RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2014

FIRST YEAR

Date : 22/05/2014 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : II Full Marks : 50

[Use a Separate Answer Book for each group]

Group – A

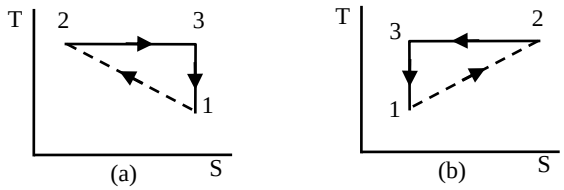
(*Answer **one** question from each unit*)

Unit – I

1. a) Prove the equivalence of Clausius' Statement and Kelvin-Planck's statement of the second law of thermodynamics. [4]

   b) A heat engine operating between 1000°C and 25°C produces work which is entirely used to run a refrigerating machine, operating between 0°C and 25°C. Calculate the ratio of the heat absorbed by the engine to that absorbed by the refrigerator, assuming ideal operation for both. [3]

   c) Consider two hypothetical irreversible adiabatic processes, shown as dotted lines in the following two diagrams.



   Give the arguments with the help of 2nd law of thermodynamics to show only one of the two above diagrams is correct. Also state the law involved. [4]

   d) Justify or criticise : Joule-Thomson expansion is an isenthalpic process as $H_f = H_i$. [2]

2. a) One mole of He is heated from 200°C to 400°C at a constant pressure of 1 atm. Given that the absolute entropy of He at 200°C is 135 $JK^{-1}mole^{-1}$ and assuming that He is a perfect gas, calculate $\Delta G, \Delta H$ and ΔS for this process. Comment on the spontaneity of the process from ΔG value. — Explain. [4]

   b) Starting from the fundamental equation to show that for a reversible process at constant temperature and pressure, maximum work done by the system is a measure of decrease in Gibbs energy. [2]

   c) Give separate example of a process for which— (A) $\Delta A = 0$ (B) $\Delta S = 0$ [2]

   d) One mole of an ideal gas at 300K and 1 atm is allowed to expand freely to twice its initial volume under adiabatic condition. Calculate ΔS_{sys}, ΔS_{surr} and ΔG for the expansion of the gas. [3]

   e) A Carnot engine works between temperatures T_H and T_c. If it is possible either to increase the source temperature by 1°C or to decrease the sink temperature by 1°C, which of these will be causing more increase in the efficiency? Explain your answer in a general way. [2]

Unit – II

3. a) Which of the following functions, when multiplied by a normalization constant, would be acceptable wave founction? Why?

   i) $\psi(x) = e^{-bx^2}$ for $x < 0$ and $2e^{-bx^2}$ for $x \geq 0$.

   ii) $\psi(x) = \tan x$. [1½×2]

   b) Give a pictorial description of an experiment other than the photoelectric effect, that demonstrates the particle nature of light. Also write down the associated expression. [3]

   c) Show that— Any linear combination of the 'n' wave functions of the degenerate level is an eigenfunction of the Hamiltonian with eigenvalue 'w'. w is the eigenvalue for individual function. [2]

d) Find the eigenfunctions and eigenvalues of the operator $\frac{d}{dx}$. [2]

e) Evaluate the commutator, $[\hat{x}, \hat{p}_x^2]$. [2]

4. a) A photon and an electron have the same de Broglie wavelength.
   i) Which one of these has higher kinetic energy?
   ii) Which has greater total energy? —Explain. [2+2]

   b) Find the expectation value of p_x for a particle in a 3D cubic box of length 'L'. Comment on the result obtained. [2]

   c) Show that the wavefunction $\psi(x) = A \sin kx$ satisfies the Schrowdinger equation for an electron in a 1D box. Determine the constant 'k' by requiring the wavefunction to have the value zero at L i.e. $\psi(L) = 0$ and also determine the constant 'A' by applying appropriate condition. [4]

   d) Calculate the probability of finding a free particle confined in a one-dimensional box of length L within the region from $\frac{L}{4}$ to $\frac{3L}{4}$. [2]

Group – B

(*Answer **one** question from each unit*)

Unit – I

5. a) Between NH_3 and $NH_2 - NH_2$, which one is the better nucleophile in bimolecular substitution reaction? Give explanation. [3]

   b) Predict the products when R-Cl is separately treated with AgCN and NaCN. Explain product formation. [3]

   c) Alcohols are not good substrate for S_N reaction—Why? How can alcohols be converted into good substrate for S_N reaction? Hence propose a scheme for the conversion of (S) 2-pentanol to (R) 2-pentanol. [4]

   d) Predict the products when erythro-3-bromo-2-butanol is treated with HBr. Show the stereochemical course of the reaction using sawhorse formulae. [3]

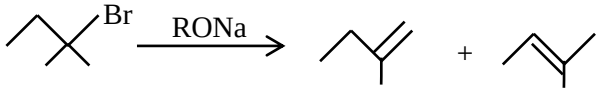
   e) Carry out the following transformation : [2]
   cyclohexene $\rightarrow$ trans-cyclohexane-1,2 diol

6. a) Among the halides, which one is the best nucleophile in polar aprotic solvent? Give reason for your answer. [2]

   b) Both CH_3CH_2I and Me_3CCH_2I are primary iodides, but the former undergoes solvolysis reaction ~10^5 times more rapidly than the later —why? [2]

   c) How can you convert (outline the steps with reagent) (R)–α–deutero ethanol to its (S)–stereoisomer? [3]

   d) How can you explain the observed ratio of products in the following reaction? [2]



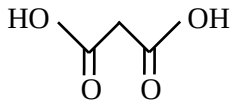
	(I)	(II)
R = Et	30%	70%
= Et_3C	90%	10%

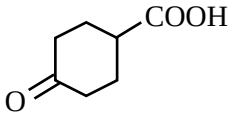
   e) Predict major product when propene is treated with HBr in presence of benzoyl peroxide. Give mechanism. Why does only HBr among other halogen acids behave in different way in presence of peroxide? [3]

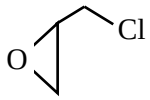
   f) Active threo isomer of 1,2-diphenyl-1-bromopropane reacts 10 times more rapidly than the active erythro isomer, when both are treated with EtONa base to give substituted propenes. Explain the higher rate of reaction of the threo isomer and classify the reaction as stereoselective / or stereospecific. [3]

Unit – II

7. a) Give IUPAC name of the following compounds (**any two**) : [2]

i) 

ii) 

iii) 

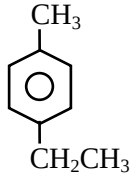
b) Predict the major product and give mechanism of the following reaction : [3]

$$Ph-CH_2-CH=CH-CH_3 \xrightarrow{NBS(1eqv)\,in\,CCl_4}$$

c) Draw energy profile diagram indicating starting material, transition states, intermediate and product for the reaction given below which shows no primary kinetic isotope effect ($k_H / k_D \approx 1$). Indicate rate determining step. [2½]

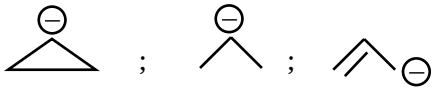
$$ArH + NO_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\overset{+}{\underset{NO_2}{\overset{H}{<}}} \xrightarrow{k_2} ArNO_2 + H^+ ; k_2 >> k_{-1}$$

d) Indicate the relative acidity of three different kinds of aliphatic protons in the following compound. Explain. [2½]

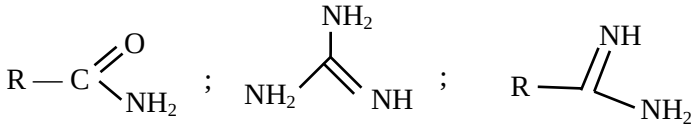


8. a) Sulphonation of naphthalene at 80°C gives naphthalene-1-sulphonic acid as the major product, while at 160°C the major product is naphthalene-2-sulphonic acid. Explain with a suitable energy profile diagram. [3]

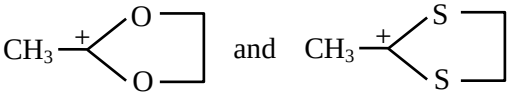
b) Arrange with reason the following ions in order of increasing stability. [1½]



c) Compare the base strength of the following compounds. [2½]



d) Compare stabilities between the following pair of ions [3]

i) 

ii)