

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2019

FIRST YEAR (BATCH 2019-22)

CHEMISTRY (Honours)

Paper : II [CC 2]

Date : 13/12/2019

Time : 11.00 am – 1.00 pm

Full Marks : 50

(Use a separate Answer Book for each Group)

Group A

[34 marks]

Unit –I

[12 marks]

Answer **any one** from question nos. 1 & 2:

1. a) In the mythical world of Flatland, everything is two dimensional. Write down the distribution of speeds and determine the most probable speed of the molecules at a temperature T. [1+2]
b) Consider the following equation of state for a gas : $P\bar{V} = RT\left(1 + \frac{b}{\bar{V}}\right)$ would it be possible to liquefy the gas? Explain. [2]
c) i) Draw a family of Z vs P curve for a real gas at different temperature (below, at and above Boyle temperature).
ii) Show how would you interpret the above behaviour with the help of van-der Waals of equation (in all the three regions : below, at and above Boyle temperature; at low, intermediate and high pressure). [2+3]
d) Write down the expression for the potential energy function V(r) for Lennard-Jones potential (6-12) and plot V(r) as a function of intermolecular distance(r). [2]
2. a) Find an expression for $\left\langle \frac{1}{c} \right\rangle_{av}$ in the case of a three dimensional Maxwellian distribution of molecular speeds. [3]
b) Write down the Dieterici equation of state for a real gas and hence show that $\frac{RT_c}{P_c V_c} = \frac{1}{2} e^2$ [3]
c) Calculate the volume of 1 mole of CO₂ at a pressure 1 atm and temperature 300 K using the van-der-Waals equation of state to a reasonable accuracy. $[a = 3.64 \text{ atm L}^2 \text{ mol}^{-1}, b = 0.042 \text{ L mol}^{-1}]$ [3]
d) The critical temperature and pressure for NO gas are 177 K and 64 atm, respectively, and for CCl₄ they are 550 K and 45 atm, respectively, Which gas
i) Has the smaller value of the van der Waals constant b?
ii) Has the smaller value of the van der Waals constant a?
iii) Is most nearly ideal in behavior at 300 K and 10 atm? [3]

Unit –II

[10 marks]

Answer **any one** from question nos. 3 & 4:

3. a) Consider a gas at constant temperature. If the pressure is doubled what effect does this have on (b) the total number of collisions per second occurring in 1m³ of gas? (c) the mean free path of a gas molecules? [3]
b) What is the trend in Diffusion coefficient (D) as (i) temperature increase? (ii) molar mass increases? (iii) pressure increases? [3]

- c) Derive a relation between viscosity coefficient of gas and the mean free path of the gas molecules. [4]
4. a) Assume that the ammonia is diffusing through an atmosphere of helium. Will diffusion be faster or slower than through air? [2]
- b) Neon and mercury vapor have almost equal van der Waals constant b. Would you expect any difference in the viscosities of these gases (at the same temperature)? [2]
- c) Two separate bulbs are filled with neon and argon gas, respectively. If conditions are such that the Ar is at twice the absolute temperature and half the density of the Ne, what is the ratio of wall collision frequencies?
- At wt of Ne = $0.020 \text{ kg mol}^{-1}$
 Ar = $0.040 \text{ kg mol}^{-1}$ [3]
- d) How will you determine the viscosity of a liquid using Stokes law (falling sphere method)? [3]

Unit –III

[12 marks]

Answer any one from question nos. 5 & 6:

5. a) True or False ? Explain (**any two**) [2×2]
- i) U remains constant in every isothermal process in a closed system.
- ii) $PV^\gamma = \text{constant}$ for an adiabatic process.
- iii) Joule-Thomson expansion is an isenthalpic process for an ideal gas.
- b) A perfect gas with $\bar{C}_v = 3R$, independent of T expands adiabatically into a vacuum, thereby doubling the volume. Two students present the following analyses –
- 1st student wrote $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{3R}} \Rightarrow T_2 = \frac{T_1}{2^{1/3}}$
- whereas 2nd student wrote $\Delta U = q + w = 0 + 0 = 0$, so $T_2 = T_1$. Which student is correct? What error the other student make? [3]
- c) Calculate $\Delta H_f^\circ (298\text{K})$ of sucrose (s) from the following data : [2]
- $\Delta H_f^\circ (\text{H}_2\text{O}, l) = -285.8 \text{ KJ mol}^{-1}$
 $\Delta H_f^\circ (\text{CO}_2, g) = -393.5 \text{ KJ mol}^{-1}$
 $\Delta H_{\text{combination}}^\circ (\text{sucrose}, s) = -5665 \text{ KJ mol}^{-1}$
- d) One mole of an ideal gas of $\bar{C}_v = 6 \text{ cal K}^{-1} \text{ mol}^{-1}$ expands adiabatically from STP to 0.1 atm. Calculate the final state (T_f, V_f) and q, w, ΔU and ΔH if the expansion is reversible. [3]
6. a) For the ideal gas, prove that $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$ [2]
- b) Show that reversible work of expansion is the maximum work. [3]
- c) The average bond enthalpy of OH bond in water is defined as $\frac{1}{2}\Delta H_r^\circ$ for $\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g)$ ΔH_f° for H(g) and O(g) are 218.0 and 249.2 KJ mol^{-1} , respectively at 298.15 K. And ΔH_f° for $\text{H}_2\text{O}(g)$ is $-241.8 \text{ KJ mol}^{-1}$ at same T.
- i) Use this information to determine the av. bond enthalpy of OH bond in water at 298.15 K.
- ii) Determine average bond energy (ΔE) of O-H bond in water at same T. [3]

d) Show that for an ideal gas,

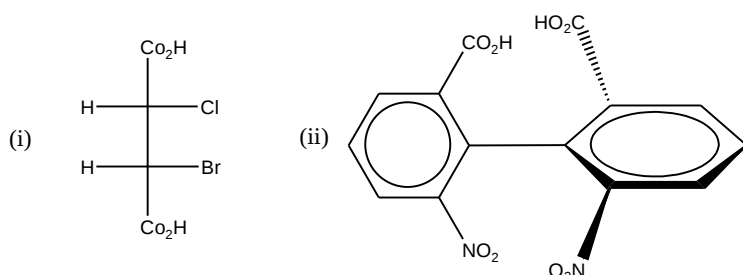
$$\text{i) } \left(\frac{\partial U}{\partial V} \right)_T = 0 ; \text{ ii) } \left(\frac{\partial C_P}{\partial P} \right)_T = 0 \quad [2+2]$$

Group B

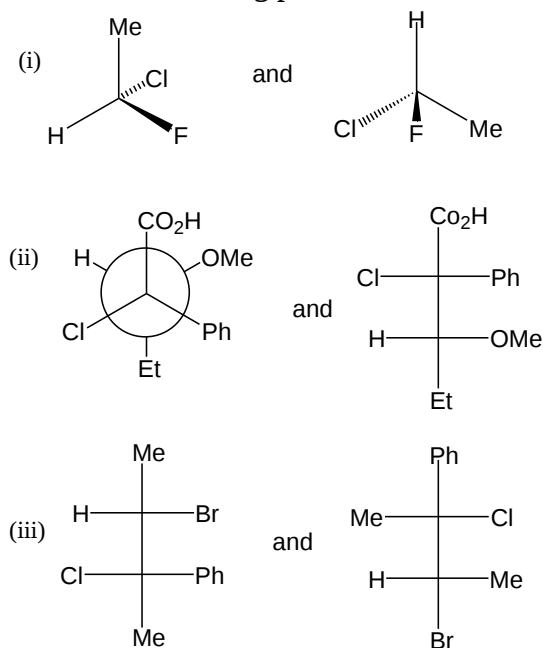
[16 marks]

Answer any one from question nos. 7 & 8:

7. a) Assign the following compounds with absolute configuration (R/S descriptor) [2]



b) Label the following pairs of molecules as homomers, enantiomers or diastereomers. [3]



c) Write the Fischer projection formula of erythro-3-phenyl-2-butanol and represent it in Newman projection formula. [2]

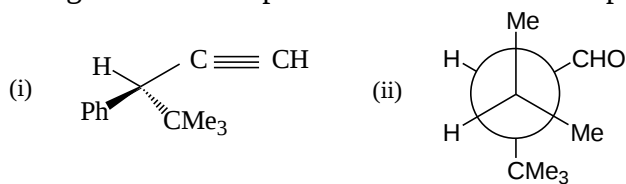
d) Indicate the symmetry element present in (i) bromoform (ii) anti conformation of ethylene glycol. [2]

e) A sample of 2-methyl-1-butanol has an observed specific rotation, $[\alpha]_D^{25} = +1.151^\circ$. Calculate the enantiomeric excess of the sample [the specific rotation of the pure enantiomer is $+5.756^\circ$]. What is the stereoisomeric composition of the mixture? [2]

f) Explain the stereoisomerism of 6,6'-dinitro-diphenic acid and draw the energy profile for racemisation of its enantiomers. [3]

g) Stereo isomers of $H_3C-CH=CH-CH_3$ differ widely in chemical properties but those at $H_3C-CH=C=CH-CH_3$ do not. — why? [2]

8. a) Indicate the symmetry elements present in (i) Chloroform, (ii) 1,2-dibromethene and (iii) CO_2 . [3]
 b) Define with example (i) axial chirality (ii) atropisomerism. [2+2]
 c) Assign R/S – descriptors for the chiral centres present in the following molecules. [2]



- d) Draw the Fisher projection formulae of the following :- [1]
 (2S,3R)-3-phenyl-2-butanol
 e) Draw the Fischer projection of a meso-isomer of $\text{H}_3\text{C}(\text{CHOH})_3\text{CH}_3$ and point out the stereogenic and achirotopic centre(s), if any in it. Explain. [2]
 f) Explain why (+)-1-phenyl ethyl alcohol loses its optical activity in presence of acid. [2]
 g) Ethyl isopropylamine is a chiral molecule – Justify or criticise. [2]

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