

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

FIRST YEAR [BATCH 2016-19]

B.A./B.Sc. SECOND SEMESTER (January – June) 2017

Mid-Semester Examination, March 2017

Date : 15/03/2017

Time : 11 am– 1 pm

CHEMISTRY (Honours)

Paper : II

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

[Attempt one question from each Unit]

Unit - I

[8]

1. a) The following rate data are found for gas phase reaction $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$.

	$P^0(\text{H}_2)$ (mm Hg)	$P^0(\text{N}_2)$ (mm Hg)	$-d[P_{\text{tot}}]/dt$ (mm Hg Hr ⁻¹)
Set 1	100	1.00	0.01
Set 2	200	1.00	0.04
Set 3	400	0.5	0.08

[P^0 being the initial pressure]

i) For the rate law, rate = $k[P(\text{H}_2)]^x[P(\text{N}_2)]^y$, find x and y.

ii) Calculate $d[P(\text{N}_2)]/dt$ for set 1 and time for $P(\text{N}_2)$ to drop to 0.05 for the same set.

[4]

- b) For a 1st order reaction, show that $t_{1/n}$ is proportional to 'n'. $t_{1/n}$ is the time for [A], reactant, to decrease from $[A]_0$ to $\frac{1}{n}[A]_0$.

[2]

- c) Determination of order using differential method can be disturbed if the reaction is a catalytic one. Justify.

[2]

2. a) The reaction $n-\text{C}_3\text{H}_7\text{Br} + \text{S}_2\text{O}_3^{-2} \rightarrow \text{C}_3\text{H}_7\text{S}_2\text{O}_3^{-1} + \text{Br}^{-1}$ in aq. solution is 1st order with both $\text{S}_2\text{O}_3^{-2}$ and $\text{C}_3\text{H}_7\text{Br}$. At 37.5°C the following data are obtained.

$10^3[\text{S}_2\text{O}_3^{-2}]$	96.6	90.4	86.3	76.6	66.8
t/ks	0	1.11	2.01	5.05	11.23

The initial concentration $\text{C}_3\text{H}_7\text{Br}$ was 39.5 m mol/cm³. Find the rate constant.

[3]

- b) For a 1st order opposing reaction, between A and A₂, find the integrated rate law in terms of x_e , where x_e is the amount of A₂ at equilibrium. [A = anthracene].

[3]

- c) True or False?

[0.5×4]

i) For an elementary reaction, the partial orders are determined by the reaction stoichiometry.

ii) Elementary reactions with molecularity greater than 3 don't occur, normally.

iii) KCP can never be TCP.

iv) Rate expression for the gaseous reaction is same to that in solutions.

Unit – II

[8]

3. a) With the help of a labelled schematic diagram prove that an engine with efficiency equal to one can be coupled with another engine to transfer heat spontaneously from low to high temperature.

[4]

- b) What is the maximum possible efficiency of a heat engine that has a hot reservoir of water boiling under high pressure at 125°C and a cold reservoir at 25°C?

[2]

- c) Starting with Clausius inequality argue that the entropy of the universe is ever increasing.

[2]

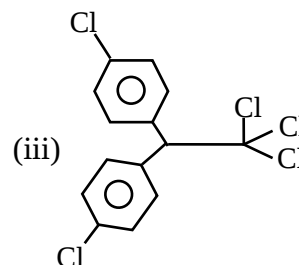
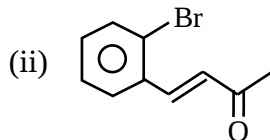
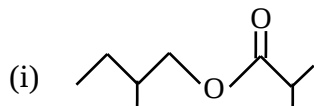
4. a) Write down the thermodynamic definition of entropy. [2]
 b) Prove that $dS > \frac{q}{T}$ for any irreversible process (Hint : For any irreversible cycle $\oint \frac{q}{T} < 0$) [2]
 c) Prove that $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa}$ [the terms have their usual significance] [4]

Group – B

(Answer any two questions)

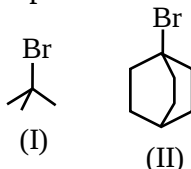
[2×8]

5. a) Put IUPAC name to each of the given structures :

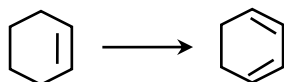


[3]

- b) Both the given compounds (I) and (II) are tertiary bromides, but (I) undergoes ethanolysis 10^6 times more rapidly than (II) — Explain. [2]

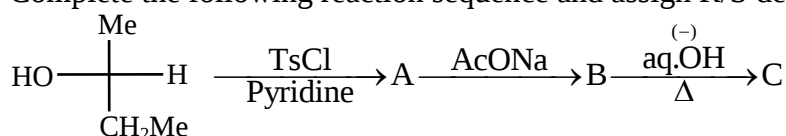


- c) State and explain, with an example, the principle of microscopic reversibility. [3]
6. a) Convert : [2]

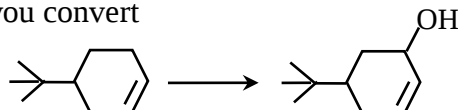


Cyclohexene Cyclohexa-1,3-diene

- b) How can you establish that direct displacement reaction takes place with inversion of configuration at the reaction centre? [3]
 c) Complete the following reaction sequence and assign R/S descriptor to each product [3]



7. a) How would you convert

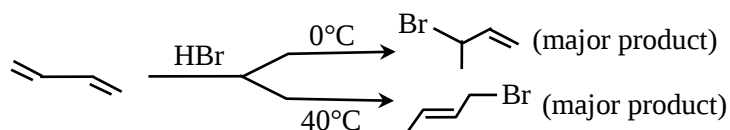


(Give mechanism and explain the reaction)

[3]

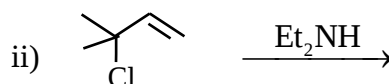
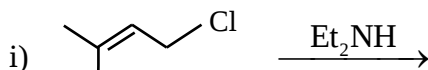
- b) Explain the following observation with an energy profile :

[3]

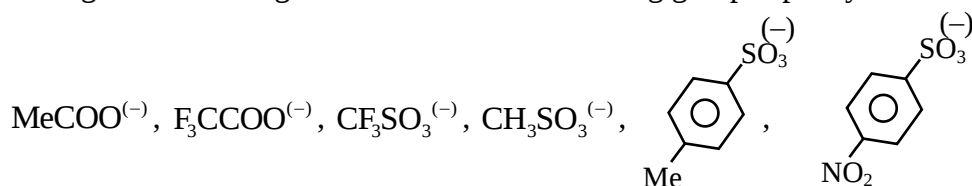


- c) Write down the major product with reason

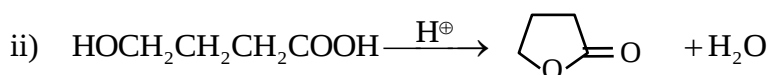
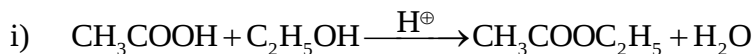
[2]

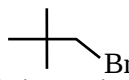


8. a) Arrange the following ions in order of their leaving group capacity : [2]

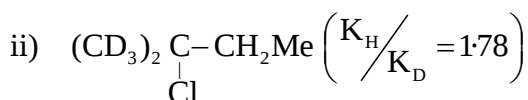
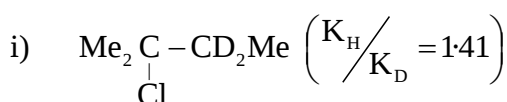


- b) The following two reactions are basically esterification reactions having nearly same ΔH value, but more of ester is obtained from the second reaction than the first reaction —explain [2]



- c)  (neopentyl bromide) is very much inert towards direct displacement reaction, though it is a primary halide —explain. [2]

- d) In the investigation of the mechanism of solvolysis (in 80% ETOH) of 2-chloro-2-methyl butane following results were obtained. [2]



Account for the above result

Group – C

[Attempt one question from each Unit]

Unit – I

[9]

9. a) Explain with reasons : [2×2]

- i) Magnesium does not impart any colour to flame, while calcium does.
 ii) Alkaline earth metals are harder, denser and have higher melting and boiling points than alkali metals.

- b) Discuss the structure of basic beryllium acetate. [2]

- c) Discuss the complexation reaction of alkali metal ions with crown ethers. [3]

10. a) Describe the diagonal relationship of beryllium with aluminium. [3]

- b) The heat of reaction for $\text{Li(solid)} + n\text{H}_2\text{O} \rightarrow \text{LiOH(soln)} + \frac{1}{2}\text{H}_2(\text{g})$ is -508.3 KJ/mol whereas it is -469.5 KJ/mol for the reaction $\text{Na(solid)} + n\text{H}_2\text{O} \rightarrow \text{NaOH(soln)} + \frac{1}{2}\text{H}_2(\text{g})$. Why is the reaction of lithium with water much less vigorous than that of sodium with water? [3]

- c) How is lithium extracted from its ore? [3]

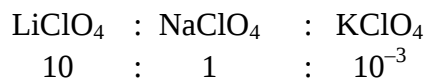
Unit – II

[9]

11. a) Explain the following :

- i) The thermal stability of gr.II metal carbonate— BeCO_3 (100°C), MgCO_3 (400°C), CaCO_3 (900°C), SrCO_3 (1290°C), BaCO_3 (1360°C) [2]

ii) The solubility of alkali metal perchlorate [2]



- b) SbCl_6^{3-} is regular octahedral where as XeF_6 is distorted octahedral, comment. [3]
- c) Electron affinity of chlorine is higher than fluorine but fluorine is much more oxidising explain. [2]
12. a) ZnO is yellow when hot but white when cold, comment. [2]
- b) Formation of divalent cations and anions are endothermic, yet MgO is a stable ionic solids, explain. [2]
- c) Calculate the limiting radius ratio for tetrahedral lattice (C.N.4) and comment. [2+1]
- d) What happens when Na vapour was passed through NaCl crystals. [2]

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