RAMAKRISHNA MISSION VIDYAMANDIRA

(A Residential Autonomous College under University of Calcutta)

First Year, Second Semester (January – June), 2011
Mid-Semester Examination, March, 2011

CHEMISTRY (Honours)

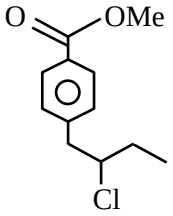
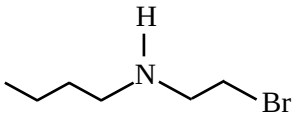
Date : 9 March 2011 Full Marks : 50
Time : 11am – 1pm

(Use separate answer script for each group)

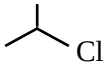
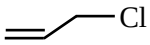
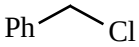
Group – A

Answer any three questions :

1. a) Write the IUPAC name of the following compounds :

i)  ; ii) 

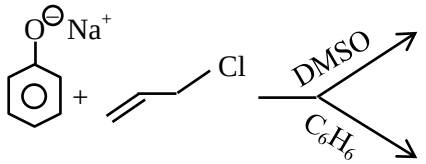
b) Comment on the following S_N2 reaction rate with $I^{\ominus}$

alkyl chloride	relative rate
	0·02
	79
	200

[2+3]

2. a) Cite an example of a S_N2 reaction which is attended by racemisation. On the basis of the result how would you proceed to draw the conclusion regarding the stereochemistry of S_N2 reaction.

b) Predict the major product of the following reactions :



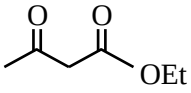
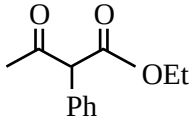
c) Comment on the relative nucleophilicity of RS^- and RO^-. [2+2+1]

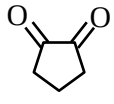
3. a) Carry out the following conversion :

(R) - 2-butanol ⟶ (S) - 2-butanol

b) Write the structures of keto and stable enol forms of 2,4-pentanedione. The enol content of this dicarbonyl compound is 92% in n-hexane and 15% in water— Explain. [3+2]

4. a) Which one of the following pair has higher enol content? Justify your answer.

i)  and 

ii) $CH_3COCOCH_3$ and 

b) Give the structure of A

$CH_3CH = CH_2 + H^+ \longrightarrow A$ [(2+2)+1]

5. a) Between $H_3C^{\bullet}$ and $F_3C^{\bullet}$ which one is bent and why?

b) Cyclopropylmethyl cation is more stable than benzyl cation— explain.

c) What is state of hybridisation of the radical carbon in the following structure. [2+2+1]

Group – B

Answer <u>any four</u> questions :

6. a) Construct the correct Lewis structures of—
$[ONC^-]$ and $[NCO^-]$ and assign formal charges to each atom of each species.

b) Explain the solubility of $NaClO_4$ and $KClO_4$ in water. [3+2]

7. a) Write down the differences of Lithium with other alkali metals.

b) Sketch the box diagram and explain the bonding and hybridisation of carbonate ion. [3+2]

8. a) i) Arrange the increasing order of bond angle in NO^+, NO, NO^-

ii) Explain the structure of ClF_3 with the help of Bent's rule

b) K^+ and F^- have almost similar radii but which one posses higher hydration energy? Explain. [(1·5+1·5)+2]

9. a) Compare the alkali metals with respect to their physical properties.

b) CO_2 is linear but SO_2 is a bent molecule. Explain. [3+2]

10. a) Explain the solubility of covalent HCl compound in water thermodynamically and chemically. Ionisation energy of hydrogen is 1311 KJ mol^{-1}, electron affinity of chlorine is 348 KJ mol^{-1} Hydration energy of H^+ and Cl^- is 1091 and 381 KJ mol^{-1}.

b) i) Write down the uses of Lithium.

ii) How can you detect the presence potassium ion chemically with proper chemical equation. [3+(1+1)]

11. a) What do you mean by radius ratio and what information can be obtained from radius ratio.

b) Write notes on Covalent Hydrides. [3+2]

Group – C

Answer <u>any three</u> questions : [5+5 = 10]

12. a) Show that the two statements of 2nd law of thermodynamics - Kelvin Planck and Clausius are equivalent.

b) Give the molecular interpretation of entropy. [4+1]

13. a) What is efficiency of an engine?

b) 0·5 mole of an ideal monatomic gas initially at 5 atm. pressure and 0°C is allowed to expand against a constant external pressure of 0·5 atm. Conditions are such that the final volume is 10 times the initial volume; the final gas pressure equals the external pressure.

Calculate ω, ΔE, ΔH and ΔS for the process. [1+4]

14. a) An ideal gas is subjected to the following reversible cycle in the given steps :

Step I : Isobaric expansion, Step II : Adiabatic expansion,

Step III : Isobaric compression, Step IV : Adiabatic compression

Draw the TS diagram for the above cycle.

b) Show that if A undergoes two simultaneous reactions producing B and C according to $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$ then E_a, the observed activation energy for the disappearance of A is given by

$$E_a = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

where E_1, E_2 are the activation energies for the 1st and 2nd reactions, respectively. [2+3]

15. a) Consider the following reversible reaction, 1st order in both the reactions $A \underset{k-1}{\overset{R_1}{\rightleftharpoons}} B$

Derive that $(k_1 + k_{-1})t = \ln \frac{x_e}{x_e - x}$

b) What are the characteristics of a zero order reaction? [3+2]

16. a) Draw a rough energy profile diagram to distinguish kinetically and thermodynamically controlled product. Mention the activation energy and rate constants.

b) The reaction $A \rightarrow P$ gives a linear plot of $\frac{1}{[A]}$ vs. time, of intercept 100 lit mol^{-1} and slope 3×10^{-2} lit $mol^{-1}sec^{-1}$. What is the order of reaction? Calculate the $t_{1/2}$ of the reaction. [2+3]