2019

CHEMISTRY

[Honours]

PAPER – I

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

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

GROUP – A

(*Organic*)

Subgroup – A (a)

Answer any **one** question : 15 × 1

1. (*a*) (*i*) Draw the Fischer projection formula of (2S, 3R)-3-chlorobutan-2-ol and convert it to Newman projection formula (any conformer). 3

(*ii*) In a given solution a compound shows optical rotation of $+300^{\circ}$. How will you prove that it is dextrorotatory ? 2

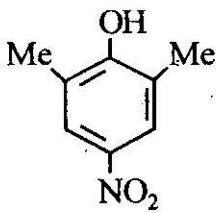
(*iii*) Give an example where an optically active compound possess a C_2-axis. 1

(*b*) (*i*) Draw all the possible stereoisomers of the following molecule with R/S or E/Z nomenclature : 2 + 1

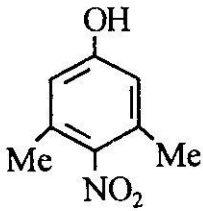
$$CH_3 - CH = CH - CH(OH)CH_3$$

(*ii*) Why [10] annulene is not considered as an aromatic compound ? Explain. 2

(*c*) (*i*) Among the following compounds which one is more acidic and why ? 2



(A)



(B)

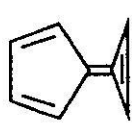
(*ii*) Arrange the following molecules with their increasing order of dipole moments : 2

$CH_3 - CH_2 - Cl$, $CH_2 = CH - Cl$, $HC \equiv C - Cl$

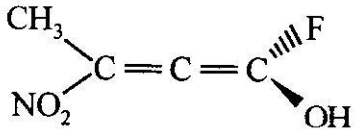
2. (*a*) (*i*) Rank the following in order of increasing basicity with reasons : 3

$CH_3C\overset{\ominus}{O}_2$, $CH_3CO\overset{\ominus}{N}H$, $\overset{\oplus}{N}H_3 - CH_2 - C\overset{\ominus}{O}_2$

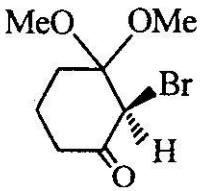
(*ii*) The following hydrocarbon has an unusually high dipole moment. Explain. 2



(*b*) (*i*) Assign R/S descriptors to the following compounds and also show the priority order of the groups : 3



(A)



(B)

(*ii*) (R)-2-Benzoyl propanoic acid undergoes racemization when treated with NaOEt in. ethanol. Give an explanation. 2

(*c*) Draw the following as indicated : 3

(*i*) (Z, E) isomers of benzildioxime.

(*ii*) anti-conformer of PhCH(Br) – CH(Br)Ph.

(*iii*) Fischer projection formula of (2S, 3R)-2,3-dichloro propanoic acid.

(*d*) Why lactic acid is optically active ? 2

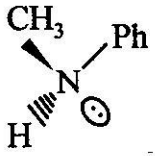
Subgroup – A (b)

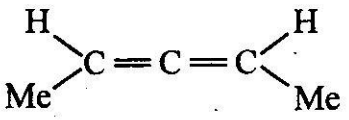
Answer any **two** questions : 10×2

3. (*a*) Draw all the π-M.O.S. of [6] annulene. Arrange them in order of increasing energy levels. Identify the HOMO and LUMO in the ground state. 3

(*b*) Enol content of acyclic 2,3-butanedione is slightly greater than normal ketone but in case of cyclobutane-1,2-dione is much higher. Explain. 2

(*c*) Explain whether the following compounds are resolvable or not ? 2

(*i*) 

(*ii*) 

(*d*) Draw the potential energy diagram of 2, 3-butanediol for rotation around $C_2 - C_3$ bond showing the conformers. Explain the relative stabilities of the conformers. 3

4. (*a*) *Trans*-4-butylcyclohexanol is oxidized four times more slowly than *cis*-isomer, when treated with CrO_3 at 25 °C. Give an explanation with mechanism. 3

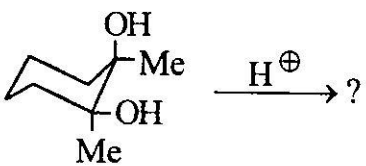
(*b*) Draw the preferred conformation of the following compounds : 3

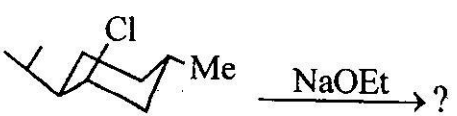
(*i*) trans-1-ethyl-2-methylcyclohexane

(*ii*) 1-t-butyl-1-methyl cyclohexane

(*iii*) Ethane-1,2-diol

(*c*) Write down the product(s) of the following reaction with mechanism (any *two*) : 2 × 2

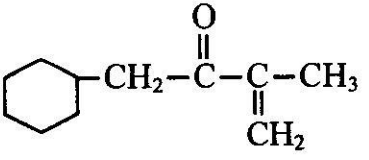
(*i*) 

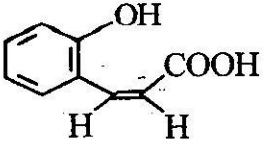
(*ii*) 

(*iii*) 

5. (*a*) The pKa of cycloheptatrienyl anion is around 36 but pKa of trimethyl cyclopropenyl anion is 62. Explain. 2

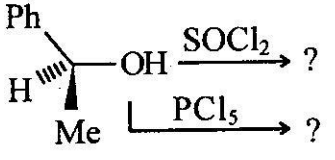
(*b*) Give the IUPAC name of the following compounds : 3

(*i*) 

(*ii*) 

(*iii*) $CH(CO_2H)_3$

(*c*) Predict the product(s) of the following reactions with proper explanation : 3



(*d*) Why $\left(Me_3\overset{\overset{O}{\|}}{C}-C\right)_3CH$ fails to show enol form ? 2

6. (*a*) Compare nucleophilicities of the following compounds with proper explanation : 2

CH_3CONH_2, $NaNH_2$, NH_3, NH_2-NH_2

(*b*) How does land polarity differ from bond polarisability ? Explain with examples. 2

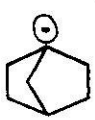
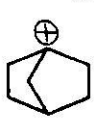
(*c*) How would you resolve

$(\pm)\ CH_3CH(OH)CH_2CH_3$? 3

(*d*) The rate of reaction of MeI with $N_3^{\ominus}$ at 0°C becomes 10^9 times faster if the soluent methanol ($\epsilon \simeq 33$) is changed to DMSO ($\epsilon \simeq 46$). Justify. 3

Subgroup – A (c)

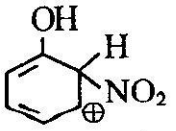
7. Answer any *five* questions : 2 × 5

(*a*)  is much more stable than  . Explain.

(*b*) α-chloro carbonyl compounds (R–CO–CH_2–Cl) is a very good substrate for S_N2 process. Explain.

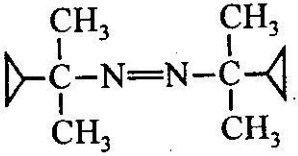
(*c*) CH_3–CH(OH)CH_2–SEt and CH_3–CH(SEt)–CH_2–OH give same product when treated with dry HCl. – Explain.

(*d*) Draw the resonating structure for

(*i*) 

(*ii*) $CH_3 - \overset{\oplus}{C}H - OCH_3$

(*e*) The azo compound (A) decomposes 20 times faster than compound (B). Explain.



(A)

$(CH_3)_3C-N=N-C(CH_3)_3$

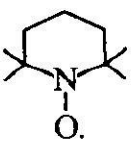
(B)

(*f*) Draw the stereo structures of $(CH_3)_3C^{\oplus}$. How does it differ from the corresponding carbanion ?

(*g*) Why dipole moment of cyclo pentandienone is less than cyclopentanone ?

(*h*) What is purple benzene ?

(*i*) Why the following radical is highly stabilized ?



GROUP – B

(*Inorganic*)

Subgroup – B (a)

Answer any **one** question : 15 × 1

8. (*a*) Why electron can not stay in the nucleas ? 2

(*b*) Draw the radial distribution curve for 3d and 2p orbital. 2

(*c*) Calculate the effective nuclear change for 2+, Fe^{3+} ion. 2

(*d*) Explain the electronic configuration of following metals : 2

Ni, Pd, Pt

(*e*) State the uncertainty principle and explain the situations in which it becomes insignificants. 2

(*f*) The photoelectric work function of a metal is 2·489 eV. Calculate the threshold wavelength. 3

(*g*) Arrange the following compounds according to their acid strength : 2

BBr_3, BI_3, BF_3, BCl_3

9. (*a*) Write a short note on "ion dipole interaction". 2

(*b*) Compare the IP of Cu, Ag and Au. 2

(*c*) Calculate the ionic radii of the Na^+ in NaF according to Pauling's method. The inter ionic distance is 1·08 Å. 2

(*d*) Draw the structures of ICl_2^+ and XeF_6 using VB theory. 2

(*e*) Explain the bond angles of CH_2F_2. 2

(*f*) Why nitrogen shows abnormal electron affinity ? 2

(*g*) $CaO + SiO_2 = CaSiO_3$
Find out the acid and base according to LUX theory. 2

(*h*) Write the IUPAC name of the element having atomic number 105. 1

Subgroup – B (b)

Answer any **two** questions : 10 × 2

10. (*a*) Write the physical significance of wave-function. 2

(*b*) Compare the solubility of $MgSO_4$ and $BaSO_4$ in water. 2

(*c*) Calculate the lattice energy of Th O_2 using Born-Lande equation. The radii of the Th^{4+} and O^{2-} ions are 108 pm and 126 pm. The

Madelung constant for fluorite structure = 2·519 Born exponent for Th^{4+} ($6S^2 6P^6$) may be taken only. 3

(*d*) Write the conjugate base of HS^-. 1

(*e*) What do you mean by the levelling effect of water ? 2

11. (*a*) Compare the thermal stability of PH_4Cl, PH_4Br, PH_4I. 2

(*b*) How the pH will change when 2 + 2

(*i*) $CuSO_4$ is added to the aqueous solution of $(NH_4)_2SO_4$.

(*ii*) $KHSO_4$ is added to sulfuric acid.

(*c*) The first IP of Be is lower than B, but the 2nd IP is reverse. Explain. 2

(*d*) Write atleast one example for each of μ bond and S bond. 2

12. (*a*) All the Arrhenius acid are the Bronsted acid but all the Arrhenius base are not the Bronsted base. Explain. 2

(*b*) Compare the melting point of NaCl and Cu_2Cl_2. 2

(*c*) The acidity of HF is lower than HCl. – Explain. 2

(*d*) Write one example where H_2SO_4 acts as base. 2

(*e*) What are super acid and per acid ? 2

13. (*a*) The bond angle of NH_3 is 107·3 whereas in PH_3 93·3°. Explain the difference in bond angle. 2

(*b*) Why the solubility of AgCl is lower than AgF in water ? 2

(*c*) The acidity of $ClCH_2COOH$ is higher than CH_3COOH. Explain. 2

(*d*) Showing the structure, prove that NO_2 is an odd electron molecule. 2

(*e*) MgO is highly stable, though the second electron affinity of oxygen is very high. Explain. 2

Subgroup – B (c)

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

(*a*) Why the solubility of AgCl decreases after the addition of NaCl ?

(*b*) Which one will be strong base toward a proton – NH_2^- and PH_2^-.

(*c*) Find out the ground state term symbol of Cr^{3+}.

(*d*) Why the Zr and Hf show almost similar chemical property.

(*e*) O-nitrophenol has lower melting point than P-nitrophenol. Explain.

(*f*) The bond angle of F_2O is $103{\cdot}2^\circ$ whereas in H_2O it is $104{\cdot}5^\circ$ – Explain .

(*g*) $HgCl_2$ is colourless whereas HgI_2 is red colour – Explain.

(*h*) p-orbital is dumble shaped. Explain.
