

2016

## CHEMISTRY -I

Time Allowed: 3 Hours

Full Marks: 200

If the questions attempted are in excess of the prescribed number, only the question attempted first up to the prescribed number shall be valued and the remaining ones ignored. Answer may be written either in English or in Bengali but all answers must be in one of 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. He<sub>2</sub> does not exist, but He<sub>2</sub><sup>+</sup> exists. Explain. 4
2. Manganate is not stable in solution. Explain. 4
3. The structure of PCl<sub>3</sub> is different in solid and gaseous state. Explain. 4
4. Compare the ground state energies of H and Li<sup>2+</sup> ion. 4
5. Electron affinity of oxygen is less than sulphur. Comment. 4

GROUP B

6. Write down the expression representing a one dimensional Maxwellian velocity distribution of an ensemble of ideal gas molecules. Hence, show that the number of collisions with the wall of area A is  $\frac{1}{4} N\langle c \rangle$  where N is the number of molecules per volume of the container and  $\langle c \rangle$  is the average speed. 4

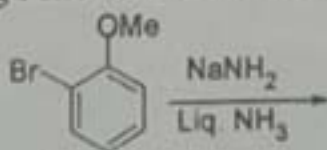
$$\text{Given: } \int_0^\infty x e^{-\beta x^2} dx = 1/2\beta$$

7. Write down the expression of the 'spreading co-efficient',  $\phi$ , of a liquid 'a' on another liquid 'b'. Water has a surface tension of 72.8 dynes/cm and benzene has a surface tension of 28.9 dynes/cm and the interfacial tension between water and benzene is 35.0 dynes/cm. What is  $\phi$ ? What is the significance of the sign of  $\phi$ ? 4
8. Distinguish between number of atom in a unit cell of a bcc and fcc lattice. 4
9. Write down the expression for the 'Clausius inequality'.  
1 mole of an ideal gas is expanded adiabatically and inversibly to twice its initial volume. What will be the  $\Delta S$  if you are to choose between +ve, -ve and zero? If the same expansion in volume is carried out irreversibly, would your choice differ? Explain with the help of a schematic diagram. 4

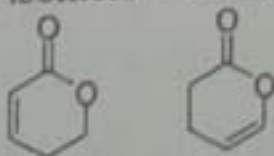
10. Prove that for a reaction involving ideal gas  $\frac{d \ln K_c}{dT} = \frac{\Delta \mu^\circ}{RT^2}$   
(The term have the usual significance) using the van't Hoff equation. 4

GROUP - C

11. (a) Identify the aromatic, non aromatic and antiaromatic species from the following: cyclopropenyl anion, cis-trans-cis-cis-trans-[10]annulene, 1,6-methano[10]annulene. Explain. 4
12. Identify the major product of the following reaction. Give mechanism. 4



13. Malonate radical readily adds to a vinyl ether but not so to acrylonitrile. Explain. 4
14. Addition of LiClO<sub>4</sub> in the acetolysis of some tosylates produces an initial steep acceleration which then decreased to the normal linear acceleration. Explain. 4
15. How can you distinguish the isomers from their IR spectral feature? 4



P.T.O



## SECTION - II

This section comprises 6 questions in three groups. Answer any four questions taking at least one question from each group.

## GROUP A

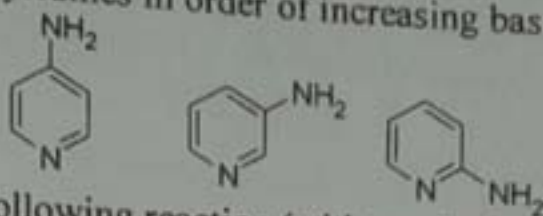
16. (a) Compare the spin states and bond orders of  $O_2$ ,  $O_2^+$ ,  $O_2^{2-}$  and  $C_2^{2-}$  ions. 8  
 (b) Illustrate the 3s, 3p and 3d orbital and calculate the number of nodes of each. 8  
 (c) 50 ml 0.1(N)  $Fe(II)$  solution was titrated with 50 ml 0.1(N)  $MnO_4^-$  solution. Calculate the redox potentials in the following steps ( $E^*_{Fe(III)/Fe(II)} = 0.76$  V and  $E^*_{MnO_4^-/Mn^{2+}} = 1.55$  V). 8  
 (i) When 5 ml  $MnO_4^-$  solution as added.  
 (ii) When 25 ml  $MnO_4^-$  solution was added.  
 (iii) When 50 ml  $MnO_4^-$  solution as added.  
 (iv) When 50.1 ml  $MnO_4^-$  solution was added.  
 (d) Compare the structure of  $BF_3$ ,  $CF_4$ ,  $NF_3$  and  $XeF_2$  molecules. 8  
 (e) Compare with example the Pauling and Allred-Rochow electronegativity scales. 8  
 17. (a)  $NaCl_2$  and  $CaF$  do not exist, while  $NaCl$  and  $CaF_2$  are stable. Explain. 8  
 (b) Illustrate the MO diagram of the CO molecule and compare it with that of  $CN^-$ , particularly mentioning the donation and acceptance property. 8  
 (c) Compare the origins of Balmer, Lyman and Paschen series of H- spectra. Illustrate with a diagram. 8  
 (d)  $Fe(III)/Fe(II)$  redox potential decreases in the presence of excess  $F^-$  and  $H_3PO_4$ . Explain. Depict the analytical importance of it. ( $E^*_{Fe(III)/Fe(II)} = 0.76$  V) 8  
 (e) The composition of interhalogen is different from that of polyhalides. Explain. Compare the reactivities of inter-halogens with halogens. 8

## GROUP B

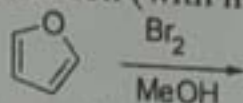
18. (a) Derive  $\mu_{J-T} = \frac{V}{Cp}(\alpha T - 1)$  where  $\alpha$  is the coefficient of thermal expansion of a system. For a certain gas  $\mu_{J-T} = 0$ , what does it imply? 8  
 (b) Calculate the density of elemental silver which crystallizes in a fcc lattice with unit cell length of 4.086 Å. 8  
 (c) Two van der Waals gases have the same value of 'b' but different 'a' values. Which of these would occupy greater volume under identical conditions? Why? Estimate the molar volume of  $CO_2$  at 500 K and 100 atm by treating it as a van der Waals gas. ( $a = 3.592$  dm<sup>6</sup> atm mol<sup>-2</sup> and  $b = 4.267 \times 10^{-2}$  dm<sup>3</sup> mol<sup>-1</sup>). 8  
 (d) Describe any one of the suitable methods employed for the determination of viscosity of a liquid. 8  
 (e) Discuss the origin of surface tension of a liquid. Show that the surface tension and surface energy have the same dimensions. 8  
 19. (a) Derive the condition for reflection to give constructive interference, when the X-rays are incident on a crystal face. Calculate the separation of (i) the {123} planes and (ii) the {246} planes of an orthorhombic unit cell with  $a = 0.82$  nm,  $b = 0.94$  nm, and  $c = 0.75$  nm. (a, b and c are the length of the three sides of the unit cell). 10  
 (b) Prove that for a hexagonal closest packed structure occupied space is 74.05%. 10  
 (c) If for a substance  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  and  $\left(\frac{\partial H}{\partial p}\right)_T = 0$ , show that the equation of state is  $\frac{pV}{T} = \text{constant}$ . (all the terms have their usual significance). 8  
 (d) Prove that  $\left(\frac{\partial H}{\partial p}\right)_T - V = -T \left(\frac{\partial V}{\partial T}\right)_p$  (all the terms have their usual significance). 6  
 (e) A van der Waals gas changes its state from  $T_1, V_1$  to  $T_2, V_2$ . Derive the expression for its entropy change. (T for temperature, V for Volume) 6

## GROUP - C

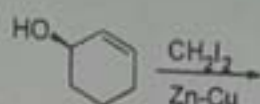
20. (a) Arrange the following aminopyridines in order of increasing basicity. Give reason. 6



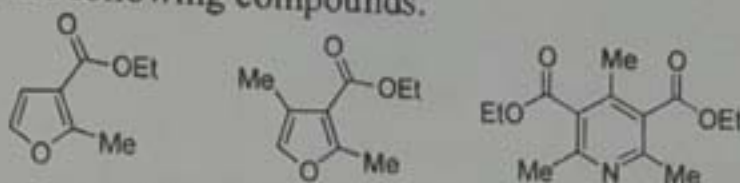
- (b) Predict the product(s) of the following reaction (with mechanism). 6



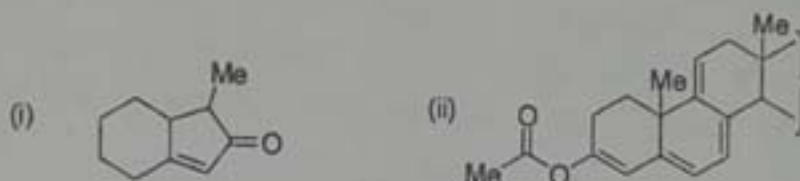
- (c) Predict the product in the following reaction. Comment on the stereochemical feature of the reaction. 5



- (d) Outline the synthesis of the following compounds. 3x5

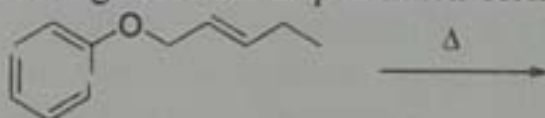


- (e) Calculate the  $\lambda_{\text{max}}$  values for the following compounds. 4x2

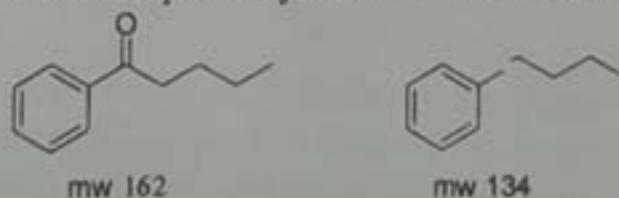


21. (a) Outline the synthesis of  $\text{C}_6\text{H}_5\text{CH}(\text{CO}_2\text{Et})_2$  using anthranilic acid as one of the starting materials. Explain the key step. 5

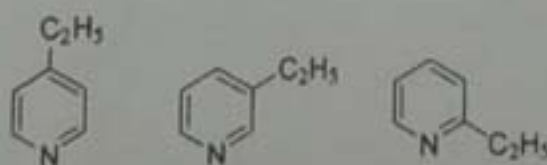
- (b) Predict the products of the following reaction. Explain their formation. 6



- (c) Depict the major mass fragmentation pathways for the following compounds. 4x2



- (d) How can you distinguish the following aromatic compounds with the help of mass spectrometry? 3x3



- (e) An organic compound with molecular formula  $\text{C}_5\text{H}_7\text{NO}_2$  exhibits the following spectral data. 6

IR:  $\nu_{\text{max}}$  2260, 1747, 1200 (several strong bands)  $\text{cm}^{-1}$

$^1\text{H}$  NMR:  $\delta(\text{ppm})$  1.3 (3H, t), 3.5 (2H, s), 4.3 (2H, q)

Suggest the structure of the compounds. 6

- (f) Identify [A] and B. Explain the formation of B from [A]. 6

