2010

CHEMISTRY (Honours)

First Paper

Full Marks : 90   Time : Four Hours

*The figures in the margin indicate full marks.*

Group - A

(Organic Chemistry)

Answer any *four* questions.

1. Explain the following (any *four*) :   4×2½ 10

   (a) Monochloro acetic acid is stronger acid than acetic acid.

   (b) *p* Nitroaniline is less basic than aniline.

   (c) The gauche conformation of ethane –1, 2- diol is more stable than the anti form.

   (d) Toluene chiefly gives *o*- and *p*- products on nitration.

   (e) The distance between the end carbons of *n* butane is less than the three times of C-C single bond.

2. (a) Designate the chiral centres of the following compounds as R-/S-notation by mentioning the priority order of the ligands attached to the chiral centres.   3+1+2
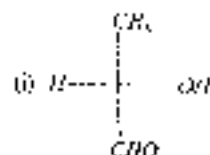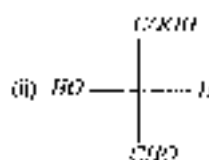
(i) H_2N———H

COOH

CHO

or

(ii)
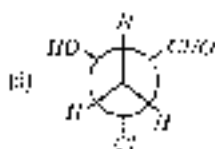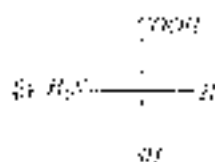
(b) Designate the following compounds as Z-E tion (you must mention the priority order of the ionic ligands) : 1+1=2

(i)

(ii)
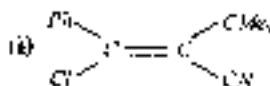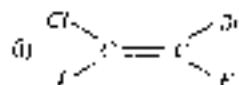
(c) Designate the following compounds by D-/L-me : 1+1=2

(i) H————OH

CH₃

CHO

(ii) HO——————D

COOH

CHO

(d) Predict the product/products with proper stereochemical notations (i.e. by R-/S- notations) : 2+2=4

(i)

$$\frac{OsO_4}{NaHSO_4}$$

(ii)

$$Br_2/CCl_4$$
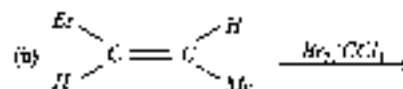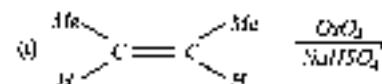
3. (a) Which one is more stable in the following pairs? Give reasons. 2+3=5

(i) $Ph \quad CH - CH \quad \overset{+}{C}H_2$ and

$Me \quad CH - CH \quad \overset{+}{C}H_2$
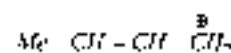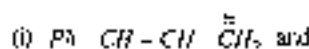
(b) 1-Butene and 2-butene

(n) Addition of chlorine to an alkene is less stereospecific than the addition of bromine. Explain 3

(c) Predict the product with mechanism : 2

$CH_3 \quad C - CH_2 \xrightarrow{O_3/..}$

CH_3

P.T.O.
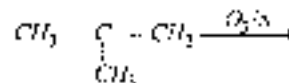
4. (a) Cyclopentadienyl anion is an aromatic species.— ... 3

(b) Benzene and deuterated benzene (C_6D_6) are nitrated with the same rate though C–D bond is ... than C–H bond. Explain. $3\frac{1}{2}$

(c) Give interpretation of the fact that phenol ... rapid nitration with dilute HNO_3. $3\frac{1}{2}$

Group - B

(Inorganic)

Answer any three questions.

5. (a) Atomic radius is difficult to define— Explain. 2

(b) The 1st I.P. of Cu is greater than that of K ... both have almost similar radii— Explain. 2

(c) Deduce the ground state term symbol of nitrogen. 2

(d) Calculate the ionisation energy for hydrogen atom ... the Balmer equation. 2

(e) Mulliken scale of electronegativity is more rational ... any other scale— Explain. 2

6. (a) Mention the principal features of H-spectrum. 4

(b) How molecular geometry can be predicted from concept of hybridisation ? 3

(c) Discuss the factors which affect the value of electronegativity. 3

7. (a) Describe Slater's rule for determining effective nuclear charge for an electron in an atom. What are the limitations ? 4

(b) Formulate lattice energy of $NaCl$ from the following data :

$$d = 1.75; r_0 = 2.8 \text{ Å}; n = 9; N = 6.02 \times 10^{23};$$

$$e = 4.8 \times 10^{-10} \text{ e.s.u.}$$ 2

(c) Explain why $NaCl$ is more ionic than $CuCl$? 3

8. (a) Using VSEPR theory predict the structure of ClF_3, NO_3^- and XeF_4.

(b) The melting point of MgO and NaF are 2853°C and 988°C respectively— Explain.

(c) Explain the term 'Formal charge'.

(d) What is inert pair effect ?

(e) Covalent radii do not increase regularly from ... to ... — Explain.

Group - C

(Physical Chemistry)

Answer any three questions.

9. (a) What is the physical significance of 'a' and 'b' in the van der Waals' equation ?

P.T.O.

(b) Comment on the nature of the gas whose n of state for a mole is

(i) $P(V - b) = RT$ and

(ii) $\left(P + \frac{a}{V^2}\right) V = RT$, with respect to a plot of compressibility factor vs pressure and attractive or repulsive forces between the molecules. 2+2

(c) The temperature of a gas is to be lowered below a critical value before it can be liquified— Explain. 1

(a) What do you mean by the term viscosity and coefficient of a fluid ? 3

(b) Establish the relation $\eta = \frac{1}{3} \rho u \lambda$, where the ... their usual significance. 3

(c) Derive Clausius-Clapeyron equation and discuss its application. 4

Write short notes on : 5×2=10

(i) Second law of thermodynamics

(ii) Joule Thomson coefficient and its variation with temperature for different real gases

(a) If a gas of molecular weight 80 contained in a ... of fixed volume of 1m³ at a temperature of 320K pressure of 1 atm on its wall of area 1m² what will

... the ... pressure if the gas is replaced by an equal weight of another gas of molecular weight 60 ? 3

(b) Calculate the mean free path of NTP of H_2 molecule. 3

(c) Derive Graham Dalinhouse equation 4

P - a [3+3+4]H/10

2010

CHEMISTRY [Honours]

THIRD PAPER

Full Marks : 60   Time : Four Hours

The figures in the margin indicate full marks

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

1. Explain why ? *(any four) :* $4 \times 2\frac{1}{2} = 10$

   (a) Aryl diazonium salts are more stable than alkyl diazonium salts.

   (b) The migrating group retains its configuration in Beckmann degradation.
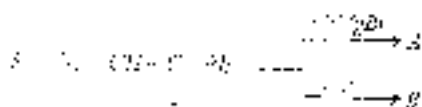
   (c) With aqueous bromine phenol gives 2, 4, 6-tribromophenol but with CS_2 as solvent it gives only 4-bromophenol.

   (d) Diazoacetic ester is more acidic than diazomethane.

   (e) The reaction rate of MeI with N_3^- at 0°C is increased by 4.5×10^4 fold on transfer from methanol to dimethyl formamide as solvent.

2. (a) What is abnormal Grignard reaction ? Illustrate your answer with suitable example. How the abnormal reaction can be avoided ?
   5

P T O

(3)

(b) Indicate the products obtained in the following ....

$$\text{...} \xrightarrow{\text{...Zn}} A$$

$$F \quad \text{...} \quad CH_2 = C - CH_2 \longrightarrow$$

$$\xrightarrow{\text{...}} B$$

(c) What do you understand by nucleophilicity ? How does it differ from basicity ?   2

3. (a) Why trans-2, 3-dibromobutane reacts with ... ion more readily than does a d- or l- form ? What ... the respective alkenes formed ?   3

(b) The alkyl group to the ... group always goes on ... Beckmann rearrangement. Illustrate with suitable ...   3

(c) Acylation of alcohols with acyl chloride is ... by pyridine. Explain the diverse role of pyridine in ...   4

4. Give Chemical evidence in support of the following :
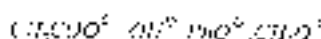
$$(2\tfrac{1}{2} \times 4) = 10$$

(a) Hydride ion transfer in Meerwein Ponndorf and Verley reduction.

(b) Intermolecular nature of Cannizzaro reaction.

(c) Dichloro Carbene is involved in Reimer Tiemann reaction.

(d) Reversibility of benzoin condensation.

(3)

5. (a) Account for the fact that in dimethyl sulphoxide the order of reactivity of halide ion with methyl ... is $I > Cl > Br > F$ which is opposite to that observed in methanol solution.   3
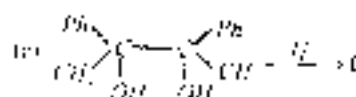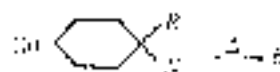
(b) Increasing solvent polarity cause a large decrease in the rate of SN^2 attack by OH^- on trimethyl sulphoxide ion $OH^- + Me_3S^+ \rightarrow MeOH + Me_2S$. Explain why?   3

(c) Treatment of EtI with aqueous alkali gives EtOH but treatment with alcoholic alkali gives ethene. Explain   3

(d) Arrange the following ions in decreasing order of nucleophilicity.   1

$$CH_3COO^-, \; OH^-, \; PhO^-, \; CH_3O^-$$

6. Predict the products with suitable mechanism :   10

(a)

(b)

(c)

P. T. O.

(c)

$\xrightarrow{\text{Strong KOH}}$ D

(e)

$\xrightarrow{KOH}$ E
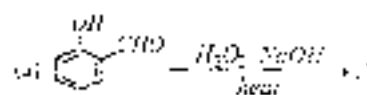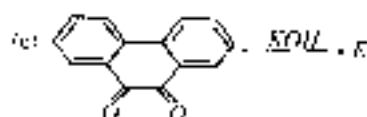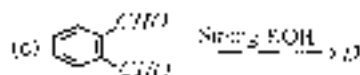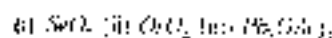
7. Write short notes on :　　　　　　4+3=3

(a) Hofmann and Saytzeff rule of β-elimination reaction.

(b) E1CB mechanism.

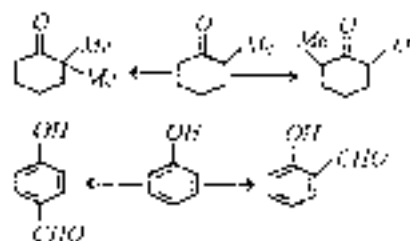(c) Michael Reaction or Mannich reaction.

8. Give the preparation of the following compounds (any four) :　　　$2\frac{1}{2}\times4=10$

(a) Cyclopentanone to Cyclohexanone.

(b) Aniline to Chlorobenzene.

(c) Acetaldehyde to acetone using 1,3-dithian as intermediate.

(d) Methylamine to diazomethane.

(e) Acetic acid to acetone using organo lithium compounds.

(f) Phenol to p-hydroxyacetophenone.

(g) Nitrobenzene to m-bromoaniline.

(a) Write down the important use of the following reagents in organic chemistry.

(i) SeO_2 (ii) OsO_4 (iii) $Pb(OAc)_4$

(b) Describe the following conversions and suggest mechanism with proper reason.　　2½

(c) Give one method of converting a carbonyl compound to a hydrocarbon.

(a) For a given substrate elimination is favoured with respect to substitution by rise in temperature. Explain. 2

(b) Acid catalysed bromination of 2-Butanone give 3-bromocompound whereas base catalysed bromination give 1-bromocompound. Explain. 2

(c) With acetone, di- and tri-bromination in the presence of $NaOH$ takes place on the same carbon atom. Explain why? 2

(d) What are ylide reagents? How are they prepared? Discuss the mechanism. 3

P - II ( )+)+ 1F/10

2010

CHEMISTRY (Honours)

Fourth Paper

Total Marks : 60   Time : Four hours

The figures in the margin indicate full marks

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

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

    (a) Why packing fraction may be positive or negative whereas mass defect can not ?

    (b) What happens when NH_3 gas is passed through Nessler's reagent ?

    (c) *PF₅* exist but *PH₅* does not exist. Explain.

    (d) Explain why alkali metals are soft.

    (e) Coinage metals are less reactive compared to alkali metals. Explain why ?

    (f) Trimethyl amine forms addition compound with $B(CH_3)_3$ but triethyl amine does not. Explain.

2. (a) Explain the working principle of G.M. counter.
                                                              5

    (b) What is spallation reaction ? How does it differ from fission ?   4

    (c) What are fertile and fertile materials ?   2

                                                         T. T. O.

    2/8

(2)

3. (a) Discuss the working principle of Beckmann's spectrograph. 5

(b) Write notes on application of radioactivity. 5

4. (a) Discuss a criteria for stability of nucleus. 3

(b) How would you show that two Cl atoms in PCl_5 occupy different positions than the other three (3-atoms)? 2

(c) In an old Egyptian mummy C^{14}/C^{12} was found to be 50% of the human body. Calculate how many years the man had died? $(t_{1/2}$ of $C^{14} = 5730$ yrs) 5

5. (a) Give a comparative account of coinage metals respect to their electronic configurations, oxidation state, atomic, valence state and complexes. 5

(b) Dithionic acid is not a member of polythionic group — Explain. 3

(c) Alkali metals when dissolved in liq. NH_3 give a conducting solution — Explain. 3

6. (a) Show with the help of resonance sulphur (VI) two 'S' atoms in $S_2O_3^{2-}$ are not equivalent. 3

(b) Explain with appropriate examples the Lewis concept of acids and bases. 3

(c) Urea can act both as acid as well as base-couples. 2

(d) Why is BBr_3 a better Lewis acid than BF_3? 2

(3)

7. (a) Reducing character of group V hydrides are as follows: $NH_3 < PH_3 < AsH_3 < SbH_3$ — Explain. 4

(b) Reactivity of halogen molecules from I to F — Explain. 3

(c) Mercury differs from Zn and Cd on the same group. Why? 4

8. (a) Discuss the principle of redox couple dialog. 4

(b) Aluminium chloride exist as dimer Al_2Cl_6 where as boron chloride exist as monomer — Explain. 3

(c) Explain why diamond is non-conducting graphite like structure. 3

9. Write notes on (any four): 2.5×4

(a) Counting of nucleus.

(b) Composition of atom.

(c) Basic properties of Lewis.

(d) Meson Theory of nuclear forces.

2010

CHEMISTRY [Honours]

Fifth Paper

Full Marks : 80   Time : Four Hours

The figures in the margin indicate full marks.

Answer any six questions.

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

   (a) In a solution of low conductance, the platinum electrodes are kept closer and the area of the electrodes is kept larger during conductance measurement. Why ?

   (b) On dilution the equivalent conductance increases but the specific conductance decreases —Explain.

   (c) The degree of hydrolysis of a salt of a weak acid and a weak base is independent of concentration.—Explain.

   (d) Quinhydrone electrode is not suitable for *pH* measurement in strongly alkaline solution.— Why ?

   (e) Ionic product and dissociation constant of water are not identical. Account for.

   (f) Water wets glass, but mercury does not.— Why ?

P. T. O.

(g) The neutralisation of all bases by acids do not necessarily occur at pH 7.0 —Explain.

(h) H^+ and OH^- ions in aqueous media have exceptionally high ionic conductance —Explain.

2. (a) Arrange the following electrolytes in order of valent conductance: $NaOH$, $NaCl$, CH_3COOH —all at same concentration. Will there be any change in order equivalent conductance at infinite dilution ? $1\frac{1}{2}+1+2\frac{1}{2}$

(b) Discuss how conductance measurement may be used for the determination of solubility of a sparingly soluble
    3

(c) The specific conductivity of a saturated solution gCl is 1.55×10^{-6} ohm^{-1} cm^{-1}. The mobilities of Cl$^-$ Ag$^+$ ions are 5.6×10^{-4} and 6.2×10^{-4} cm sec^{-1} ectively under unit potential gradient. Calculate the ility product of $AgCl$. $2\frac{1}{2}$

(d) Explain the nature of conductometric titration es for CH_3COOH vs. $NaOH$.   2

3. (a) Arrange the following aqueous solution of molar concentration in order of increasing osmotic sure : (i) KCl, (ii) glucose, (iii) $Ba(NO_3)_2$, (iv) Urea, botassium ferricyanide. $2\frac{1}{2}$

(b) Show that the relative lowering of vapour sure is a colligative property   2

(c) How will you determine the molecular mass of non-volatile substance by the study of the relative lowering of vapour pressure of the solution ? $2\frac{1}{2}$

(d) Find the boiling and freezing points of a solution containing 0.92 g of glucose dissolved in 50.2 g of water for water $K_b = 1.86$ and $K_b = 0.52$.   3

4. (a) Derive an expression for the equilibrium constant of a chemical reaction from thermodynamic consideration. 3

(b) The heat of a reaction can be determined from the measurement of the equilibrium constant of this reaction as a function of temperature —Justify.   3

(c) When an alcohol and acetic acid are mixed together in equi molar proportion, 66.5 per cent are converted into esters, calculate the equilibrium constant.

How much of the ester will be formed if 1 mole of acetic acid is treated with 0.5 mole of the alcohol ?

5. (a) Describe briefly how would you determine the pH of a solution using a glass electrode.   3

(b) What are the advantages and disadvantages of using a glass electrode ?   2

(c) "Activity co-efficient of ions can be determined from e.m.f. measurements." —Discuss.   2

(d) Calculate the e.m.f. of the cell in which the reaction is

P. T. O.

$Mg(s) + 2Ag^+ (aq) \to Mg^{2+} (aq) + 2Ag(s)$
on $[Mg^{2+}] = 0.130\ M$ and $[Ag^+] = 1 \times 10^{-3}\ M$ at 298 K.
er.

$E^0_{Ag^+/Ag} = -0.80\ V$ and $E^0_{Mg^{2+}/Mg} = -2.34\ V$
298K.   3

6. (a) Distinguish between surface tension and surface
rgy. Under what condition they are measured ?   2

(b) What is meant by 'specific refraction' and 'molar
action' of a substance ? How do you experimentally
un the refractive index of a solid substance ?   3

(c) Temperature has different effects on viscosities of
ids and gases — Explain. $2\frac{1}{2}$

(d) Para-dinitrobenzene is non-polar but o-dinitrobenzene has a dipole moment of 1.04 Debye. — Explain. $2\frac{1}{2}$

7. (a) Explain the terms — eutectic point, azeotrope,
hydrate, cryohydrate and monotropy.   4

(b) What are neutralisation indicators? Explain their
king and selection giving suitable examples.   2+2

(c) State and explain the law which governs the
ribution of solute between two immiscible solvents.   2

8. (a) pH-scale lies between 0 and 14. Can the pH
solution have a value greater than 14 or less than zero ?   2

(b) Calculate the pH of a 0.01 M solution of
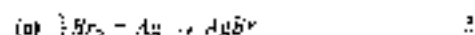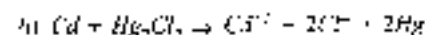NH_4OH given that $K_w = 1 \times 10^{-14}$ and $K_b = 1.85 \times 10^{-5}$.   2

(c) The reaction in a fuel cell is

$$H_2 + \frac{1}{2}O_2 \to H_2O$$
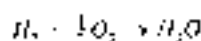
$E^0(O_2, H^+, H_2O) = 1.23\ V$

Calculate maximum amount of electrical work
available per mole of hydrogen.   3

(d) Construct the cells for which the cell reactions

(i) $Cd + Hg_2Cl_2 \to Cd^{2+} + 2Cl^- + 2Hg$

(ii) $\frac{1}{2}Br_2 + Ag \to AgBr$ 3

9. Write notes on in short (any four) : $2\frac{1}{2} \times 4$

(i) Common ion effect.

(ii) Parachor.

(iii) Abnormal Colligative properties.

(iv) Le-Chatelier Principle.

(v) Vant Hoff equation.

(vi) Buffer capacity.

2 0 1 0

CHEMISTRY (Honours)

FIRST PAPER

(Revised New Syllabus)

Time : 4 hours   *Full Marks* : 90

The figures in the margin indicate full marks.

Answer **three** questions from each Group.

GROUP—A

(Organic)

1. Explain the following :   2×5=10

   (i) The addition of fluorine to ethylene double bond is non-stereospecific whereas addition of bromine to double bond is *trans*.

   (ii) Acrylic acid is stronger than propanoic acid.

   (iii) $C_2—C_3$ bond length in propene is shorter than C—C bond in propane.

Group - B

[Inorganic]

5. (a) What are the four quantum numbers? Explain the significance of these numbers in relation to atomic structure.

(b) Determine the ground state term symbol for d^2 electronic state.

(c) Calculate the radius of Li^{2+} in its first excited state.

(d) Mention the significance for the negative sign in the energy expression of an electron in hydrogen like electronic systems.

6. (a) Using VSEPR theory, explain the geometry of the following species : $1.5 \times 2 = 3$

(i) XeF_4

(ii) ClF_3

(b) Calculate formal charges on the different atoms of the ions

(i) CO_3^{2-}

(ii) NO_3^-

(c) Discuss Slater's rule for determining effective nuclear charge.

(d) Draw the shape of PF_5 molecule and mention the hybridization of the central atom in this molecule.

(e) When calcium electrons enter the 4s orbital before going to the 3d-orbitals but when a transition metal ionizes, the 4s electrons are removed first. Why?

(f) State and explain Fajan's rule to explain covalent character in ionic compounds.

(g) Differentiate between electron affinity and electronegativity. Also mention their periodic variation.

(h) Why are van der Waals radii generally higher than covalent radii? Explain.

(a) Write short notes on

(i) Diagonal relationship

(ii) Pauli's exclusion principle

(b) Both of the radius ratio condition and the relative ionic-covalent character should be taken into account when considering the structure of coordinate compounds. Explain with an example.

(c) What are f-block elements? Mention their position in the periodic table and comment thereon.

Group-C

[Physical]

9. (a) What is the nature and significance of van der Waals' constants a and b?

   (b) What do you understand by law of corresponding states? Obtain the reduced equation of state for a gas obeying van der Waals' equation. 2+1+

   (c) Explain the term collision frequency. On what factor does it depend? 2+1

10. (a) What is meant by degrees of freedom?

    (b) Calculate the degrees of freedom for CO_2 and C_2H_6

    (c) Derive the barometric formula

    (d) Show that the height at which the atmospheric pressure is reduced to half the value is given by $h = 0.6909\, RT / Mg$.

11. (a) What are the limitations of the first law of thermodynamics? State the second law of thermodynamics.

    (b) 10 moles of ... are heated from 0 °C to 100 °C at constant pressure of 1 atm. Calculate ΔS.

(c) Deduce the relationship ...

What do you understand by inversion temperature? Why do He and H2 show heating instead. Explain.

12. (a) Calculate the efficiency of a reversible Carnot engine working between 300 K and 600 K. Calculate the minimum work obtained or gained if the engine absorbs ... kJ of heat from source.

    (b) Show that entropy of mixing is always positive for gases or substances. What is ideal mixture?

    (c) Define and explain third law of thermodynamics.

* * *

B. II. (Three Year II)

Under 1+1+1 System

2 0 1 0

CHEMISTRY (Honours)

THIRD PAPER

(Revised New Syllabus)

Full Marks : 50

The figures in the margin indicate full marks.

Answer question No. 1 and **five** from the rest.

1. Explain (any five) : 2×5=10

(a)

(b)

(c)

(d)

(e)

(f) The bond strength of $C=C$ is less than twice that of $C-C$ bond.
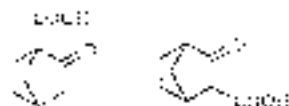
(Turn Over)

1. 5. Say type of reactions are examples uncommon in the gas phase.

2. (a) Give examples with explanation of the following :

   (i) Compound reacting on more than one but gives specific products.

   (ii) Compound containing more than one structure but does not give one specific product.

   (b) What difference do you think between saturated illumination of all $BrCH_2(CH_2)_2CH_2$? Give, what you think why?

3. (a) What is potassium ferricyanide often used to prepare K_2 compound?

   (b) Give the structure of the major products of the following reaction and explain.

   Benzaldehyde + acetone + dilute.

   (c) What is major ..... chemical reaction bisulphate?

4. (a) An organic compound $C_4H_8O_2$ is readily oxidised by HNO_3 at low temperature but oxidised to $C_3H_6O_2$, which on treatment gives compound A on boiling with dilute H_2SO_4.

3. compounds described as ...... cyclohexene and ...... cyclohexene results in the formation of different compounds structure.

(b) ..... chloride reacts with dimethyl amine in known medium to give conjugated product whereas bromide chloride reacts with acetone in slightly acidic medium to yield final product why?

(c) Which of the following will be most and least reactive hydrolysed with NaOH and why? 2

   MeCOOMe   MeCH2COOMe   MeCOOBu

4. Write short notes on any **three** of the following :   3×3 = 9

   (a) Say reactions.

   (b) Claisen rearrangement.

   (c) Reaction with CH_3COCl

   (d) Quinone structure.

5. (a) Give evidence to establish that in the structure corresponds to the group and to the same hydroxyl group migrates.

[4]

6. How do you fail to prepare a ketone from acylchloride by Grignard reagent ? How can you prepare it using an substituted reagent?

(b) How can we distinguish acetone and ether by boiling point? 5×2=10

(i) Nature, stabilisation and nucleophilicity

(ii) Nature and stabilisation

7. (a) Give an example of nucleophilic reaction in S_N2 reaction.

(b) Iodine acts as an effective leaving group as well as an efficient nucleophile. Explain.

(c) What is meant by inversion of configuration and racemisation?

(d) Chloral usually forms a stable gemdiol, and whereas butanal normally fails to do so. Explain.

8. (a) (i) What is ring expansion?

(ii) Between two acids which one will dissociate readily? Explain your answer.

2-10=20

[5]

(a) ...... movement ...... in front ...... the ...... compound ...... formation ...... involves ...... intra-molecular ...... rearrangement.

(b) ...... an acylation reaction to get ...... rearrangement ...... Barton-Meyer.

2×2=

9. Given compound C-2, and P with possible mechanism. 5+2×

(a)

$$ \text{...} + Br_2/NaOH \longrightarrow $$

(b)
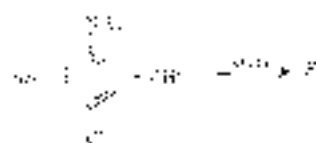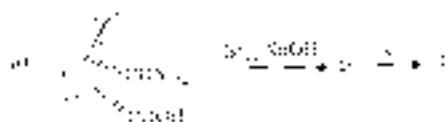
10. Explain the following transformations :

(a) ...... + ... \longrightarrow

(b) ...... + ... \longrightarrow

11. ......

of KI with two equivalents in formation
yields HI — $C_{14}H_{12}O_2$, which on
treatment with caustic soda followed by
acidification forms a compound. I.
C_9H_8O. The acid liberate CO_2 on
treatment with $NaHCO_3$, gas is released.
What are G, HI and I? Give
mechanism of formation of I from HI.

9. Three compounds G, H, I have
common molecular formula $C_6H_9O_4$.
On oxidation with hot alkaline
$KMnO_4$, G gives m-p-N_2O$_2H_2O_2$, H
gives p- and N-$C_6H_4O_2$, but I
remains unchanged. Treatment with hot
alk-NH_3 produces G, $C_6H_9O_4$
under similar conditions H gives I
which on treatment with HI... gives
m-$dihydroxy$... I gives simple
... reactions and products also gives
... gives a deep colour formation
when reacted with $NaNO_2$. Identify
G, H, I and mention your line of
approach.

11. Describe the use of NaS HCl_3 and P_2O_5.
... in organic synthesis.   (10)(4+6)+10

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2 0 1 0

CHEMISTRY (Honours)

FOURTH PAPER

(Revised New Syllabus)

Time — ...   *Full Marks — 90*

The figures in the margin indicate full marks

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

1. Explain why (any **five**)   5×2=10

(a) Lighter elements generally undergo fusion while heavier elements undergo nuclear reaction.

(b) P exhibits two half lives.

(c) NH_3 is pyramidal but BF_3 is planar.

(d) $AgCl$ dissolves in NH_3 solution with AgI does not.

(e) H_3PO_2, H_3PO_3 and H_3PO_4 are mono-, di- and tri- basic acids respectively.

(f) ... red hot when hot and white when cold.

(Turn Over)

[2]

2. (a) Give a brief account on GM counter.

(b) Discuss the principles of Thomson's method of determination of e/m ratio of electron and positive rays.

3. (a) Discuss the principle of radiocarbon dating.

(b) What are Oppenheimer-Phillips reactions?

(c) Fission is used to trigger a fusion reaction. Justify.

(d) What is the principle of breeder reactors? 3+3+2+2

4. (a) Spallation reaction is always accompanied by fission. Explain.

(b) Write short notes on
(i) Nuclear reaction cross-section
(ii) Nuclear forces

(c) The binding energy per nucleon for ^6_3Li is 7.08 MeV and that for ^7_3Li is 7.47 MeV. Calculate the energy required to remove a neutron from ^7_3Li. 1+(2+2)+3

5. (a) How can the radioactivity be used to study the mechanism of esterification reaction?

[3]

(b) What is nuclear binding energy and how is it related to nuclear stability?

(c) Thorium is a natural radioactive element whereas hydrogen is inactive. Explain. 1+1+2

6. (a) Compare the chemistry of Zn, Cd and Hg with respect to (i) size (ii) oxidation states and complex formation.

(b) Give a comparative discussion on the properties of hydrides of N, P, As, Sb and Bi. 5+5

7. (a) Give reasons why PF_5 is known but NF_5 is not.

(b) Give a method of preparation of NH_3 and mention its uses.

(c) In Marsh's test SbH_3 gives metallic mirror before the flame whereas AsH_3 gives the mirror after the flame. Explain.

(d) Freons deplete ozone layer of the atmosphere. Explain. 3+2+2+3

8. (a) Give evidences for I^- and I^{3-}.

(b) Fluorides may be oxidised electrolytically but not chemically. Explain.

(e) NO_2 readily dimerises while NO does not. Explain.

(f) Solution of alkalimetals in liquid ammonia are blue coloured and reducing in nature. Explain.

9. (a) SF_6 is unreactive towards H_2O while TeF_6 reacts. Explain.

(b) Coinage metals are less reactive than Alkali metals. Explain.

(c) Classify the following as hard/soft acids/bases :

H^+, Na^+, I^-, CH_3COO

(d) Which of the following reactions is expected to proceed towards right according to HSAB concept?

$CH_3MgI + HCl \rightleftharpoons CH_3MgCl + HI$

$Cu[(CN)_2](aq) + 2CN^- (aq) \rightleftharpoons$

$2Ag[CN]_2(aq) + X^- (aq)$

10. Write short notes on :

(a) Phosphazine

(b) Siloxanes

(c) Polyhalides

* * *

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 any **five** *from the rest.*

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

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

(b) 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 Autophoresis?

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

(Turn Over)

(i)   Whether gas and solid have 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? Derive an expression for the reaction isotherm What is the significance of the isotherm?

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

(c)   Assuming that the degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2, calculate the pressure at which this substance will be half dissociated at the same temperature.

3. (a)   What will be the pH of 10^{-8} (N) HCl?

(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.

(c)   Calculate the pH of a normal solution of sodium acetate and (i) a cent normal solution of ammonium hydroxide in water at 298.1 K

[Given $K_{w} = 1.8 \times 10^{-5}$]

(i)   Define transference number. How are the transference number by Moving Boundary methods   4

(ii)   State down Kohlrausch's law of independent migration. How can one determine the equivalent conductance at infinite dilution using this law   3

(iii)   If the resistance of 0.1 (N) KCl in a conductivity cell is 86.8 ohm and that of 0.01 (N) NaCl is 203 ohm. What is the specific conductance and equivalent conductance of 0.01 (N) NaCl? (Specific conductance of 0.1 (N) KCl is 0.01118 ohm⁻¹cm⁻¹)   3

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

(v)   A soap bubble rises 1.42 cm in a capillary tube of radius 0.3412 mm. Find the surface tension of solution the density of solution at 20°C is 0.994 gm/cc   4

(vi)   Explain why viscosity of a gas increases with temperature   1

(vii)   Define the terms phase, component and degrees of freedom of a system.

(4)

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

(c) Derive the phase rule introduced by Gibbs.

7. (a) What are colligative properties?

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

(c) A solution of 3×10^{-4} kg of compound $(C_{14}H_{12}O_2)$ in 25.9×10^{-3} kg of chloroform boils at 335.9 K. Boiling point of chloroform is 334 K. Calculate ΔH_{vap} and K_b for chloroform.

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

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

$2KMnO_4 + 3H_2SO_4 + 5H_2O_2$
$\rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

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

H_2(g)(1 atm.)|HCl(a = 1)|Cl_2(g)(1 atm)|Pt(?)

(5)

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

(b) Derive an expression of pH of an aqueous solution of CH_3CO_2Na. 3

(c) Explain the nature of the conductometric titration curve for KCl vs. $AgNO_3$ taken in the burette. 3

(d) H^+ and OH^- have abnormal equivalent conductance in water. Explain. 1

10. Write short notes on any four of the following : 2½×4=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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