

2016

CHEMISTRY

[Honours]

PAPER – I

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

(Use Separate Answer Scripts for each group)

GROUP – A

(Organic)

Subgroup – A(a)

Answer any one question : 15×1

1. (a) Compare the following pairs with explanation as indicated in the parenthesis : $1\frac{1}{2} \times 4$
- (i) n-BuOH and t-BuOH (miscibility with H_2O)

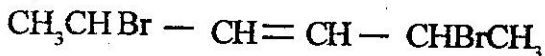
(Turn Over)

(ii) *n*-pentane and neopentane (melting point)

(iii) $\text{Cl} - \text{CH}_2 - \text{COOH}$ and $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ (dipole moment)

(iv) *o*-Nitrophenol and *p*-nitrophenol (steam volatility).

(b) How many stereomers are possible with the structure



Draw one each of optically active and inactive forms. Designate their stereochemistry by R/S ; E/z notations. 1 + 2 + 1

(c) Pro-R Hydrogen of propanoic acid is replaced by Br with retention of configuration. Draw the structure and assign the configuration. 1 + 1

(d) What is the difference between polarity and polarizability ? Explain with example. 2

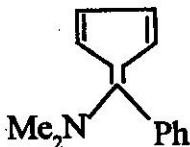
(e) Mention the hybridisation states of all carbon atoms in allene.

1

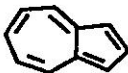
2. (a) Predict the following molecules as aromatic, antiaromatic, non aromatic or homoaromatic with justification.

 $1\frac{1}{2} \times 4$

(i)



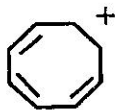
(ii)



(iii)



(iv)



- (b) What is gauche-butane interaction? Draw the stable form of trans-1, 2-dimethyl cyclohexane. How many gauche-butane interactions are there?

 $1 + 1 + 2$

- (c) Draw the energyprofile diageam of a two step exothermic reaction where activation energy

of the first step is greater than that of the second step, but the second step is rate limiting step. Justify your drawing. 3

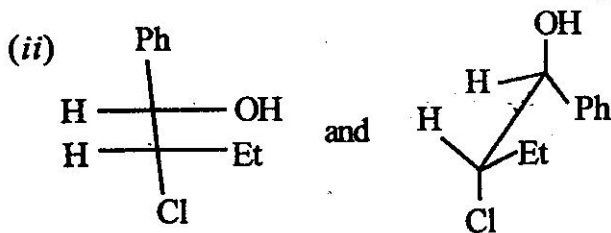
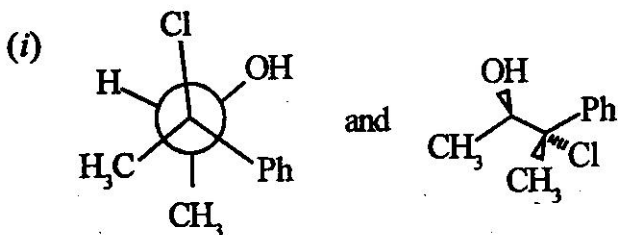
- (d) Which C – H bond of ethylbenzene will be halogenated readily and why? 2


Subgroup – A(b)

Answer any two questions : 10 × 2

3. (a) Draw the preferred conformation of 1-methyl-1-phenylcyclohexane and support your drawing by proper justifications. $1 + 1\frac{1}{2}$
- (b) Acetolysis of both 4-methoxy-1-pentyl brosylate and 5-methoxy-2-pentyl brosylate gave the same mixture of products – explain. 3
- (c) Draw the Newman projection formula of 2R, 3S-2-chloro-3-phenylbutane. Designate it as erythro or threo. $1\frac{1}{2} + 1$
- (d) What is the difference between "kinetic isotope effect" and "non-kinetic isotope effect"? Explain with example. 2

4. (a) Assign the following pairs of compounds as homomer, enantiomer or diastereomer : $1\frac{1}{2} \times 2$



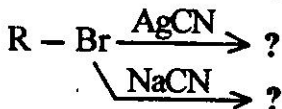
- (b) Indicate the elements of symmetry and point group in any *one* of the following : 2
- (i) Twist boat form of cyclohexane;
- (ii) Naphthalene ()
- (c) What are 'heat of hydrogenation' and 'heat of combustion'? Which method is appropriate

for determining relative stability of the following alkenes and why?

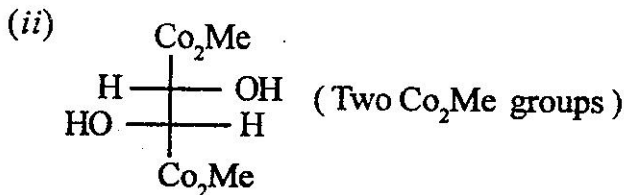
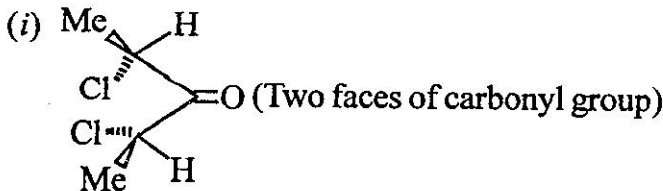
cis-2-butene, *trans*-2-butene, 1-butene and isobutene. $\left(\frac{1}{2} \times 2\right) + 1 \frac{1}{2}$

(d) What is 'purple benzene'? 1

(e) Predict the major product with proper explanation of the following reactions: $1 \frac{1}{2}$



5. (a) Assign the topic relationship between the indicated atoms, groups or faces in the following molecules: 2



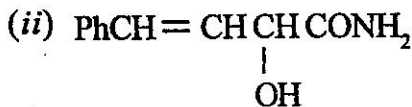
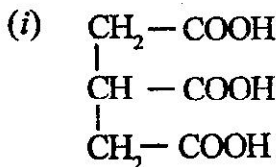
(b) Compare the following with explanation : 3 × 2

(i) Basicity of acetamidine and urea.

(ii) Acidity of $\text{CH}(\text{NO}_2)_3$ and $\text{CH}(\text{CN})_3$.

(iii) Conformational energy barrier for rotation across c-c and c-si bonds in $\text{CH}_3 - \text{CH}_3$ and $\text{CH}_3 - \text{SiH}_3$.

(c) Write the IUPAC nomenclature of the following : 2



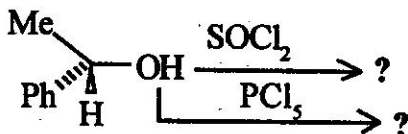
6. Explain the following :

(a) In presence of light, bromination of Me_3CH by Br_2 gives almost exclusively Me_3CBr , but chlorination under similar condition with Cl_2 is not so selective. 4

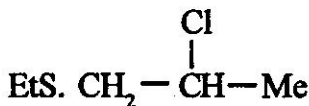
- (b) Optically active α -phenethyl chloride loses its optical activity during distillation at atmospheric pressure. 2
- (c) Optically active 2-iodooctane racemises on reacting with NaI in acetone. 2
- (d) $(\text{Me}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH})_3$ fails to show enol form. 2

Subgroup - A(c)

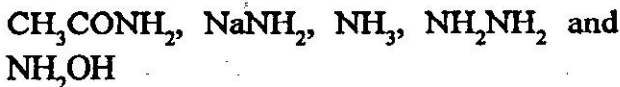
7. Answer any *five* questions from the following : 2×5
- (a) Compare the Pka^1 and Pka^2 values of the diastereomers of cyclohexane-1, 2-dicarboxylic acids.
- (b) Predict the product of the following reactions with proper explanation.



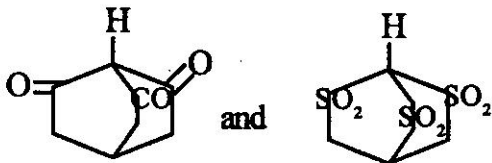
- (c) Why does neopentyl chloride fail to show S_N2 reaction despite of the presence of primary halide ?
- (d) Predict the major product obtained by hydrolysis of



- (e) Compare the nucleophilicities of the following compound giving proper explanation :



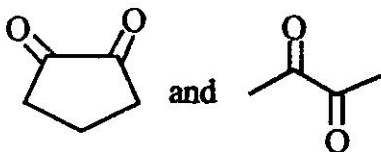
- (f) Which one of the following compound is more acidic and why ?

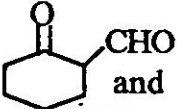


- (g) Trans - 1, 2,-Dichloro cyclohexane exists exclusively in the e, e-conformation in solid

state, shows some α, α -conformer in liquid state but mainly in α, α -form in gaseous state – Explain.

- (h) Which one of the following shows higher enol content and why ?



- (i) Draw all the enol forms of  and indicate the most populated form in C Cl_4 .

GROUP – B

(*Inorganic*)

Subgroup – B(a)

Answer any **one** question : 15 × 1

8. (a) Calculate the frequency of light emitted for transition of an electron from the sixth to

the second orbit of the hydrogen atom. In what region of the spectrum does this light occur ? 3

(b) Account for the large difference in electron affinity between Li and Be despite the increase in nuclear charge. 2

(c) Find the solubility of AgCl in a solution where $C_{Cl^-} = 10^{-1} N$. To a saturated solution of AgCl in water, $10^{-8} N Cl^-$ is added. Find out the amount of AgCl precipitated in gm/litre. The solubility product of AgCl is 1×10^{-10} at $25^\circ C$. 3

(d) Construct a Born-Haber cycle for the formation of LiF crystal and calculate the electron affinity of F atom from the following data given in kJ/mol

Heat of sublimation of Li metal = 161

Bond dissociation energy of F_2 molecule = 79

First ionization energy of Li = 530

Enthalpy of formation of LiF = - 1240

Lattice energy of LiF = -796. 2 + 2

(e) When AlCl_3 and OPCl_3 are mixed, the product $\text{Cl}_3\text{Al}-\text{O}-\text{PCl}_3$, has a nearly linear $\text{Al}-\text{O}-\text{P}$ arrangement. Suggest an explanation for this unusually large angle. 3

9. (a) Calculate the pH of 0.15 molar solution of CH_3COONa at 25°C . (K_a of $\text{CH}_3\text{COOH} = 1.792 \times 10^{-5}$). 3

(b) Counter ions of similar size provide high lattice energy where those of much difference in size provide high solvation energy. How for this statement is true? Discuss with justification. 2

(c) Why are the 4-coordinated boron compounds always tetrahedral but never square planar? 2

(d) Calculate the percentage of ionic character in LiH and Comment on the nature of bonding.

Given $\mu_{\text{LiH}} = 5.88 \text{ D}$ and $r_{\text{LiH}} = 1.6 \text{ \AA}$. 2

- (e) Calculate the electronegativity of lead following Allred-Rochow procedure : (Given covalent radii of Pb = 1.53 Å and atomic number of lead = 82) 3
- (f) State radius ratio rules and hence find the limiting radius ratios (r_+/r_-) for tetrahedral coordination. 3

Subgroup – B(b)

Answer any two questions : 10 × 2

10. (a) Explain the physical significance of magnetic quantum number. Determine the ground term of p^2 electronic configuration. 2 + 2
- (b) Calculate the screening constants of the following electrons and the effective nuclear charge of the given atoms applying Slater's rules :
- (i) the 4s electron in Ca ($z = 20$)
- (ii) a 3d electron in Mn ($z = 25$). 2

- (c) The solubility of a sparingly soluble salt in water increases in presence of added salt without common ion – Explain. 2
- (d) What will be the coordination number of each ion in NaCl, if the ionic radius of $\text{Na}^+ = 0.95\text{\AA}$ and that of $\text{Cl}^- = 1.81\text{\AA}$. Predict the shape of NaCl crystal. 2
11. (a) Depict with proper equation the autoionisation of liq. NH_3 and liq. SO_2 and hence complete the following chemical equations : 3
- (i) $\text{PCl}_5 + \text{SO}_2$ (in liq. SO_2) \rightarrow
- (ii) $\text{Zn}(\text{NH}_2)_2 + \text{KNH}_2$ (in liq. NH_3) \rightarrow
- (b) The speed of an electron is 1.2×10^6 m/s. What is its de Broglie wavelength? 2
- (c) Predict the shapes of the following molecules using VSEPR Theory : 3
- (i) F_2O



- (d) What happens when I_2 is added to NaBH_4 in diethylene glycol ? Give chemical reaction. 2
12. (a) What are eigen functions ? What are their characteristics. 3
- (b) Although In and Tl occur in the same group of the periodic table, while In is (+3) valent in most of its compounds Tl is mostly (+1) valent. Why is it so ? 2
- (c) Why NH_4Cl is mixed before the addition of NH_4OH to precipitate Gr. III A basic radicals analytically. 2
- (d) Discuss the structure and bonding of B_2H_6 . What is the speciality of this structure ? 3
13. (a) What happens when pure Be reacts with carbon at elevated temperature (1900°C) and the product is allowed to react with water ? Write the chemical reactions. 2

- (b) Complete the reaction using the concept of HSAB principle



- (c) Why does bond angle ONO decreases in the following order $NO_2^+ > NO_2 > NO_2^-$. 2

- (d) What is acidity function ? State its utility. How does it behaves in dilute aqueous solution ? 3

- (e) Explain why $LiCl$ is soluble in organic solvents while the chlorides of other alkali metals are not. 2

Subgroup – B(c)

4. Answer any *five* questions : 2 × 5

(a) Explain your observation when ZnO is heated in a test tube.

(b) $Be(CH_3)_2$ is polymeric in the solid state. Explain the reason.

(c) TlI_3 is a compound of $Tl(I)$. Justify.

- (d) What is inorganic graphite and why is it so called ?
- (e) Why are Pb(IV) and Bi(V) compounds strongly oxidising ?
- (f) Ionic radius of La^{3+} is 1.17 Å while Lu^{3+} is 1.00 Å. – Explain.
- (g) How pH of an aq. solution of KI will be affected if solid HgO is added ?
- (h) Is it necessary for an ionising solvent to be a proton acceptor to have good solubility of ionic salts ? Give reasons.
- (i) Predict the approximate PKa values of boric acid applying Pauling's rules [Given : electronegativity of B atom on Pauling's scale is 2.04].
- (j) Explain the difference in basicity of Me_3N and $(\text{H}_3\text{Si})_3\text{N}$.
-