RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

FIRST YEAR

B.A./B.SC. SECOND SEMESTER (January – June) 2014

Mid-Semester Examination, March 2014

Date : 24/03/2014 **CHEMISTRY (Honours)**

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

[Use a separate Answer Book for each group]

Group – A

(*Attempt **all** questions*)

1. a) Show the followings : (**any one**) [3]

   i) $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

   ii) $C_P - C_V = \frac{\alpha^2 VT}{\beta}$

   b) Carnot cycle is a very standard cycle in texts, normally plotted in P vs V axis. Plot the same cycle in S vs T axis. [1]

   c) An ideal operative Carnot cycle operates on a temp. dif. of 200°C and one-third of the heat absorbed at the higher temp., T_2, is wasted as heat discharged at the lower temp., T_1. The cycle does 400J of work. Calculate q_1, q_2, T_1 and T_2. [2]

   d) Show what percent T_1 is of T_2 for a heat engine whose ideal efficiency is 10%. [2]

   Or,

   a) Derive from the 1st and 2nd laws and related definitions $\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}$. [3]

   b) 1 mole of a perfect monatomic gas initially at vol. v_1 = 5 liter, pressure, P_1 and temperature, T_1 = 298 K experiences the following reversible changes, (i) isothermal compression to one half of vol. with new pressure, P_2. (ii) cooling at const. vol., until the pressure is returned to original pressure is retained, the final temp. being T_2.

   Calculate P_1, P_2, T_2. Also calculate ΔH and ΔS for two processes. [5]

2. a) If a source of 58·5nm wavelength photons irradiates a sample of neutral hydrogen atoms, it is possible to eject electrons from the atoms and generate protons. The most stable H atoms (gr. st.) bind the electrons with about 13·6 ev of energy. Use energy conservation to deduce the K.E of photoejected electron. If you were trying to measure K.E. with P.E instrument, what stopping voltage would you need to apply? [3]

   b) A typical value for a particle's K.E. at 25°C is $6{\cdot}21\times10^{-21}$J. Use this value of K.E. to estimate the speed of spheres with dif. mass— i) ping pong ball (2·60 gm)
   ii) Buckminister fullerene (C_{60}) (0·720 Kg/mol)

   Comment on the different results. [3]

   c) If α, β, γ are linear operators, prove that $[\alpha,[\beta,\gamma]]+[\beta,[\gamma,\alpha]]+[\gamma,(\alpha,\beta]] = 0$. [2]

   Or,

   a) Complete the followings : [2×2]

   i) $[H, p_x] = -i\hbar F$, show this

   ii) $[x^n, p_x] = ?$

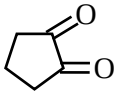
   b) Describe an experiment other than P.E effect which demonstrates the particle nature of light. Comment on the invariance of the result w.r.t. the source of light used. [2+1]

c) In particle in 1D box problem, $\Delta E = E_2 - E_1$ is not an arbitrary value rather quantized. —Explain. [1]

Group – B

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

3. a) Which one of the following two compounds has higher enol content and why? [2]

$CH_3COCOCH_3$, 

b) Comment on the fact that phloroglucinol but not phenol reacts with hydroxylamine to give oxime. [2]

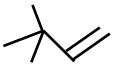
c) Carry out the following conversion : [4]

(R)-2-butanol $\longrightarrow$ (S)-2-butanol

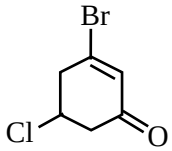
d) Complete the following reactions and give mechanism in each case.

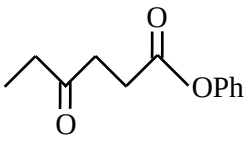
i)  $+Br_2 \xrightarrow{CCl_4}$

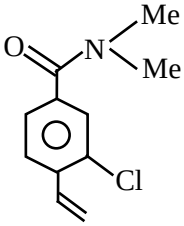
ii) $F_3C-CH=CH_2 + HCl \rightarrow$

iii)  $+HCl(aq) \xrightarrow{\text{nitromethane}}$ [3+2+3]

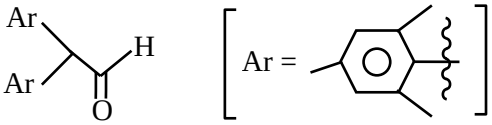
4. a) Write the IUPAC name of the following compounds : [4½]

i) 

ii) 

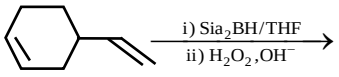
iii) 

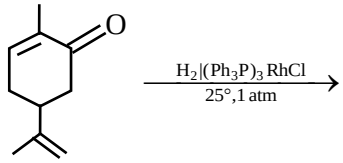
b) Comment on the enol content of the following compound : [1½]



c) Give a S_N^2 reaction which is attended by racemisation. [2]

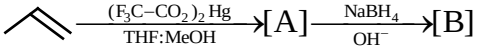
d) Give the product for each of following reactions with explanation :

i) 

ii) 

[2×2]

e) The peroxide effect is usually observed only for HBr addition, not for HCl and HI —why? [2]

f) Write the structures of [A] and [B] :  [2]

Group - C

5. Explain the shape of the following :

a) $SbCl_6^-$ b) XeF_6 c) BH_4^- d) ClF_3 [4×1½]

Or,

a) Explain the bond angle in the series : $\overset{+}{N}O_2$ (180°), NO_2(132°), NO_2^-(115°) [2½]

b) Predict the shape of— i) $\overset{+}{C}F_3$ ii) $SOCl_2$ [1+1]

c) Explain with reasons the position of lone pair(s) in TBP stereochemistry. [1½]

6. a) The calculated Lattice energy obtained from Born-Lande equation and the the experimental Lattice energy is not always in good agreement. —Explain [2½]

b) Why the Madelung constant (A) is different for different geometry of the crystal? —Comment on. [2]

c) Calculate the Lattice energy of sodium chloride using the following data. A = 1·748; r_0 = 2·79Å; electronic charge = $4{\cdot}8\times10^{-10}$ e.s.u. [1½]

Or,

a) E^o of $\frac{1}{2}F_2 \mid F^- = 2{\cdot}87v$; E^o of $\frac{1}{2}Cl_2 \mid Cl^- = 1{\cdot}33v$, yet the electron affinity of Cl_2 is greater then F_2. Explain. [2]

b) $\frac{r+}{r-}$ for LiCl is 0·33. From this value comment about the predicted and the observed structure of LiCl. [2]

c) Explain the solubility of $MgSO_4$, $CaSO_4$, $SrSO_4$ and $BaSO_4$ with respect to the size of cation and anion. [2]

7. a) How can you extract Beryllium from one of its important occurances (with name and composition). [3]

b) Write notes on Beryllium complexes. [3]

Or

a) Write anomalons behaviour of Lithium with other alkali metals. [2]

b) Write notes on Hydrides. [2]

c) Write a short note on (**<u>any one</u>**) [2]

i) Zintil Salts ii) Crown-ether complexes