**2021**

CHEMISTRY

PAPER-I

*Time Allowed — 3 Hours* *Full Marks — 200*

*If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.*

*The figures in the margin indicate full marks for each question.*

*Answers may be written either in* ***English*** *or in* ***Bengali*** *but all answers must be in one and the same language.*

## Section-I

This Section comprises 15 questions in three Groups.

Answer *any ten* questions taking *at least three* questions from each Group.

### Group-A

1. An electron in a hydrogen atom in its ground state absorbs 1.50 times as much energy as the minimum required for it to escape from the atom. Calculate the wavelength of the emitted electron. (Given ionisation energy of H–atom = 13·6 eV. $m_e = 9{\cdot}109 \times 10^{-31}$ kg, $h = 6{\cdot}63 \times 10^{-34}$ JS). 4

2. Predict the species among $SF_4$, $I_3^-$, $SbCl_6^-$ and $PCl_5$ in which the central atom has used different type of hybridisation for chemical bonding from the others. 4

3. Aqueous solution of borax function as buffer solution of pH 9·18— why? 4

4. Using Pauling's rules, explain the $pk_{a_1}$ -values of $H_3PO_3$ (~2·0) and $H_3AsO_3$ (~9·0) with respect to their structural difference, if any. 4

5. Establish Nernst equation for the couple $VO_3^-/VO^{2+}$ standard potential of this couple at 25°C in 1(M) acid medium is + 0·92 volt. Find the formal potential at pH = 7·0. 4

### Group-B

6. For an ideal gas show that the word done for a reversible adiabetic expansion is $W_{ad} = C_v \Delta T$. 4

7. What is mean free path? How does it depend on the size of gas molecules? 4

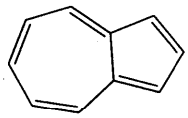
8. Write van der Waals equation for real gases. Derive a and b in terms of the critical parameters $V_c$, $T_c$ and $P_c$. 4

9. What is atomic packing factor? Calculate that for a body centered cubic crystal structure. 4

10. Define Joule-Thompson coefficient. It is an intensive property. Justify your answer. 4

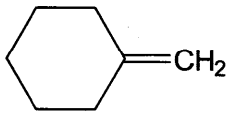
## Group-C

11. Azulene ($C_{10}H_8$) is a deep-blue compound having dipole moment (1.0 D).—Explain. 4



12. The room temperature $^1H$ NMR spectrum thiophene-3-carboxamide ($C_4H_3SCONH_2$) contains five signals. Give a reason for this observation. 4

13. Which alkyl bromide and what conditions would be used to prepare the following alkene in good yield by E2 elimination? Justify your choice. 4




14. (S)-1-bromo-1-fluoroethane reacts with $CH_3ONa$ in ethanol to give pure (S)-1-fluoro-1-methoxyethane. Is this result consistent with reaction by $S_N2$ mechanism? Explain. 4

15. Draw a reaction free-energy diagram for a reaction $A \rightleftharpoons B \rightleftharpoons C$ that meets the following criteria. The starting free energy are in the order C<A<B, and the rate limiting step of the reaction is $A \rightleftharpoons B$. 4

## Section-II

This Section comprises *six* questions in three Groups. Answer *any four* questions taking *at least one* question from each Group.

## Group-A

1. (a) An electron circles a nucleus of charge 'Ze'. Of the two orbits 1 and 2 of radii $r_1$ and $r_2$ respectively, its total energy is greater while in orbit-1. Prove that $r_1 > r_2$. Also show that the velocity and acceleration in orbit-2 are higher than those in orbit-1. 8

   (b) State the Heisenberg uncertainty principle. Suppose an electron is confined within the nucleus of diameter $10^{-14}$ metre. Find the uncertainty in determination of its velocity. Hence show that an electron can never reside inside the nucleus. 8

   (c) Write down the Born-Lande equation and explain the significance of the terms present. 2+4=6

   (d) Calculate the value of lattice energy of NaCl using the given data: A = 1·74, $r_0$ = 2·79Å, n = 8. 6

(e) Can you develop a pH-like scale in liquid $NH_3$? Given: $K_{H_2O} = 10^{-14}$ at 298K, $K_{NH_3} = 10^{-33}$ at 223K. 4

(f) Explain the basis of Mulliken electronegativity scale. 4

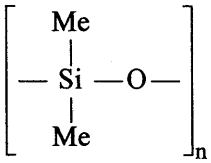
(g) Calculate the Pauling electronegativity value of fluorine from the following data (kcal/mole): $D_{H-H}$=104·2, $D_{F-F}$=36·6 and $D_{H-F}$=135·6. 4

2. (a) Consider the ethers $H_3SiOSiH_3$ and $H_3COCH_3$.

(i) Which ether has more Lewis base character and why?

(ii) Which angle $\left[\text{Si}-\hat{\text{O}}-\text{Si and C}-\hat{\text{O}}-\text{C}\right]$ is greater and why? 3+3=6

(b) Starting from $SiO_2$, show how the following polymer is prepared industrially. 4



(c) (i) $Al_2Cl_6$ and $Al_2Me_6$ are dimeric in gas phase. Draw their structures. Which compound is more Lewis acid character? Explain.

(ii) Arrange the halides $SnCl_2$, $PbCl_2$, $SiCl_2$ in the increasing order of their stability and explain your arrangement. 6+6=12

(d) What is formal potential of a redox couple? Give its an analytical importance. 8

(e) Calculate the pH of a solution made by mixing 50ml of 0·10M $NH_3$ and 50ml 0·040M HCl. The $K_b$ of $NH_3 = 1{\cdot}8\times10^{-5}$ at 298K. 6

(f) Arrange the following: (i) Acidic nature: $Ag_2O$, $V_2O_5$, $N_2O_5$ (ii) Stronger base towards a proton: $NH_2^-$, $PH_2^-$ 2+2=4

## Group-B

3. (a) Define thermal expansivity ($\alpha$) and isothermal compressibility ($\beta$) for an ideal gas. Verify that $\left(\partial P/\partial T\right)_{V_m} = \alpha/\beta$ where $V_m$ is the molar volume. 9

(b) What is mean-square speed? For 1·00 mol of $CH_4(g)$ at 0°C and 1 atm, find the number of molecules whose speed lies in the range 90·000 m/s to 90·002 m/s. 6

(c) What is Bragg's law? Explain with a suitable diagram. For a given wavelength of X-rays what is the lower limit of the spacings that can give observable diffraction?

For X-rays with X 3·0Å, what angles of incidence produce a diffracted beam from the (100) planes in a simple cubic lattice with side 5·0Å? 12

(d) A cylinder is fitted with a frictionless piston containing 3·00 mol of He gas at 1atm pressure and is in a large constant temperature bath at 400K. The pressure is reversibly increased to 5·00 atm. Find $w$, $q$ and $\Delta U$ for this process. 6

(e) Derive Laplace equation $p_{in} = p_{out} + {}^{2\gamma}/_{r}$ for curved surfaces where the terms have their usual meaning.

Calculate the pressure difference across the surface of an ethanol droplet of radius 220 nm at 20°C. The surface tension of ethanol at 20°C is 22·39 $mNm^{-1}$. 7

4. (a) Define heat capacity at constant volume. Show that $q_v = C_v dT$ where $q_v$ is the heat supplied at constant volume. What does a large heat capacity imply?

What will be the heat capacity at a phase transition, such as boiling point of water? Explain your answer. 8

(b) Calculate the change in entropy when the pressure of a fixed amount of perfect gas is changed isothermally from $P_i$ to $P_f$. What is this change due to? 5

(c) Using the relation $\left({}^{\partial S}/_{\partial V}\right)_T = \left({}^{\partial P}/_{\partial T}\right)_V$ show that the entropy of a perfect gas is $ln V$. 4

(d) State Nernst heat theorem.

Calculate the entropy of transition between orthorhombic sulfur (α) and monoclinic sulfur (β) at 369K $\left[Given: S_m(\beta) - S_m(\alpha) = -\ 402\,Jmol^{-1}\right]$. 4

(e) Show that $d\,ln\,k \Big/ d\left({}^{1}/_{T}\right) = -\Delta H^{\circ}/_{R}$. 4

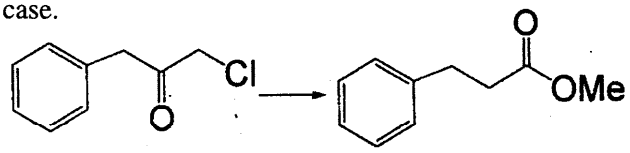
(f) For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ establish a relationship between K and $K_c$. 6

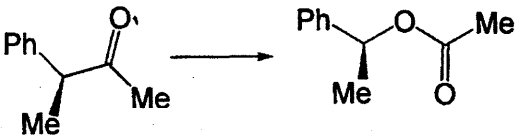
(g) What are Miller indeces? How are they obtained? For a simple cubic lattice draw the (100) and (111) planes. 6

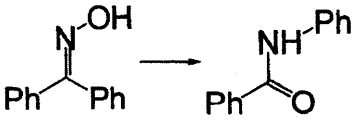
(h) What are point defects in solids? Give two examples. 3

**Group-C**

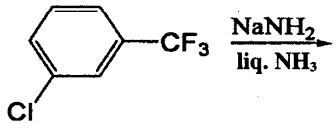
5. (a) Show how you would carry out the following conversions. Give reasonable mechanism in each case. 4×3=12

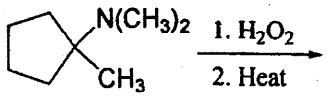
(i) 

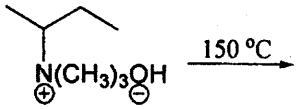

(ii) 


(iii) 


(b) Predict the major product formed in each of the following reaction. Propose plausible mechanism that account for the formation of each product: 5+3+3=11

(i) 


(ii) 


(iii) 

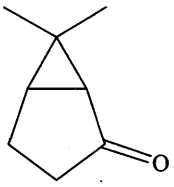

(c) An unknown compound ($C_3H_2NCl$) shows moderately strong IR absorptions around 1650 $cm^{-1}$ and 2200 $cm^{-1}$. Its $^1H$–NMR spectrum consists of two doublets (J = 14Hz) at δ 5·9 and δ 7·1. Propose a structure consistent with these data. 6

(d) Suggest a structure for each of the following ions in the mass spectrum of butyrophenone ($PhCOCH_2CH_2CH_3$), and the mechanism by which each is formed. 7

(i) m/z = 106 and

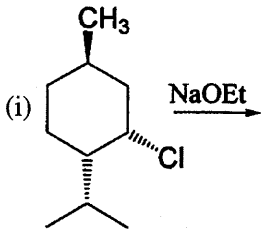
(ii) m/z = 120

(e) Show with a reasonable mechanism how a carbene might be used in the synthesis of the following compound: 4



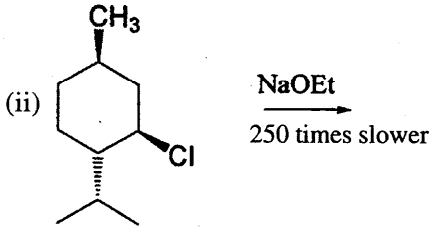
6. (a) Predict the major organic product formed in each of the following reaction. Explain why E2 elimination of diastereoisomer A proceeds 250 times faster than that of diastereoisomer B. 8

(i)



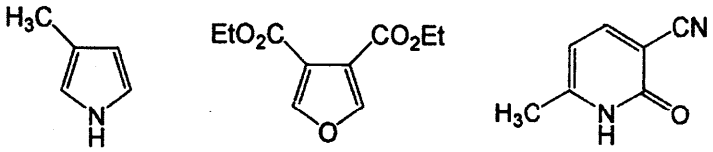

Diasteroisomer A

(ii)

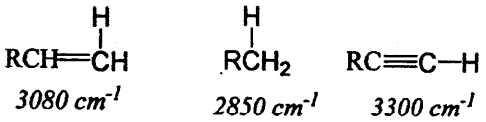



Diastereoisomer B

(b) How would you synthesize these aromatic heterocycles? 4×3=12



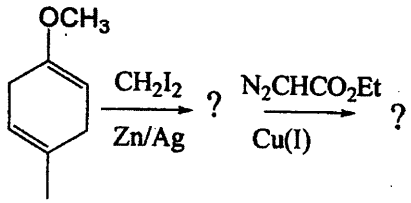

(c) Given the stretching frequencies for the C–H bonds shown, arrange the corresponding bonds in order of increasing strength. Explain your reasoning. 4




(d) Using 60 MHz spectrometer, a chemist observes the following absorption: doublet, J = 7 Hz at $\delta_H$ 4·00. How many hertz from the TMS peak is this absorption? Where would this peak be located (in ppm and in hertz) in the 100 MHz spectrum of this sample? What would J (coupling constant) be in the 100 MHz spectrum? 4

(e) Identify the geometric isomers of stilbene ($C_6H_5CH=CHC_6H_5$) from their $\lambda_{max}$ value of 294 and 278 nm. 3

(f) Predict the product in these two reactions and then comment on the selectivity shown. 5




(g) Treating 3-methyl-2-butanol with HBr yields 2-bromo-2-methylbutane as the sole product. Propose a mechanism that explains the course of reaction. 4

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