

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIRST SEMESTER EXAMINATION, DECEMBER 2012

FIRST YEAR

CHEMISTRY (Honours)

Date : 14/12/2012

Time : 11 am – 1 pm

Paper : I

Full Marks : 50

(Use separate answer-book for each group)

Group – A

UNIT-I

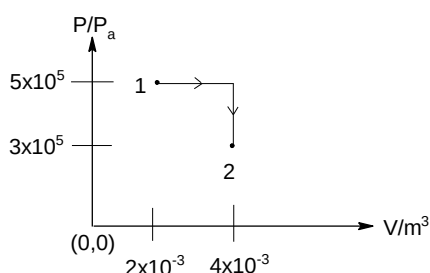
(Answer **any one** question)

1. a) (i) Calculate the average velocity of a gas constrained to move only on a single dimension. [2]
(ii) Explain the significance of the result. [1]
b) 'Temperature is a measure of the width of the speed distribution of the gas molecules' — explain. [2]
c) Out of the three types of intermolecular forces – dipole-dipole attractive force, dipole-induced dipole attractive force and London dispersion force only the first one depends on temperature — explain. [1]
d) Suppose that at some initial time all the molecules in a container have the same translational energy, $2.0 \times 10^{-21} \text{ J}$. As time passes, the motion becomes chaotic and the energies finally are distributed in a Maxwellian way.
(i) Compute the final temperature of the system.
(ii) What fraction of molecules would finally have energies in the range $1.98 \times 10^{-21} \text{ J}$ to $2.02 \times 10^{-21} \text{ J}$? [Hint: since the range of energy is small, the differential form to the Maxwell distribution may be used] [3]
e) Explain from van der Waals equation why the initial slope of the Z vs P (or PV_m Vs P) isotherm at very low temperature is negative. [2]
f) Explain in the light of intermolecular forces that although the *o*-, *m*- and *p*- isomers of dinitrobenzene have very different dipole moments but their boiling points are nearly same. [2]
2. a) Define Boyle temperature (T_B) of a gas. Obtain an expression for the Boyle temperature of a van der Waals gas. State what makes T_B of He gas to be very low. [2+3+1]
b) The mean free path of oxygen gas at 25°C and 1 atm is $1.6 \times 10^{-5} \text{ cm}$. Estimate the van der Waals constant ' b ' of oxygen gas. [3]
c) The critical temperature and pressure for NO gas are 177K and 64 atm, respectively, and for CCl_4 they are 550K and 45 atm, respectively. Which gas (a) has the smaller value of the van der Waals constant ' b '. (b) The smaller value of the van der Waals constant ' a '. (c) has larger critical volume. (d) behaves more ideally at 300K and 10 atm. [4]

UNIT-II

(Answer **any one** question)

3. a) A system undergoes a reversible change of state ($1 \rightarrow 2$) following the path indicated below when it absorbs 500J of heat. Calculate the work done in this process. Also estimate the work done when the same change of state occurs adiabatically. [2+2]



b) Verify whether dz as given below is an exact differential or not. [2]

$$dz = \frac{RT}{P} dP - R dT \quad (R = \text{constant})$$

c) Using the thermodynamic definition of an ideal gas, show that for an ideal gas

(i) $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ [1½]

(ii) $\left(\frac{\partial H}{\partial P}\right)_T = 0$ [1½]

d) Develop an equation for the work produced in the isothermal, reversible expansion from $\bar{V}_1$ to $\bar{V}_2$ of a gas with the equation of state $p\bar{V} = RT + (bRT - a)\left(\frac{1}{\bar{V}}\right)$. [2]

e) Arrange the following gases in order of increasing μ_J (Joule's coefficient) value:

$\text{NH}_3, \text{He}, \text{H}_2$ [1]

4. a) Prove that for a reversible adiabatic change of state for a gas obeying the equation of state $p(V-b) = RT$, the term $T(V-b)^{nR/C_V}$ remains constant. [3]

b) One mole of an ideal gas ($C_V = 20 \text{ JK}^{-1} \text{ mol}^{-1}$) initially at STP is put through the following reversible cycle –

(A) State 1 to state 2 – heated at const. volume to twice the initial temp.

(B) State 2 to state 3 – expanded adiabatically back to the initial temp.

(C) State 3 to state 1 – compressed isothermally back to the initial state.

Calculate $q, w, \Delta E$ and ΔH for (i) Step A (ii) Step B (iii) The whole cycle. [6]

c) Obtain the expression $C_p - C_V = \left[P + \left(\frac{\partial u}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$
(notations have usual significance). [3]

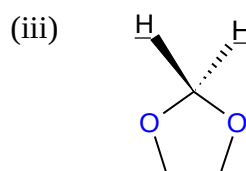
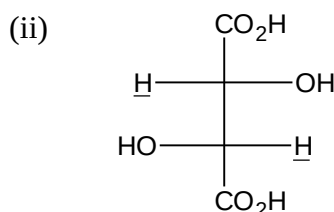
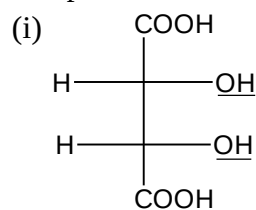
Group – B

UNIT-I

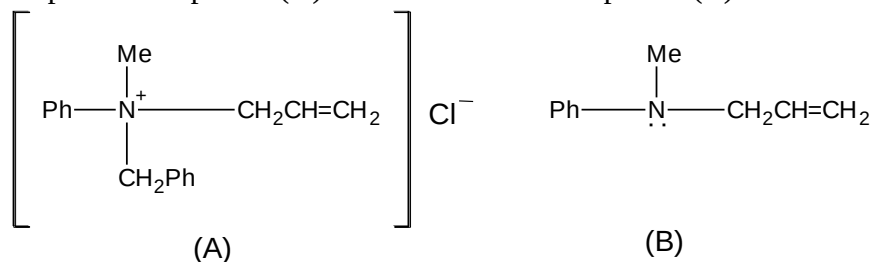
(Answer **any one** question)

5. a) (i) What is the necessary and sufficient condition for the existence of enantiomerism? [2]
(ii) Does enantiomerism possible in molecules having no chiral carbon atoms? [2]

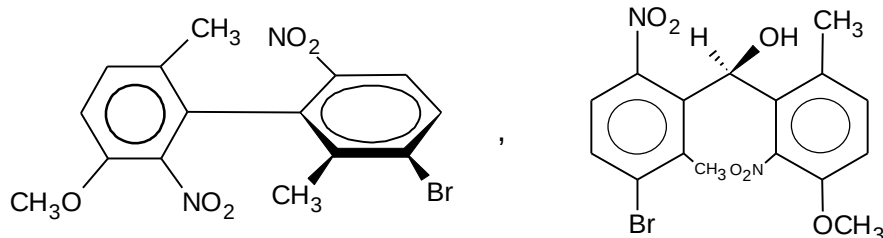
b) Identify the underlined ligands as homotopic, enantiotopic or diastereotopic of the following compounds with reason: [3]



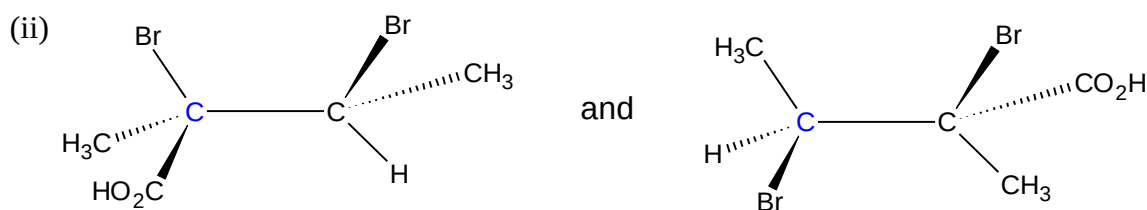
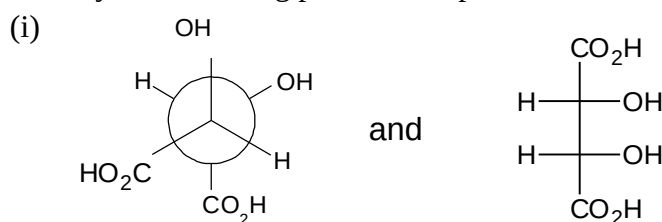
c) Explain: Compound (A) is resolvable but compound (B) is not resolvable. [2]



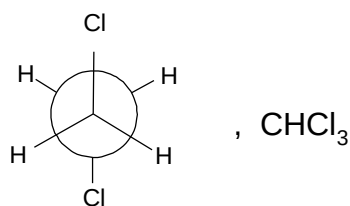
- d) A 2.0% solution of a sample of 2-phenylpropanal in benzene shows an optical rotation of -3.6° when measured using a polarimeter tube of 10 cm length. Specific rotation of pure (+) -2-phenylpropanal is reported as $[\alpha]_D +240$. Calculate the molar ratio of the two enantiomers in the above sample. [3]
- e) Write down a Newman projection formula of any one conformer of (2R, 3R)-2,3-dibromobutane. State whether the bromine atoms in the above compound are homotopic, enantiotopic or diastereotopic. [2]
- f) Designate the following structures with *R/S* notations. [3]



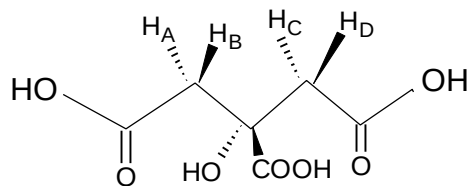
6. a) Identify the following pairs of compounds as enantiomers, diastereomers or homomers. [3]



- b) C_5H_8 represents two isomeric allenes. One is achiral and the other is resolvable. Identify the allenes. [2]
- c) Find, if present, the simple axes of symmetry (C_n), planes of symmetry (σ) and centre of symmetry (i) of the following: [2]



- d) Explain the following observations: [2]
Optically active mandelonitrile ($PhCHOHCN$) gives optically inactive mandelic acid ($PhCHOHCOOH$) upon hydrolysis with dilute NaOH followed by acidification with dilute HCl.
- e) Find the topic relationship (homotopic, enantiotopic or diastereotopic) of H_A with H_B , H_C and H_D separately in the following structure (citric acid). Designate H_A by Pro-R / Pro-S notation. [3]



- f) How will you resolve a racemic mixture of $(\pm)$ 2-phenylpropanoic acid? [2]

g) Justify the following statement:

The meso isomer of butane-2, 3-diol boils at higher temperature than the active isomer.

[1]

UNIT-II

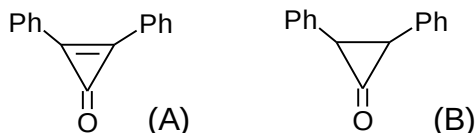
(Answer **any one** question)

7. a) Explain why the C = C bond length of allene are shorter than those of an ordinary alkene.

[2]

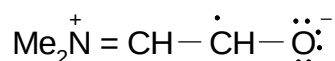
b) Which of the following two compounds has higher dipole moment? Give reason.

[2]



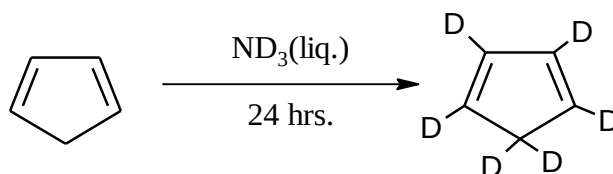
c) Draw the contributing resonating structures of the following indicating the major contributor.

[2]



d) Explain the following transformation

[2]

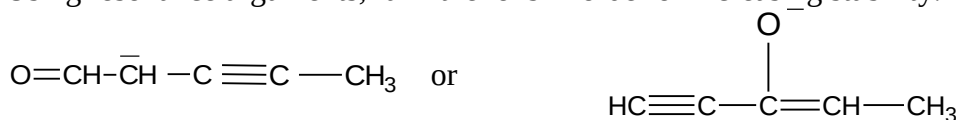


e) Compare the boiling points of n-pentane and neo-pentane.

[2]

8. a) Using resonance arguments, rank the ions in order of increasing stability.

[2]

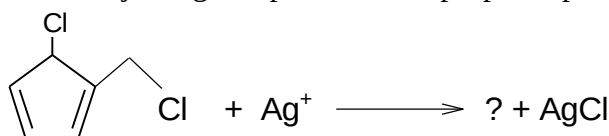


b) The experimentally determined enthalpy of hydrogenation of cyclooctene and cyclooctatetraene to cyclooctane are -23 and $-98 \text{ kcal mol}^{-1}$, respectively. Comment about the value of resonance energy.

[2]

c) Predict the structure of the major organic product with proper explanation.

[1]



d) Compare the dipole moments of the following pair with explanation.

[2]



e) Sketch the π Mo_5 of allyl carbanion indicating the HOMO and LUMO.

[2]

f) Draw the orbital picture of $\text{CH}_2 = \text{C} = \text{O}$ indicating the hybridisation states of the C atoms.

[1]

