Total Pages—17

UG/I/CHEM/H/I/15

2015

CHEMISTRY

[Honours]

PAPER – I (Group-A + B)(New)

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

Illustrate the answers wherever necessary

Use separate answer scripts for Group—A and Group—B

GROUP – A

(*Organic*)

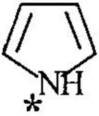
GROUP—A(a)

Answer any **one** question

1. (*a*) Calculate Double Bond Equivalent for the formula C_2NOH_5. Write IUPAC name of one compound of this formula which posseses geometrical isomerism. Label it by E/Z system. 1

(*b*) Using Frost Diagram lebel bonding and anti-bonding pi-molecular orbitals of cyclobutadienyl dianion. Comment of its aromaticity and sketch LUMO energy diagram. 2 + 1 + 1

(*c*) Write the state the Hybridisation of the atoms marked by * 1 + 1



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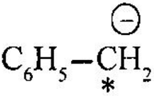
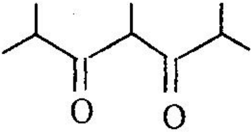


$C_6H_5-\underset{*}{\overset{\ominus}{C}}H_2$

(*d*) Which of the following compounds will have higher enol content ? Why ? 1 + 1



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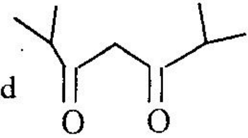
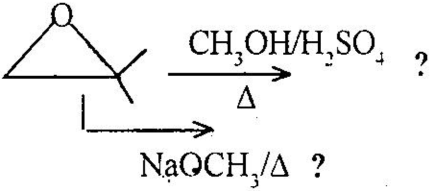


(*e*) Predict the products with mechanistic explanation 2 + 2



2. (*a*) Give an example of each of the following : 1 + 1 + 1

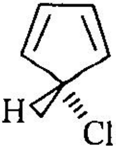
   (*i*) Psuedo rotation

   (*ii*) Umpolung effect

   (*iii*) Captodative carbon radical.

   (*b*) Explain– why S-phenyl butanone looses optical acitivity in alkali medium. 2

   (*c*) Which of the following compounds will more readily hydrolyse by aquoes silver nitrate solution ? Why ? 2



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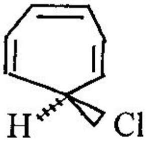


   (*d*) What happens when (*R*)-2-chloro butanoic acid is treated separately with dilute KOH solution and concentrated KOH solution. 4

   (*e*) Arrange the following compounds as directed. Give brief explanation; 2 + 2

   (*i*) $(CH_3)_2C{=}CH_2$; cis-Butene and Trans-Butene

   – according to thermal stability.

(*ii*) *n*-pentane, Isopentane and Neopentane –according to their boiling points.

GROUP–A(b)

Answer any **two** questions :

3. (*a*) Write *true* (T) of *false* (F) for the following statements : $\frac{1}{2} \times 4$

(*i*) All stereogenic centres are chirogenic

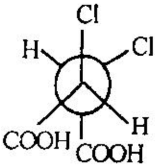
(*ii*) Carbonium ion act as sigma bond electrophile

(*iii* Racimisation process is entropy driven

(*iv*) Electron donating group at ortho-position of benzoic acid increase its pKa value.

(*b*) Identify whether the following pair of compounds represent homomer, enantiomer or diastereoisomer ; 2

(*i*)



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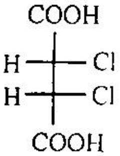
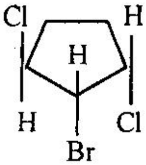


(*ii*)



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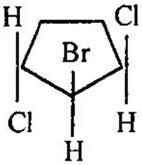
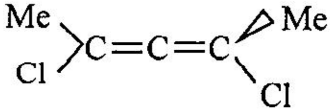


(*c*) In a given solution a compound shows optical rotation of +300°. How will you prove that it is dextrorotatory ? 2

(*d*) Indicate the elements of symmetry and point group in any *one* of the following : 2

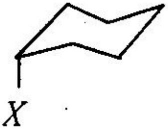
(*i*)



OR

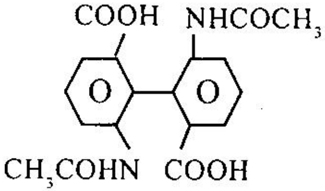
(*ii*) Boat conformation of cyclohexane.

(*e*) Explain why conformational energy of halocyclohexanes remain almost same for $X = \mathrm{Cl}$, Br, I. 2



4. (*a*) Draw Fischer Projection Formula of (1R, 2S)-1-chloro-1, 2-diphenyl propane and lebel it as Erythro or Threo. 2

(*b*) Which compound is resolvable and why ? 2



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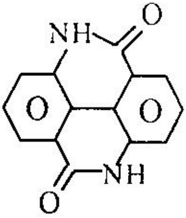


(*c*) Draw potential energy diagram of butane arrising out of rotation arround $C_1 - C_2$ bond lebelling the conformations. 2

(*d*) Define Buttressing effect with suitable example. 2

(*e*) Comment on optical activity of trans 1, 2-dimethyl cyclohexane. 2

5. (*a*) Explain why $C{=}O$ double bond energy is higher and double of $C{-}O$ single bond energy. 2

(*b*) Which compound possesses higher dipole moment ? Why ? 2

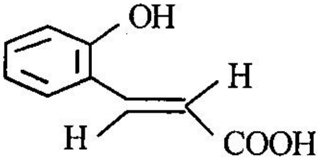
(*c*) Which compound will decompose readily on heating ? Why ? 2

$Ph-N=N-Ph$ and $Ph-CH_2-N=N-CH_2-Ph$

(*d*) Write IUPAC name of 2

(*i*) $HC(CO_2H)_3$

(*ii*)



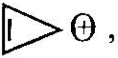
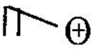
(*e*) How will you resolve an amino acid. 2

6. (*a*) Explain why Bromination of methane retards in presence of excess HBr but rate of chlorination of methane does not change on addition of HCl. 3

(*b*) Why R-2 butanol reacts with $SOCl_2$ to give R-2-chlorobutane ? What will happen if the reaction is carried out in presence of puridine ? 3

(*c*) What is primary kinetic isotopic effect ? Give an example. 2

(*d*) Arrange the carbocations according to their stability with explanation 2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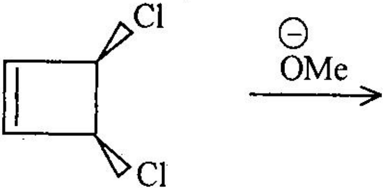
GROUP—A(c)

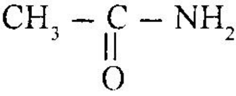
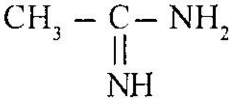
Answer any **five** questions from the following :

7. (*a*) Give example of an homoallylic carbocation. Why it is called non-classical carbocation ? 2

(*b*) Predict the product (with mechanism) 2



(*c*) Compare the basicity of $CH_3-CH_2NH_2$,


$CH_3-\underset{\underset{O}{\|}}{C}-NH_2$ and

$CH_3-\underset{\underset{NH}{\|}}{C}-NH_2$ 2

(*d*) Explain why R-2-iodo octane looses optical activity on addition of KI solution ? Write relation between loss of optical acitivity and reactivity. 2

(*e*) Write most stable conformation of 1 + 1

(*i*) 1, 2-difluoro ethane

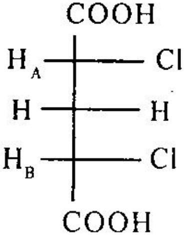
(*ii*) trans-1, 3-ditertiary butyl cyclohexane.

(*f*) Write most stable resonating structure of the following : 1 + 1

(*i*) CH_2N_2

(*ii*) CH_3CN

(*g*) Find topicity relation between marked *H* atom of 1 + 1



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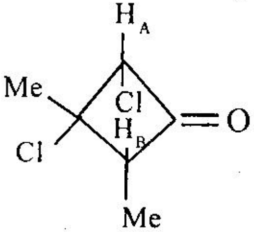
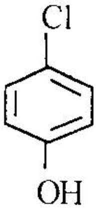


(*h*) Compare acidity of 2



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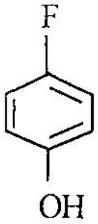
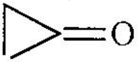


(*i*) Compare C=O bond distance of 2



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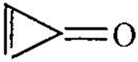

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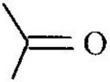

GROUP – B

(*Inorganic*)

GROUP–B(a)

Answer any **one** question 15 × 1

8. (*a*) For a certain metal the threshold frequency is $1{\cdot}4 \times 10^{15}$ Hz. Find the maximum energy which can be possessed by the photoelectrons emitted when a light of $1{\cdot}8 \times 10^{15}$ Hz is incident on the metal plate. 2

(*b*) Calculate the screening constant (σ) for the 3d electron of iron (2σ). 2

(*c*) Radius of 1st Bohr orbit of H atom is 0·529 Å. Calculate the radius of 1st and 2nd orbits of Be^{3+}. 3

(*d*) Discuss the variation of the bond angles in SF_4 and SOF_4. 2

(*e*) $MgSO_4$ is readily soluble in water whereas $BaSO_4$ is insoluble. Explain. 2

(*f*) Weak bases like acetamide and acetanilide can not be titrated by any acid in aqeous medium but these can be done by $HClO_4$ in acetic acid medium– Explain. 2

(*g*) Between NaCl and CuCl, which one has higher melting point and why ? 2

9. (*a*) Calculate the heat of formation of ionic solid NeCl and indicate weather this hypothetical solid formation is favoured or not– 3 + 1

Given,

$U_0 = -840$ KJ/mol	$D(Cl_2) = 226$ KJ/mol
$I_0 = 2080$ KJ/mol	E.A.(Cl) = – 351 KJ/mol.

(*b*) Explain the order of basic character in the following compounds 2

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2$$

(*c*) Arrange the following compounds according to their solubility in H_2O with proper explanation. 3

KI, NaI, LiI, RbI, CsI

(*d*) In B_2H_6, all hydrogens are not identical– Explain. 2

(*e*) PH_3 exists but PH_5 does not while both PCl_3 and PCl_5 exist– Explain. 2

(*f*) Calculate pH of the following solution : 2

(*i*) 50 cm^3 of 0·1 (N) HCl is mixed with 50 cm^3 of 0·2 (N) NaOH.

(*ii*) 50 cm^3 of 0·2 (N) HCl is mixed with 50 cm^3 of 0·1 (N) aqs. NH_3.

GROUP—B(b)

Answer any **two** questions 10 × 2

10. (*a*) Calculate the electronegativity of chlorine in Mulliken's scale and hence find out the electronegativity of the same element in Pauling's scale. 3

(Given : electron affinity of chlorine = 4·0 eV/atom and ionisation energy of chlorine = 13·0 eV/atom)

(*b*) Justify the ground state electronic configuration of Cr is $3d^5\ 4s^1$, and not $3d^4 4s^2$. 2

(*c*) Explain the first pKa values of H_3BO_3 (~ 2·0) and H_3AsO_3 (~ 9·0) with structural difference if any. 3

(*d*) Between $(CH_3)_2PF_3$ and CH_3PF_4, the former does not show pseudorotation. Explain. 2

11. (*a*) What is quantum mechanical interpretation of an orbital ? 3

(*b*) Account for the trend in acidity in increasing order $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$. 2

(*c*) BF_3 reacts with excess NaF in acidic aqueous solution forming BF_4^-(aq). The product of the reaction between BCl_3 with excess NaCl is different— explain. 2

(*d*) Draw the acid-base neutralisation curve for 3

(*i*) strong acid by strong base and
(*ii*) weak acid by weak base.

12\. (*a*) Formation Mg^{+2} and O^{2-} ions from Mg and O_2 are endothermic. In contrast to $O \rightarrow O^-$ process is exothermic and Mg^{2+} formation energy is about three times greater than $Mg^0 \rightarrow Mg^+$ process. Yet magnesium oxide is formulated as $Mg^{2+}O^{-2}$ rather than Mg^+O^- — explain. 3

(*b*) Write down the shapes of $\dot{C}H_3$ and $\dot{C}F_3$ using VSEPR theory. 3

(*c*) What is borazon and how it is formed ? 2

(*d*) What is the implication of the negative sign in the expression for energy of hydrogen atom in the ground state ? 2

13. (*a*) Compare the structure between $TeCl_6^{2-}$ and XeF_6. 3

(*b*) A diatomic molecule has a dipole moment of 1·2 D. If its bond distance is 1·0 Å, what fraction of an electronic charge, e, exist on each atom ? 2

(*c*) Enumerate the chemical consequences of SHAB theory. 2

(*d*) Predict the direction of the following equilibria : 1

$$2CH_3MgF + HgF_2 \rightleftharpoons (CH_3)_2Hg + 2MgF_2$$

(*e*) Explain why the conductivity of Ge is enhanced manyfolds when trace amount of As is added to it. 2

GROUP—B(c)

Answer any **five** questions 2 × 5

14. (*a*) The intrinsic spin angular moment of the electron is defined by two quantum numbers—explain.

(*b*) The radious of F^- and K^+ are same, yet the hydration energy of F^- is greater than that of K^+ – justify.

(*c*) $(SiH_3)_3N$ and $(CH_3)_3N$ react with HCl to give different products – explain.

(*d*) Predict the stronger acid and explain your answer with respect to the following pair

and $(CH_3)_2\,P(O)(OH)$

(*e*) Suggest probable structures for I_4Cl^- and ICl_4^- and give reasons why the two are probably not isostructural.

(*f*) P—N bond distances in $P_3N_3F_6$ are shorter than that in $P_3N_3Cl_6$ – explain.

(*g*) Compare the acid strength and reducing properties of the oxyacids of phosphorous.

(*h*) The valence shell electronic configuration of both Ca and Zn is $4s^2$ but first ionisation energy of Ca is lower than Zn – justify.

(*i*) Complex forming ability of Group-II A metal ion changes as $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ – explain.

(*j*) Li does not from solid bicarbonate– justify.