RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

FIRST YEAR

B.A./B.Sc. SECOND SEMESTER (January – June) 2015

Mid-Semester Examination, March 2015

Date : 18/03/2015 **CHEMISTRY (Honours)**

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

[Use a separate answer book for each group]

Group – A

Attempt any one question : [1×8]

1. a) The efficiency of a reversible engine which uses ideal gas as its working substance is found to be 0·156. What will be the same for a hypothetical diesel engine that also runs reversibly, working between the same two temperatures as the earlier one. How would you justify your answer? (no derivation required) [1+1]

   b) For a reversible engine working between the two temperatures T_1 and T_2 who have the relation $\frac{q_1}{T_1}+\frac{q_2}{T_2}=0$ (q_1, q_2 $\rightarrow$heat withdrawn at temperatures T_1 & T_2). Prove that for a reversible cycle involving temperature reservoirs T_1, T_2, T_3 ... T_n, $\sum_{i=1}^{n}\frac{q_i}{T_i}=0$. [4]

   c) Prove that for an isoentropic, isovolume process $\Delta E = W_{av}$ (work other than pressure volume). [2]

2. a) What is the thermodynamic definition of entropy? [1]

   b) Show that $S_B - S_A > \sum_i \frac{q_i}{T_i}$ where q_i's are the quantities of heat withdrawn at temperature reservoirs T_is when a change of state from A to B takes place irreversible. [3]

   c) Calculate the entropy change when a system consists of 1 mole of an ideal gas at initial state (P_i, T_i, V_i) is taken to the final state (P_f,, T_f, V_f). [2]

   d) Calculate the molar entropy change for melting of ice at normal atmospheric pressure. (latent heat of melting of ice = 80 calsgm^{-1}). [2]

Attempt any one question : [1×8]

3. Answer **any four** questions : [4×2]

   a) What is ultraviolet catastrophe? Show it in the proper spectral density vs. freq. (wavelength) curve.

   b) Arrive at the Rayleigh-Jeans law from Planck's Black body radiation law.

   c) Write down the momentum conservation equations in Compton experiment, when $\theta = 90°$.

   d) What is Compton wavelength? Find out the condition for maximum Compton shift.

   e) Time-energy uncertainty relation is not truly an uncertainty relation. Comment on it.

   f) How does one justify the Bohr's quantization rule from de Broglie relation?

4. a) de Broglie hypothesis can successfully explain the particle in 1D problem. How? Arrive at the energy expression. [3]

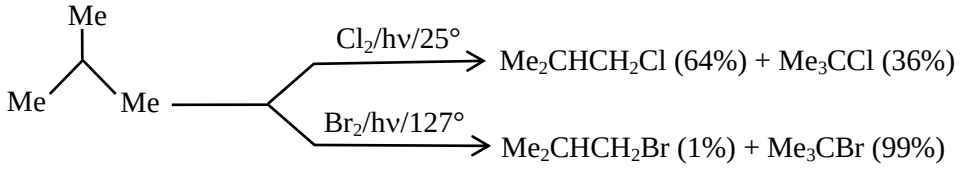
   b) Compare the wavelength for a thermal neutron ($m_n = 1{\cdot}67\times10^{-27}$kg) and a dust particle of mass 10^{-15}kg and speed v = 1 mm/sec at 300 K. Comment on the quantum nature of these particles. [3]

   c) The speed of a bullet (m = 50 gm) is measured at 300 m/sec, with an uncertainty of 0·01%. With what fundamental accuracy could we have located the position of it. [2]

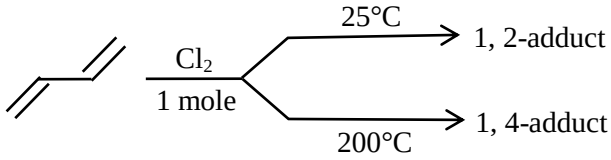
Group – B

Attempt <u>any one</u> question : [1×16]

5. a) Explain the result of following reactions on the basis of reactivity/selectivity principle. Give mechanism. [4]



b) Explain the following observation by suitable energy profile diagram. [4]

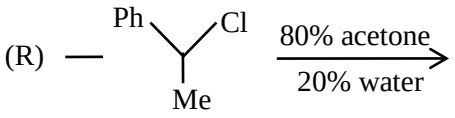


c) When the solvent polarity is increased the rate of the following S_N2 reaction is reduced slightly

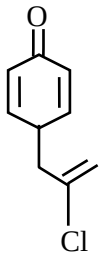
$HO^{(-)} + CH_3OSO_2Ph \rightarrow CH_3OH + PhSO_3^{(-)}$

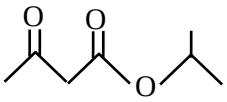
on the other hand the reaction between Me_3N and MeI is accelerated in polar solvent. Explain the above observation. [3]

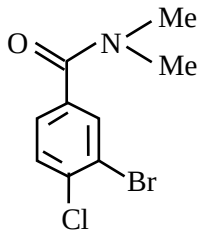
d) Predict the product(s) of the following reaction and explain their formation. [2]



e) Give IUPAC name of the following compounds : [3]

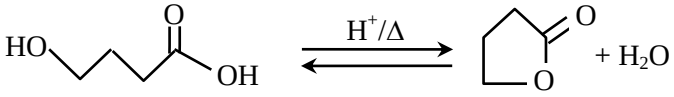
i) 

ii) 

iii) 

6. a) Compare the equilibrium constant values of the following reactions at 298K. Explain your answer. [2]

i) $CH_3CO_2H + C_2H_5OH \underset{}{\overset{H^+/\Delta}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$

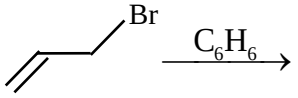
ii) 

b) What do you mean by Primary kinetic isotope effect? Nitration of benzene with mixed acid does not show PKIE but iodination of phenol in alkali shows though both the reactions belong to electrophilic aromatic substitution —Explain. [4]

c) 2, 6-Di-t—butylpyridine is a better scavanger than pyridine —Explain. [2]

d) Predict the major product of the following reactions. Explain your answer. [2+2]

i) (R) – 1 – Phynylethanol $\xrightarrow[\text{Pyridine}]{SOCl_2}$

ii) PhO^-Na^+ + 

e) Carry out the following coversion : [2]

(R) – 2 – chlorobutane → (S) – 2 – chlorobutane

f) Compare the nucleophilicity of $PhS^{(-)}$ and $PhO^{(-)}$ in DMSO. [2]

Group – C

Attempt <u>any one</u> question : [1×9]

7. a) Compare alkaline earth metals with respect to their physical properties. [3]
   b) How can you detect the presence of Mg^{2+} ion chemically? Give the balanced equation. [2]
   c) Compare and justify the melting points of Zn, Cd and Hg. [2]
   d) Though Cu, Ag and Au are same subgroup elements with similar outer electronic configuration however with different stable oxidation state. —Explain. [2]

8. a) What do you mean by—
      i) Purple of Cassious
      ii) Fulminating gold
      iii) Calomel [3]
   b) Write down the peculiarities of Mercury. [2]
   c) Answer **<u>any two</u>** : [2×2]
      i) Gold is soluble in one single acid write with proper equation.
      ii) What happens when sodium chloride is added to zinc uranyl acetate in acetic acid medium?
      iii) What happens when excess KI solution is added to a solution of mercuric chloride solution?

Attempt <u>any one</u> question : [1×9]

9. a) Describe how Heitler & London improved the idea of valence bond theory. [3]
   b) Derive the expressions for Wave functions arising out of sp hybridisation.
      Given the angular part for $\Psi_{2S} = \frac{1}{2\sqrt{\pi}}$ and for $\Psi_{2p_z} = \frac{\sqrt{3}}{2\sqrt{\pi}}\cos\theta$. [3]
   c) NMR of $P^{19}F_5$ exhibits one doublet at temperature above –22°C but two doublets at temperature below –143°C. Justify. [3]

10. a) Show that the process of sp hybridisation in carbon needs 850 $KJmol^{-1}$.
      Given, $E_{2s} = -1878\,KJmol^{-1}$, $E_{2p_x} = -1028\,KJmol^{-1}$. [3]
   b) Illustrate with examples how hybridised orbitals may become non-equivalent. [3]
   c) $\angle$<u>HOH</u> angle in water is $104°28'$. Calculate the angle between lone pairs. [3]

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