Total Pages: 9

End Semester Examination of Semester-I, 2015

Subject: CHEMISTRY (HONS.)

Paper: CEMH-101
Full Marks: 40
Time: 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

Illustrate the answers wherever necessary.

### Use separate Answer scripts for Group A and Group B

### Group A (Organic-20 Marks)

### Group A(a)

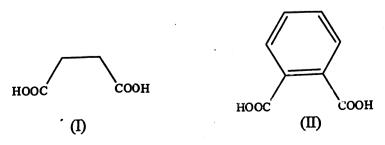
Answer any one question:

10x1=10

1. Answer any five of the following:

5x2=10

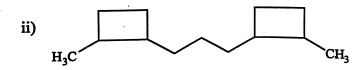
a) Compare the acidity (Pka) of following dicarboxylic acid with proper reason.



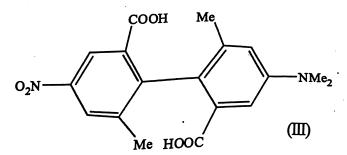
Being a diprotic acid, do you think squaric acid would be more acidic as compared to (I) and (II). Give reason.

b) State the IUPAC nomenclature of the following compounds.

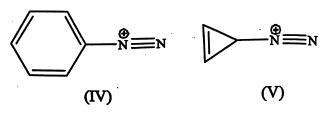
i) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)CHO

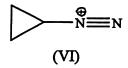


c) Which "C<sub>sp²</sub> —N" is shorter bond length in the following compound (III). Give reason.



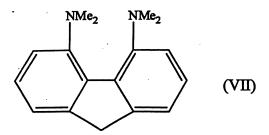
d) Predict the stability order of diazonium cations (IV, V and VI) both in gas phase and in aqueous solution.





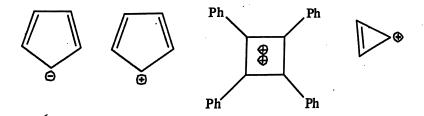
What would be the stability order if thermal decomposition of diazonium ions are considered? Provide a plausible explanation.

e) The compound (VII) is more basic than tetramethyl hydrazine. Rationalize.



f) The following compound (VIII) is converted from "diketo"-form to "diol"-form when reacted with 1, 4 cyclohexdiene. Account for the fact.

- g) Discuss the effect of temperature on dipolement for the following compounds.
  - i) 1,2 dichloroethane
  - ii) 1,4 dioxane
- 2. a) An optically active pure sample of S(+)2-butanol shows specific rotation  $\left[\alpha\right]_{D}^{25^{\circ}C} = +13.52^{\circ}$ . What will be the percentage composition of the mixture of enantiomers whose observed rotation is  $-6.76^{\circ}$ ?
  - b) What is meant by stereogenic centre? Are centres of stereogenicity always centres of chirality? Explain with suitable example.
  - c) Predict which of the followings are aromatic anti aromatic or non aromatic and why?



d) Explain why hemolytic bond dissociation energy for a benzylic hydrogen is less than that of a methane hydrogen 2

### Group A(b)

Answer any one question:

1x6

3. Answer any three of the following:

3x2=6

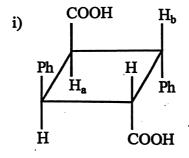
a) Explain why compound (X) is resolvable but the compound (XI) is not.

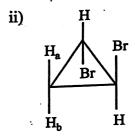
$$\begin{bmatrix} CH_3 \\ \\ \\ Ph \longrightarrow N_{\bigoplus} CH_2 - CH \Longrightarrow CH_2 \end{bmatrix} CI^{\Theta}$$

$$CH_2Ph$$
(XI)

$$\begin{array}{c}
\operatorname{CH}_{3} \\
\mid \\
\operatorname{Ph} \longrightarrow \operatorname{N} \longrightarrow \operatorname{CH}_{2} \longrightarrow \operatorname{CH} \Longrightarrow \operatorname{CH}_{2}
\end{array}$$
(XII)

b) Mention the topic relationship of the marked hydrogens  $H_a$  &  $H_b$ .



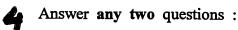


- c) Give example in each case:
  - i) A cumulene with odd number of double bonds having stereogenic axis.
  - ii) A cyclic molecule having a chirotopicnonstereogenic centre.

d)	Ring size	Heat of combustion/ CH <sub>2</sub> (Kcal/mole)
	3	166.6
	4	164.0
	5–15	157.4~158.8

Explain the above observation. Why is the Bayer hypothesis insignificant in context of experimental findings.

### Group A(c)



2x2=4

2

- 2 a) The conformational energy of an alkyl substitent at C-3 is less in cyclohexanone than that in cyclohexane. Explain the fact.
  - b) Phloroglucinol exhibits relatively more kinetic activity than resorcinol which in tern shows more Ketonic activity than phenol. Provide a suitable explanation in favour of the above statement.
  - c) Which one of the two diasteromeric 2-bromo-4-t-butyl cyclohexanones is more polar and why?

d) Write down IUPAC name of the following compounds: 1x2=2

# Group B (Inorganic-20 Marks)

# Group B(a)

Answer any one question:

10x1=10

- 1. i) What are the postulates made by Bohr to derive an equation for the energies of electron in a hydrogen atom? What are the drawbacks of Bohr's theory?
  - 2+3
  - ii) Prove that all Bronsted bases may not be Arrhenius bases.
  - iii) Applying Bohr's model, calculate the energy emitted when an electron in a hydrogen atom makes a transition from third energy level to first energy level. (h = 6.63x10<sup>-34</sup> Js)

- 2. i) What are the limitations of radius ratio rule? 3ii) What is meant by non-stoichiometric crystal? Write a note on Metal deficiency defect with example. 1+3
  - iii) How much energy in KJ is released when 1.0 gm of Chlorine atom is converted completely to Cl<sup>-</sup> ions in the gaseous state, electron affinity of Cl(g) = 349 KJ.

## Group B(b)

# Answer any one question:

1x6=6

2

- 3. i) Me<sub>2</sub>N-PF<sub>2</sub> has two donor centres-N and P. When it reacts with BH<sub>3</sub> and BF<sub>3</sub> separately two different compounds will be formed. Draw the structures of these two compounds and explain.
  - ii) The interionic distance in Chlorine molecule is 1.98 Å. Calculate the Allred-Rochow electronegativity using Slater's rule.
  - iii) How an we obtain proton affinity of NH<sub>4</sub>Cl?
- 4. i) Calculate the heat of formation (ΔHf) of MgF<sub>2</sub> from its elements using the Born-Haber Cycle. The thermochemical data are as follows:
  Sublimation energy of Magnesium, (S) = 146·4 KJ/mol Dissociation of F<sub>2</sub>, (D) = 158·9 KJ/mol Ionization energy of Mg(g), (I) = 2184·0 KJ/mol Electron affinity of F(g), (E) = -334·7 KJ/mol Lattice energy of MgF<sub>2</sub> (ν<sub>0</sub>) = -2922·5 KJ/mol

- ii) In what solution H<sub>2</sub>SO<sub>4</sub> behaves as a base? 1
- iii) Write down the IUPAC name of the elements having atomic numbers 108 and 112. What would be their symbol?

# Group B(c)

5. Answer any two questions:

2x2=4

- i) Discuss the kind of crystal defect observed when ZnO is heated. State the detectable charge.
- ii) CaO +  $P_4O_{10} \longrightarrow \Delta$

Predict the product and hence explain the above reaction by lux-flood concept.

- iii) Complete the following reactions according to SHAB

  i) Lit 2
  - i)  $Li^+ + Cs^+ + F^- + I^- \longrightarrow$
  - ii)  $Cu^{2+} + H^{+} + SO_4^{2-} + S^{2-} \longrightarrow$
- iv) Ionic radius of K<sup>+</sup> is smaller than that of Cl<sup>-</sup> though they are isoelectronic Explain.