UNIVERSITY OF RUHUNA

HELOR OF SCIENCE GENERAL DEGREE LEVEL I (SEMESTER II)-REPEAT EXAMINATION – MARCH/APRIL 2019

ECT: CHEMISTRY

RSE UNIT: CHE 1214(Repeat) TIME : **Three (03)** hours

er six **(06)** questions only by selecting **one (01)** from section **A**, **three (3)** from section **B** wo **(2)** from section **C**.

Velocity of light, (c)	$= 2.997 \times 10^8$ m s $^{-1}$
Avagadro's number, (N_A)	$= 6.022 \times 10^{23}$ mol $^{-1}$
Universal Gas Constant, (R)	$= 8.314 \times$ J K^{-1} mol $^{-1}$
Boltzmann constant, (k_B)	$= 1.381 \times 10^{-23}$ J K $^{-1}$
Faraday constant, (F)	$= 9.6485 \times 10^4$ C mol $^{-1}$
Plank's constant, (h)	$= 6.626 \times 10^{-34}$ J s
Electron Charge, (e)	$= 1.602 \times 10^{-19}$ C
Proton mass, (m_p)	$= 1.673 \times 10^{-27}$ kg
Electron mass, (m_e)	$= 9.10 \times 10^{-31}$ kg
1 amu	$= 1.661 \times 10^{-27}$ kg
1 eV	$= 1.602 \times 10^{-19}$ J

Section – A

1. Answer **all** parts

) Define the term "hydrides" and describe briefly the major three types of hydrides.

(20 marks)

) Answer the following questions related to acid base theories.

(i) How are acids and bases defined according to the Bronsted-Lowry theory and Lewis theory?

(10 marks)

(ii) Arrange the following acids/bases in the decreasing order of their acidity/basicity. Briefly explain your answer.

(I) H_3PO_4, H_3BO_3, $HClO_4$, H_2CO_3

(II) $HClO_4$, $HClO$, $HClO_2$, $HClO_3$

(III) NH_3, NH_2NH_2, $MeNH_2$, NH_2OH

(30 marks)

c) Write balanced chemical equations for the following reactions:

(i) $BeCO_3(s) \xrightarrow{\Delta}$

(ii) $Ba(OH)_2(s) \xrightarrow{\Delta}$

(iii) $LiO_2(s) + H_2O(l) \rightarrow$ (15 marks)

d) Thermal stability of the following carbonates increases as follows: $Li_2CO_3 < Na_2CO_3 < CaCO_3 < BaCO_3$. Explain your answer.

(25 marks)

02. Answer **all** parts

a) Using the relevant chemistry, explain the following:

(i) BBr_3 is a stronger Lewis acid than BF_3

(ii) BH_3 easily dimerizes

(iii) NH_3 is a better electron donor than PH_3

(30 marks)

b) Draw the structures of the following molecules

(i) $B(OH)_3$

(ii) $[B_3O_3(OH)_4]^-$

(iii) PCl_5

(iv) $Na_2[B_4O_5(OH)_4].8H_2O$ (20 marks)

c) Explain why a sharp end point is not obtained for the titration of $B(OH)_3$ with NaOH. Suggest a method to overcome this problem.

(20 marks)

d) Explain the trend in atomic size (metallic and ionic radii) of group 13 elements shown in the table below.

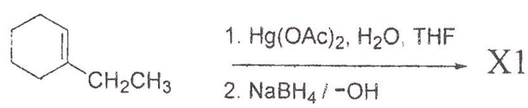
	Metallic radius (Å)	Ionic radius (Å)	
		M^{3+}(Å)	M^{+}(Å)
B	(0.885)*	-	-
Al	1.43	0.535	-
Ga	(1.225)*	0.620	1.20
In	1.67	0.800	1.40
Tl	1.70	0.885	1.50

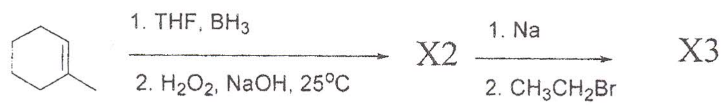
(30 marks)

Section – B

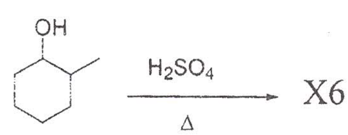
03. Answer **all** parts

a) Predict the major product(**X1-X6**) of the following reactions. Include stereochemistry where appropriate.

(i) 

(ii) 

(iii) $HC\equiv CH \xrightarrow[2.\ 2\ CH_3(CH_2)_6Br]{1.\ 2\ NaNH_2} X4 \xrightarrow[\text{Lindlar Catalysts}]{H_2/Pd/H_2SO_4} X5$

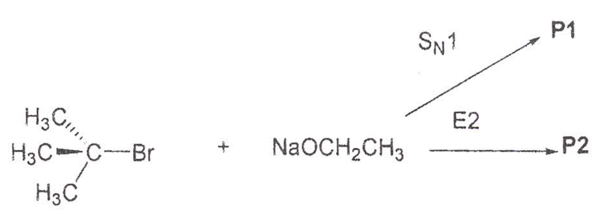
(iv) 

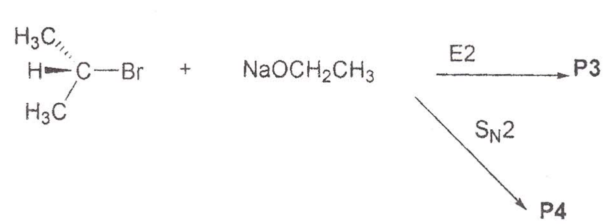
(30 marks)

b) Addition of HCl to 1,2-dimethylcyclohexene yields a mixture of two products. Draw the structures of each product indicating the stereochemistry. Explain why a mixture is formed.

(24 marks)

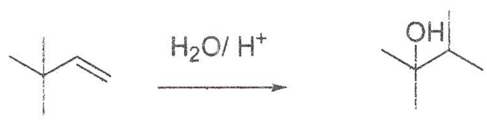
c) Giving emphasis to stereochemistry write down the products (P1-P4) of the following reactions.

(i) 

(ii) 

(28 marks)

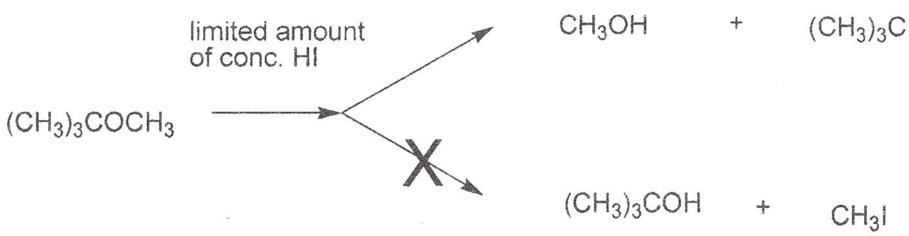
d) Propose plausible mechanisms for the following conversions.



(18 marks)

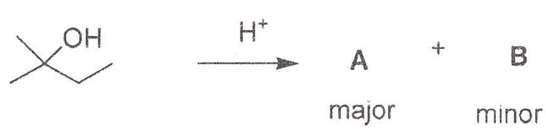
04. Answer **all** parts

a) Explain following observations



(20 marks)

b) (i) Draw the structures of the alkenes, **A** and **B** formed by acid catalyzed dehydration of the alcohol given in the following reaction.



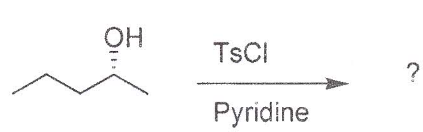
(ii) Write down the plausible mechanisms for formation of **A** & **B.**

(iii) Give reason for the prediction of the structure **A** as the major product.

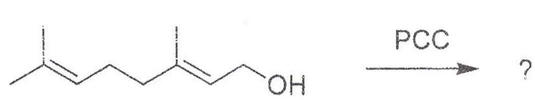
(30 marks)

c) Draw the structure(s) of the product that would be formed in the following reactions.

(i)

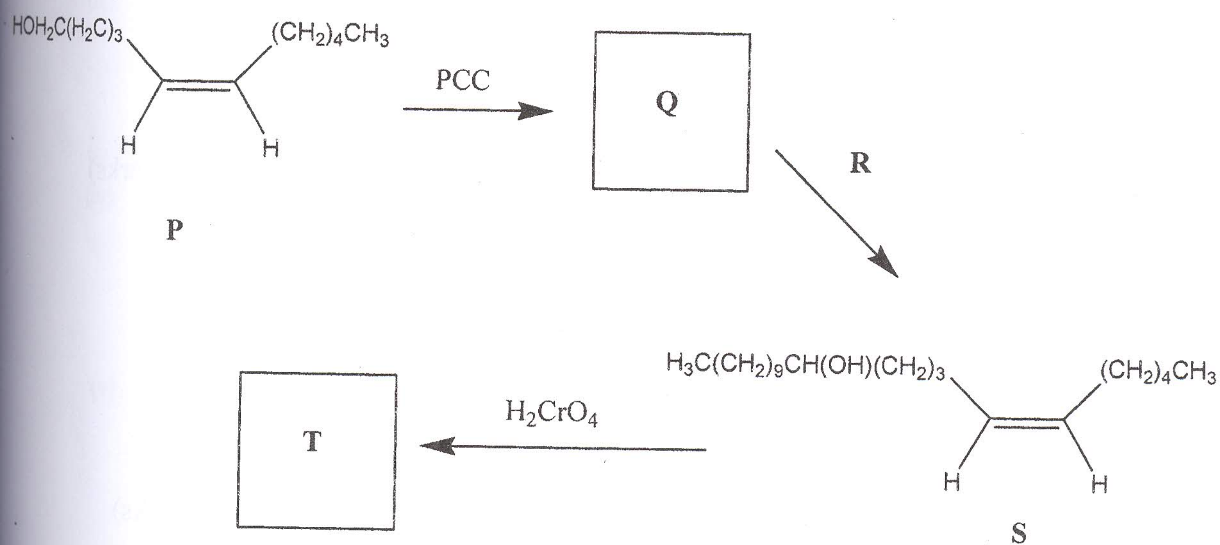


(ii)



(20 marks)

d) The sequence of the synthesis of compound **T** from the compound **P** is shown below.



(i) Deduce the structures of **Q** and **T**.

(ii) Write down the reagents **R** for converting **Q** to **S**.

(30 marks)

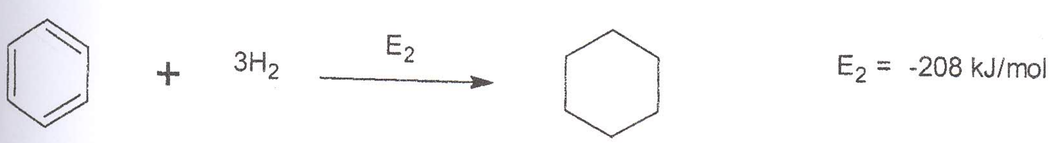
5. Answer **all** parts

(i) State two reactivity differences and structural differences of aliphatic polyenes and aromatic compounds.

(ii) What is meant by "resonance energy "of benzene. Explain your answer giving necessary structures.

(iii) Using hydrogenation energy of benzene and ethene given below, calculate the resonance energy of benzene.

$$H_2C{=}CH_2 \;+\; H_2 \xrightarrow{E_1} H_3C{-}CH_3 \qquad E_1 = -120 \text{ kJ/mol}$$



(30 marks)

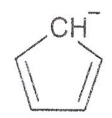
b) (i) With the help of Frost circle draw the energy diagram for π-molecular orbitals of benzene.

(ii) Fill the π-electrons to the energy levels in the above diagram drawn.

(iii) Justify the aromaticity of benzene using above diagrams.

(25 marks)

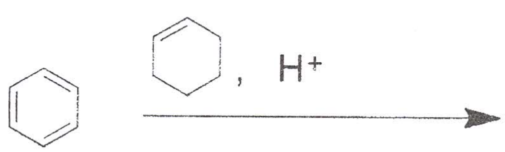
c) (i) Apply Huckel rule to show whether following ion is aromatic?



(ii) By drawing resonance structures, show the stability of above ion.

(15 arks)

d) Consider the following reaction and answer the questions (i) to (ii) given below.



(i) Write down the structure of the major product formed in the above reaction.

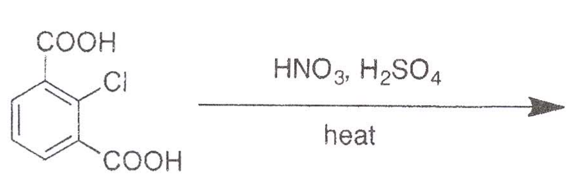
(ii) Outline a plausible mechanism for the formation of the product mentioned in (i).

(30 marks)

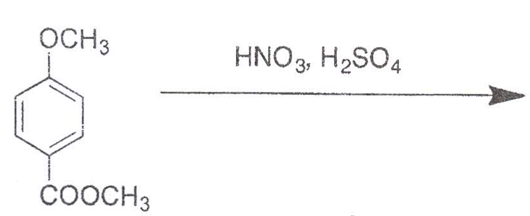
06. Answer **all** parts

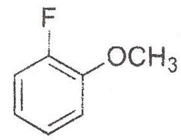
a) Give the major product(s) formed in each of the following reactions.

(i)

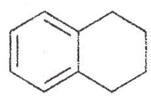


(ii)

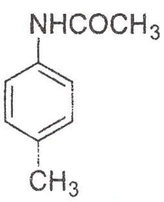


(iii) 

$\xrightarrow{CH_3COOCOCH_3,\ AlCl_3}$

(iv) 

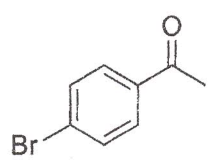
$\xrightarrow[H_2O]{KMnO_4}$

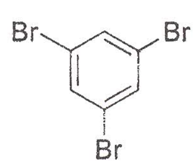
(v) 

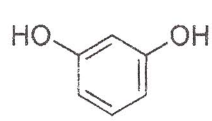
$\xrightarrow{Br_2,\ FeBr_3}$

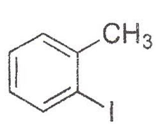
(20 marks)

b) Giving necessary reagents, reaction conditions and intermediates formed; show how you would synthesize following compounds from benzene.

(i) 

(ii) 

(iii) 

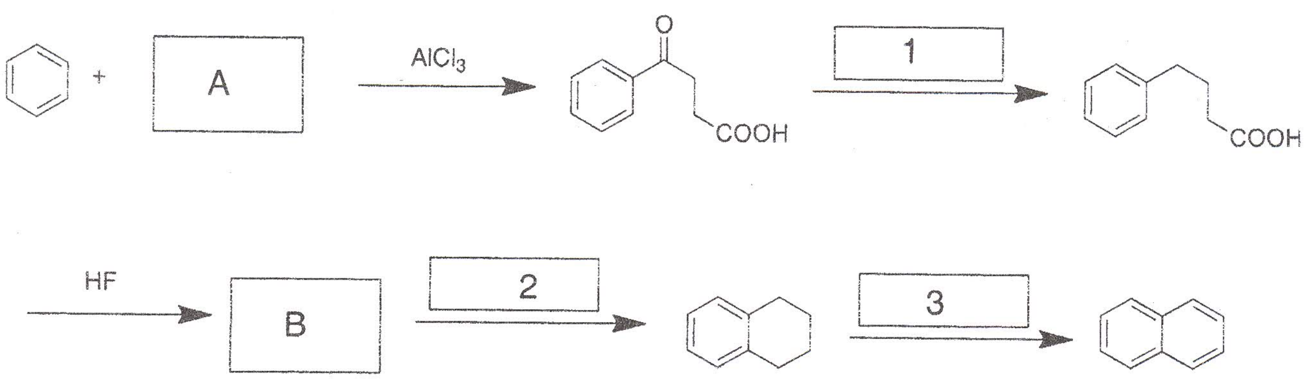
(iv) 

(40 marks)

c) Propose a plausible mechanism for the reaction given below. Be sure to use correct curved arrow notations and show all the intermediates.

(20 marks)

d) Reaction sequence for the Haworth synthesis of naphthalene is given below. Propose the structures of **A** and **B** and give the appropriate reagents and reaction conditions **1**, **2**, and **3**.



(20 marks)

Section – C

07. Answer **all** parts

a) First law of thermodynamics relates the internal energy to work performed and heat exchanged by the system with the surrounding.

(i) Write down the thermodynamic equations for work done by the system when reversible and irreversible expansions of an ideal gas take place at constant temperature from V_1 to V_2.

(20 marks)

(ii) Give the expression for the first law of thermodynamics with correct sign convention and name all the symbols in it.

(15 marks)

b) 2 moles of an ideal gas at 300 K and 6 atm pressure undergo expansion isothermally to half of its initial pressure.

(i) Calculate the work done by the system if the expansion was carried out irreversibly against zero external pressure.

(10 marks)

(ii) Calculate the work done by the system if the expansion was carried out irreversibly against 3 atm external pressure.
Hint: use pV =nRT to calculate the volume before and after the expansion.

(15 marks)

(iii) Calculate the work done by the system and surrounding if the expansion was carried out reversibly.

(20 marks)

(iv) Calculate the maximum heat exchange during this expansion.

(20 marks)

08. Answer **all** parts

a) Chemical reaction, A $\longrightarrow$ B, is found to be a first order reaction and the integrated rate law that relates the concentration to time is $ln[A] - ln[A]_0 = -k_1$t..

(i) Derive the equation for the half life ($t_{1/2}$) of the reaction. (15 marks)

(ii) Derive the equation for the relaxation time (τ). (15 marks)

(iii) The rate constant for the reaction at 10 $^{\circ}$C is 4.5×10^{3} s^{-1}. Calculate the relaxation time at this temperature.

(10 marks)

(iv) Relationship between rate constant and temperature is given by $\ln k(T) = \ln A - \frac{E_a}{RT}$
Here E_a is the activation energy and A is the Arrhenius constant. The rate constant for a reaction at 10 ^{0}C is 4.5×10^{3} s^{-1}. Calculate the temperature at which the half-life of the reaction is 6.93×10^{-5} s. The activation energy is 58 kJ mol^{-1} and it is independent of temperature. (30 marks)

b) The elementary chemical reaction by which reactants A and B yield the product P obey the rate law Rate = $k[A]^2[B]^3$.

(i) What is the stoichiometric ratio between the reactants A and B? (05 marks)

(ii) Express the rate of the reaction with respect to each species in the form of change in the concentration with time (in differential form, Rate = dx/dt). (05 marks)

(iii) How many transition states and intermediates does this reaction contain? (20 marks)

09. Answer **all** parts

a) (i) Distinguish between constituent and component pertaining to a system. (10 marks)

(ii) A gaseous mixture consists of CH_4, C_2H_6, C_3H_8 and H_2. If the amounts of these substances are related by the following independent chemical equations,

$$2CH_4\,(g) = C_2H_6\,(g) + H_2(g)$$
$$C_2H_6\,(g) + CH_4\,(g) = C_3H_8\,(g) + H_2\,(g)$$

Find the number of components of the system. (05 marks)

(iii) Write short accounts on the following characteristics pertaining to one component system at equilibrium.

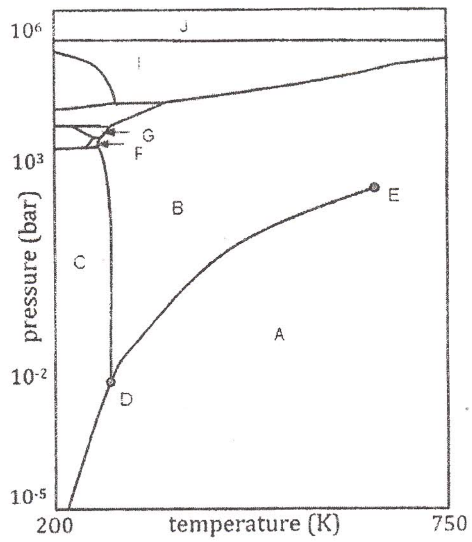
I. Critical point
II. Triple point

(15 marks)

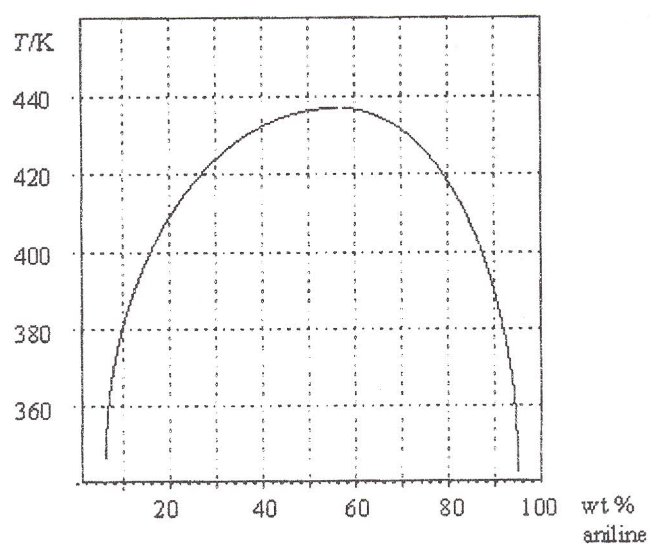
b) The schematic phase diagram of water is given below.

(i) Giving the phases in equilibrium, assign the areas, A, B, C, F, G, I and J, and the points, D and E. (18 marks)

(ii) Discuss briefly the anomalous behavior of water (Sketching of the diagram on your answer script is not expected. (14 marks)



c) Using the following miscibility diagram for aniline in water, answer the following questions.



(i) Write down the upper critical temperature of the aniline- water system.

(05 marks)

(ii) Give possible reason(s) for total miscibility of aniline in water at temperatures higher than the upper critical temperature.

(05 marks)

(iii) Estimate the ratio of the mass of the water-rich layer to that of the aniline-rich layer for 30 wt.% aniline in water at 400 K.

(13 marks)

(iv) What are the compositions of water-rich and aniline-rich layers in equilibrium mentioned in above (iii)?

(15 marks)

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