MWC(O)-CH-I/23

2023

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.

*Answer may be given either in **English** or in **Bengali** but all answers must be in one and same language.*

Attempt *any ten* questions *at least three* from each group.

Group-A

1. (a) The van der Waals constants of a gas are $a = 6.50$ atm lit^2 mole^{-2} and $b = 0.056$ lit mole^{-1}. Calculate the critical pressure and molar critical volume of the gas. 4

(b) Starting from the van't Hoff reaction isotherm, show that the equilibrium for an exothermic reaction shifts to the right on lowering of temperature. 4

(c) Define surface tension of a liquid. Write its unit in CGS and SI system. A spherical air bubble is created within a liquid of surface tension 72 dyne/cm. If the volume of the bubble is $\pi/6$ cm^3, calculate the excess pressure inside the bubble. 1+1+2

(d) What are Miller indices? Show 001 and 111 faces of a cubic crystal as Miller indices. 2+2

(e) Show that $(\partial U/\partial V)_T = 0$ for a gas obeying the equation of state $P(V - nb) = nRT$. (Assume the relevant Maxwell relation.) 4

2. (a) Write down the Maxwell's equation for molecular speed and explain the terms involved. Show graphically how the distribution curves vary at two different temperatures T_1 and T_2 ($T_2 > T_1$) for the same gas. Calculate the root mean square velocity of oxygen gas at 27°C. 2+3+3

(b) What are axis of symmetry and centre of symmetry of a crystal? Calculate the number of atoms per unit cell in a face centred cubic lattice. 2+2+2

(c) Draw the P-V and T-S diagram of an ideal gas undergoing a Carnot cycle. What do the enclosed areas of the diagram signify in the two cases? Justify your answer. 6

3. (a) Define viscosity coefficient of a liquid. Write its unit in CGS systems. Explain that viscosity of a liquid decreases with rise in temperature, but that of a gas increase with temperature. 2+2+4

(b) What is laminar flow of a liquid? How can one characterize a liquid flow turbulent or laminar? 3+3

(c) Elucidate the nature of Keesom, Debye and London interatomic forces. 6

4. (a) Prove $\frac{P_C V_C}{RT_C} = \frac{3}{8}$ for a van der Waals gas, where P_C, V_C, T_C are critical pressure, critical volume and critcal temperature of the gas respectively. 4

(b) The element polonium (atomic weight = 210) crystallizes in the cubic system. Bragg's first order reflections using X-rays of wavelength 0.154 nm occur at sin θ values of 0.225, 0.316, 0.388 for reflection from (100), (110) and (111) type planes.

(i) Show whether the unit cell is simple, face-centred or body-centred.

(ii) Calculate the value of 'a', the side of the unit cell.

(iii) Calculate the density of polonium. 5+2+3

(c) 1.0 moles of an ideal gas $\left(\overline{C}_p = 2.5R\right)$ at 1.0 atm and 300 K undergoes a reversible change so that the volume is doubled. The enthalpy change is 2078.5 J mol^{-1} and the heat absorbed is 1675 J mol^{-1}. Calculate the final temperature, final pressure and the work done during the process. 6

5. (a) Two spherical drops of mercury of diameter 0.4 mm and 0.2 mm merge to form one large drop at 27°C. Calculate the change in surface free energy during the process. Will the value increase if the same process is conducted at 100°C? Give reasons. Surface tension of mercury at 27°C = 480 dyne cm^{-1}. 5

(b) One mole of supercooled water at (–8°C) and 1 atm pressure turns into ice at (–8°C). Calculate the entropy change of the system, surroundings and the net entropy change. Heat capacity of water and ice, at 1 atm, may be taken as 75.42 JK^{-1} mol^{-1} and 37.20 JK^{-1} mol^{-1} respectively. ΔH(fusion) = 6008 J mol^{-1} at 273 K. 5

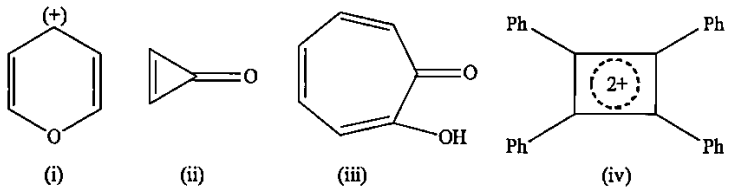
(c) Define mean free path of gas molecules. Write down its mathematical expression. How does the mean free path of a gas change with rise in temperature at constant pressure? 2+2+2

(d) What are the necessary conditions that are to be applied on van der Waals equation to obtain the expression for critical temperature (T_C), Boyle temperature (T_B) and the inversion temperature (T_i)? (No derivation required) 4

Group-B

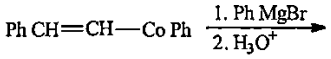
6. (a) Dimethoxycarbene fails to react with isobutylene—Explain. 4

(b) Classify the following species as aromatic, antiaromatic or nonaromatic— Justify. 4



(i) (ii) (iii) (iv)

(c) Predict the product(s) of the following reaction. 4



(d) Chlorofumaric acid undergoes dehydrochlorination at about 50 times faster than does chloromaleic acid to give the common product acetylene dicarboxylic acid. Explain this observation. 4

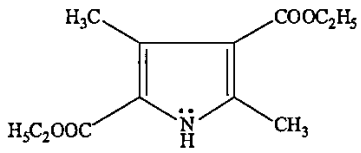
(e) How would you distinguish between the following compounds using ^{1}HNMR spectroscopy? 4

(i) $CH_3COOCH_2CH_3$ and $CH_3CH_2COOCH_3$

(ii) CH_3COCH_3 and CH_3CHO

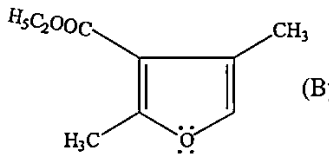
7. (a) Predict the starting materials and synthesise the following compounds. 5+5

(i)



(By Knorr synthesis)

(ii)

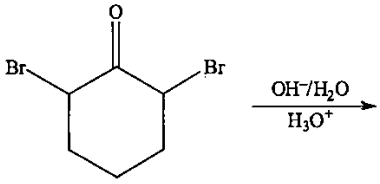


(By Feist Benary synthesis)

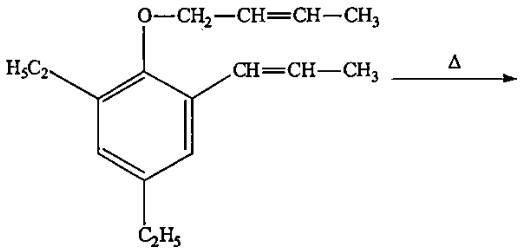
(b) Addition of HCl to 1-butene or 2-butene involves the same intermediate but the reaction of 1-butene is faster than that of 2-butene. Explain this observation with an energy profile diagram. 10

8. (a) Predict the product and suggest a plausible mechanism of the following reactions. 5+5

(i)



(ii)



(b) An organic compound (molecular mass 120) does not produce iodoform when treated with I_2/NaOH. It shows the following spectral characteristics:

UV : λ_{max} 292nm (ϵ_{max}16)

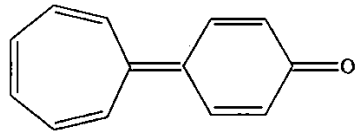
IR : 3,042 (m), 2,941 (w), 2,862 (w), 1,722 (s), 1605, 1575 (m), 1,462 (m) cm^{-1}

^{1}HNMR : δ7.27 (5H, m), 2.80 (2H, d), 9.78 (1H, t)

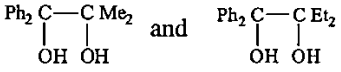
Determine the structural formula of the compound. 10

9. (a) Free rotation is possible about the double bond between the rings in the following compound. Explain.

(i)

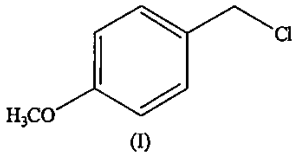


(ii) How would you prove by a cross-over experiment using the following two substrates that the pinacol-pinacolone rearrangement is intramolecular in nature? 5+5

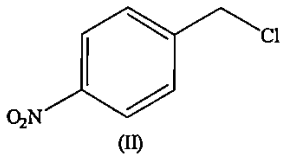


(b) (i) The azo compound dibenzyldiazene ($PhCH_2N{=}N\ CH_2Ph$) decomposes thermally to give N_2 at a rate faster than di-t-butyldiazene ($Me_3CN{=}CNMe_3$) does. Explain.

(ii) Which of the benzylic compounds will display SN^1 or SN^2 mechanism and why? 5+5



(I)

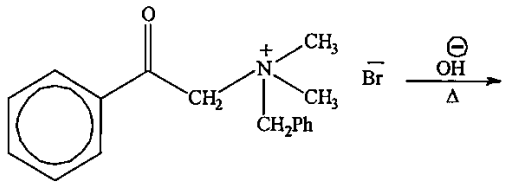


(II)

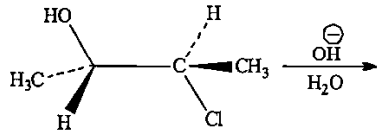
10. (a) The acetolysis of threo-3-phenyl-2-butyltosylate which is optically active gives a racemic product, while that of erythro diastereomer proceeds with retention of configuration to give optically active product— explain. 10

(b) Predict the product with a plausible mechanism (*any one*). 5

(i)



(ii)



(Optically active)

(c) Mesityl oxide ($Me_2C{=}CHCoMe$) shows two absorption bands one at 230 nm and another at 321 nm in isooctane. Assign these λ_{max} values in terms of electronic transitions. How do these absorption bands change their positions on changing the solvent from isooctane to water? 5

Group-C

11. (a) In an atom the angular momentum of an electron is $\sqrt{6}h/2\pi$. What will be the minimum value of the principal quantum number of the electron? 4

(b) Which of the following has greater melting point? RbCl and AgCl. 4

(c) The solubility of CaF_2 in water at 18°C is 2.04×10^{-4} mol/lit. Calculate solubility product. 4

(d) Find and explain the most stable dihalide among the followings: $SnCl_2$, $GeCl_2$, $PbCl_2$. 4

(e) Calculate Mulliken electronegativity of 'F' and 'Cl' from the given data: I.E. (Kcal mol^{-1}): F (401.7), Cl (299.1); E.A. (Kcal mol^{-1}): F (78.4), Cl (83.5). Convert the values to those of Pauling values using a suitable factor. 4

12. (a) The 3s and 3p orbitals have identical energies in the hydrogen atom, but in chlorine atom their energies are much different. Explain. 6

(b) Calculate the frequency of radiation emitted when an electron jumps from the third to first Bohr orbit. [Rydberg constant = 109677 cm^{-1}] 4

(c) Predict the structure of $XeOF_4$ indicating the hybridization of the central element. 4

(d) Comment the σ-donor and π-acceptor property of CN^- through MO approach. 6

13. (a) Although $N(CH_3)_3$ is a stronger base than NH_3, the adduct of the later is more stable than the former with $B(CH_3)_3$. Explain. 4

(b) $Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$ $E^0 = 0.36$ V

$I_2 + 2e = 2I^-$ $E^0 = 0.54$ V

A solution of potassium ferricyanide cannot oxidise iodide to iodine but it can do so in presence of Zn^{2+}ion — Explain. 4

(c) What is comproportionation reaction? Give example. 4

(d) Compare the reducing ability of gaseous H_2S, H_2Se and H_2Te. 4

(e) Explain the following order of ionization energies (IE_1 in KJ/mole): $_{29}Cu$ (745), $_{30}Zn$ (906), $_{31}Ga$ (579). 4

14. (a) Arrive at Bohr's quantisation principle from de Broglie equation. 4

(b) "Though the (n + 1) rule to determine the order of energy of different subshells is useful in most cases, there are some exceptions" — justify the statement with an example. 4

(c) Point out the number of radial node for 3d orbital. 2

(d) Explain why Li_3N can be formed while Na_3N is not. 6

(e) Predict and justify the order of dipole moment of CH_3Cl and $CHCl_3$. 4

15. (a) Which one is more acidic in gas phase: PH_3 or NH_3? 4

(b) What are redox indicators? Give one example with structure both in oxidised and reduced states. 3+2

(c) Using Slater' rule determine Z^* for a 4s and a 3d electron of copper. Which type of electron is more likely to be lost when copper forms a positive ion? 3+3

(d) Justify the ionization energy values of the following elements. 5

Element	I_1 (eV)	I_2 (eV)
Ga	5.99	20.51
Ge	7.89	15.93
As	9.81	18.63