graphically the variation of concentrations of A, B and C with time.
2+3+2

(b) A first-order reaction is 40% complete in 80 minutes. How long will it take to be 80% complete? 3

4. (a) Write down the Debye's T^3 law for heat capacity of solids indicating the significance of the terms involved.

(b) Show graphically the variation of the heat capacity as a function of temperature. 2

(c) Deduce Bragg equation for diffraction of X-rays from crystals. 3

(d) State and explain Pauli exclusion principle. 3

(Continued)

5. (a) Define partition function. Derive an expression for Entropy in terms of partition function.

(b) State and explain Einstein's theory of specific heat of solids.

(c) What do you mean by RNA and DNA? Draw their structure diagram. Outline three differences between them.

6. (a) Enzymes are more specific than catalysts. Justify the statement.

(b) State Lambert-Beer law.

(c) Give the mathematical expression for Lambert-Beer law. 2

(d) Distinguish between fluorescence and phosphorescence. 2

(e) The bond energy of a molecule is 340 kJ mol⁻¹. Calculate the wave length of the light required to dissociate this molecule.

7. (a) Discuss the transition state theory of reaction rates.

(b) What is the effect of temperature on reaction rates?

(Turn Over)

7. Describe how you would determine the energy of activation of a chemical reaction from the temperature dependence of reaction rate

8. (a) What do you mean by polymer? Difference between homopolymer and copolymer 2+2

   (b) Derive the following

   $$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \text{and} \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

   where the symbols have their usual significances 2+2

   (c) What is meant by zeta potential? 2

9. Write short notes on any four 2½×4=10

   (a) Chain Reactions

   (b) Stability of Colloids

   (c) Compton Effect

   (d) Heisenberg's Uncertainty Principle

   (e) Lock and Key Theory

   (f) Biodegradable Polymers

   (g) Sintering of Ceramics

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CHEMISTRY (Honours)

Revised New Syllabus

Time : 3 hours   Full Marks : 90

The figures in the margin indicate full marks

Answer Question No. 1 and five from the rest, selecting at least two from each Group

1. (a) What is Flash Point?

   (b) Write down the structure of sodium tripolyphosphate.

   (c) Give the ionic forms of H_2SO_4 and H_3PO_4

   (d) Distinguish between radioactivity and isotopy.

   (e) High energy radiations are not equally accurate? Comment.

   (f) What is ionic migration and ionic migration?

   (g) Give the binary equivalent of (12.6875)

   (h) What is Geochemistry?

(Turn Over)

8. (a) What is triple superphosphate?

   (b) What are the main differences of natural fibre from synthetic fibres?

   (c) What is Pigmentation Power?

   (d) What are Foam Rubber and Buna-S Rubber?

   (e) Give the chemical structure and name of Aspirin.

9. Write short notes on any **four** :   2½×4=10

   (a) Setting of cement

   (b) Saponification value

   (c) Cetane number

   (d) Classification of insecticides

   (e) Different types of soaps

   (f) Hydrogenation of oils

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