

EASTERN UNIVERSITY, SRI LANKA FIRST EXAMINATION IN SCIENCE - EXTERNAL DEGREE 1998/99 (Term System) Re-Repeat June - 2008 EXCH102 STEREO CHEMISTRY, ORGANIC REACTION MECHANISM

AND CHEMICAL KINETICS

TIME : 02 HOURS

ANSWER FOUR QUESTIONS ONLY. SELECTING AT LEAST ONE QUESTION FROM PART B.

PART A

- 1 (a) (i) What are the factors that determine the stability of the carbonium ions
 - (ii) Arrange the following carbonium ions in the order of increasing stability. Explain your answer.

Me₂CH⁺, Me₃C⁺, MeCH₂⁺

(b) Compare the stability of phenol and phenoxide ion.

(c) Draw all the resonance structures for the following compounds





2. a) (i) What is meant by S_N^{-1} and S_N^{-2} reactions.

(ii) The following reaction was considered to be first order.

(CH₃)₃CCI + OH → (CH₃)₃COH + CI

- (I) Give the mechanism involved in it.
- (II) Draw a fully labelled energy profile diagram for the above reaction. Indicate clearly the transition state and intermediate (if any).
- 3. a) Define the following terms.
 - i) Diastereo isomers.
 - ii) Enantiomers.

b) Indicate whether each of the following pairs of compounds is enantiomers, diastereo isomers, geometrical isomers or identical compounds.



- c) What is a racemic mixture? Explain with the help of a suitable example.
- d) Explain how you would separate a racemic mixture of CH₃OH into its pure form.

 $\frac{1}{2}$ 4. a) Giving reasons, specify the configurations of the following molecules as R or S.



b) Draw the chair conformations of trans 1,4 – dimethylcyclohexane and indicate with reasons which conformation would be the most stable.

- c) 0.3g of a compound is dissolved in ethanol to make a solution of 10 m. When this solution is placed in a 20 cm tube it showed an optical rotation of -4 12 at the sodium -D line at 25°C.
 - i) Calculate the specific rotation of this compound in ethanol at 25° C.
 - ii) If the concentration of this solution is doubled what would be the,
 - i) Optical rotation?
 - ii) Specific rotation?

PART B

- 5) (a) Define the rate law and order of the chemical reaction.
 - (b) Derive the first order rate equation to the reaction,

A product

- (c) Show that the half-life $(t_{1/2})$ for first order reaction is independent of the initial concentration.
- 6) a) Write down the assumptions made in deriving the equation for the kinetic molecular theory of gas.

b) Derive the equation $PV = \frac{1}{3} mNC^2$. Where,

m = mass of a molecule of gas.P = Pressure.

 C^2 = mean square velocity. N = no. of molecules of the gas. V = volume.

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c) Calculate the pressure exerted by 2.00 mole of ethane in a 200 ml container at 300K using Van der waals equation. What pressure will be predicted by the ideal gas equation? (a = 2.253 l^3 atm mol⁻², b= 0.04281 mol^{-1} , R = 0.0821 atm 1 mol⁻¹ K⁻¹)
