RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

FIRST YEAR

B.A./B.SC. SECOND SEMESTER (January – June) 2013

Mid-Semester Examination, March 2013

Date : 04/03/2013 **CHEMISTRY (Honours)**

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

[Use Separate Answer Books for each group]

Group – A

(*Answer **any one** question*)

1. a) The ΔH_f of CaF is negative yet we always get CaF_2 during preparation of calcium fluoride from calcium and fluorine. [2]

   ΔH_S of Ca = 210; Lattice energy of CaF = –795; I_1 of Ca = 590; ΔH_D of F_2 = 160; ΔH_{EA} of Cl_2 = –335; ΔH_f of $CaF_2(S)$ = –1243 [All data are in KJ mol^{-1}]

   b) Comment on the hydration energy of F^- and K^+ ion (Both have similar ionic radii) [2]

   c) Establish the Born-Haber cycle for the formation of $NH_4Cl(c)$ from N_2, H_2 and Cl_2. [1]

   d) Carry out the valence bond treatment on H_2. **Or,** Write notes on Resonance and delocalisation. [4]

   e) What are the limitations of the concept of Resonance in VBT. [1]

   f) Explain the following (**any four**) : [4×2]

      i) Lithium does not form alum

      ii) Lithium is sometimes referred to as super alkali metal.

      iii) CsF is more soluble in water than LiF

      iv) Alkali metals are good reducing agents

      v) Alkali metals soluble in liquid ammonia are very useful reagents.

      vi) Alkali metals form Crown ether complexes more easily than alkaline earth metals.

2. a) Explain the higher electrode potential (reduction) of $\frac{1}{2}F_2|F^-$ couple (E° = 2·87 V) than that of $\frac{1}{2}Cl_2\,|\,Cl^-$ couple (E° = 1·33 V) though electron affinity of chlorine is greater than fluorine. [2]

   b) Arrange in the increasing order and explain the solubility of phosphate and perchlorate salt of lithium, sodium and potassium. [2]

   c) Explain the solubility and insolubility of an ionic solute in water in terms of free energy change, heat of solution at infinite dilute solution and entropy change. [2]

   d) Mention the hybridisation of $BeCl_2$ and BF_3. [2]

   e) What do you mean that the resonance energy of CO_2 is 154 KJ mol^{-1}? [2]

   f) Answer **any two** from the followings : [2×4]

      A. Why ortho and para hydrogen is known as nuclear spin isomers? Compare and contrast the properties of ortho and para hydrogen.

      B. Write a short note on Hydrides.

      C. i) Why the alkali metals have very little tendency to form complex compounds.

         ii) Write note on Heavy water.

      D. What happens when (**any two**) :

         i) Sodium ferro cyaride reacts ferric sulphate.

         ii) Sodium sulphide reacts with sodium nitroprusside.

         iii) Sodium thiosulphate solution is added separately to $AgNO_3$ and $FeCl_3$ solution.

Group – B

(*Answer **any one** question*)

3. a) i) Convert (S) – 2 – pentanol to (R) – 2 – pentanol [2]

ii) Explain what is meant by primary kinetic isotope effect. Give the mechanism of oxidation of 2-propanol with chromic acid. Indicate whether kinetic isotope effect is operative here. Cite a labelling experiment and its result in favour of your answer. [4]

iii) The reaction rate of CH_3I with NaN_3 at 0°C increased several fold on transfer from methanol to DMF as solvent. —Explain [2]

b) Complete the following reactions and give mechanism in each case and mention stereochemistry of products (if any) : [2×2]

i) cis – 1,2 – dimethylcyclohexene + H_2 $\xrightarrow[1\text{atm}]{\text{Pt, heat}}$

ii) cyclohexene $\xrightarrow[25°C]{Br_2/CH_2Cl_2}$

c) Give the product for each of the following reaction with reason : [2×2]

i) $F_3C-CH=CH_2+HCl\rightarrow$

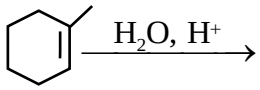
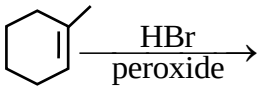
ii) $MeO-CH=CH_2+HCl(aq)\rightarrow$

4. a) List the carbocations in order of decreasing stability [2]

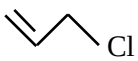
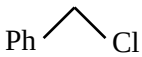
$CH_3CH_2\overset{+}{C}(CH_3)CH_3$; $CH_3CH_2CH_2\overset{+}{C}H_2$; $CH_3CH_2\overset{+}{C}HCH_3$

b) What alkene should be used to synthesize 3-bromohexane? Give reason. [2]

c) Give the major product of each of the following reactions and give their mechanisms. [2×2]

i)  ii) 

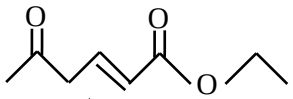
d) i) Comment on the following S_N^2 reaction rate with I^-. [2·5]

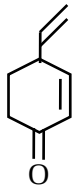
alkyl chloride	relative rate
	0·02
	79
	200

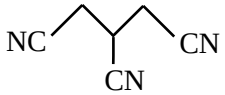
ii) Predict the product of the following reaction showing mechanism : [2·5]

(R) – α – phenylethanol $\xrightarrow[\text{ether}]{SOCl_2}$

iii) Give the IUPAC nomenclature of the following compounds : [3]

A. 

B. 

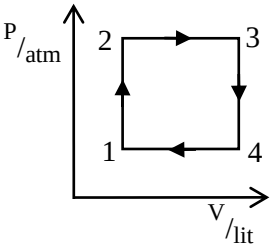
C. 

Group – C

(*Attempt all questions*)

5. a) 'Heat engine and refrigerator are acting in the reverse manner.' Justify this describing the working principle of both (outline). [2]

   b) The working of a heat engine is shown as follows



   If the working substance in the engine is 1·00 mol of a monatomic ideal gas and the cycle begins at 1 and goes clockwise, [Given, $P_1 = 1{\cdot}00$ atm, $V_1 = 24{\cdot}6$ lit, $P_2 = 2{\cdot}00$ atm and $V_3 = 49{\cdot}2$ lit]

   i) Calculate the work available in a complete cycle. [2]

   ii) Also indicate which parts of the cycle involve heat flows into the gas and calculate the efficiency of the engine in one cycle. [1+2]

   c) What is 'Clausius inequality'? State its implication. [1]

Or

6. a) Derive the expression for the efficiency of a Carnot engine directly from a TS diagram. [2]

   b) One mole of an ideal gas at 300K is isothermally compressed by a constant external pressure equal to the final pressure maintained in 10·0 Lit. vol. Initial pressure was due to volume 25·0 Lit. The temperature of the surroundings in 300K. Calculate $(\Delta S)_{sys}$, $(\Delta S)_{surr}$ and $(\Delta S)_{universe}$. Comment on the spontaneity of the process. [3+1]

   c) Comment and explain in favour of your answer —Two adiabatic curves donot cross each other. [2]

7. a) A radiation of wave length λ is incident upon a metal surface. The wave length of the scattered radiation is λ'. Prove that $\lambda' - \lambda = \frac{h}{m_e C}(1-\cos\theta)$ where θ is the angle of scattering. [5]

   b) Explain whether the following functions could be considered as 'well behaved wave-function' for Schrodinger equation :

   i) $\psi(x) = e^{-|x|}$

   ii) $\psi(x) = A\sin\alpha x$ in the range $0<x<L$ [1½×2]

Or

8. a) Explain the physical significance of $|\psi^*(x,t)\psi(x,t)|$ [1]

   b) Show that $\int_{-\infty}^{+\infty} \psi^*(x,t)\psi(x,t)dx$ is independent of time. [4]

   c) What do you mean by 'normalization condition of a wave-function. [1]

   d) Normalize the wave function given by, $\psi(x,t) = \sin\frac{n\pi x}{L}e^{-i\omega t}$ in the range $0 < x < L$

   [$n \rightarrow$ integer, $L, \omega \rightarrow$ constants] [2]