RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2019

SECOND YEAR (BATCH 2018-21)

Date : 11/12/2019 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm **Paper : III (Gr. A)** Full Marks : 40

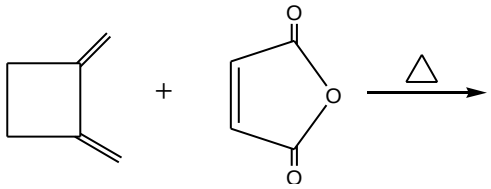
[Use one Answer Book for Unit –I and another Answer Book for Unit II & III]

(Attempt one question from each Unit)

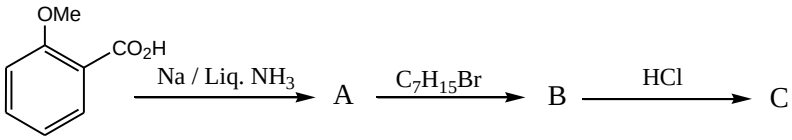
Unit-I

[15 marks]

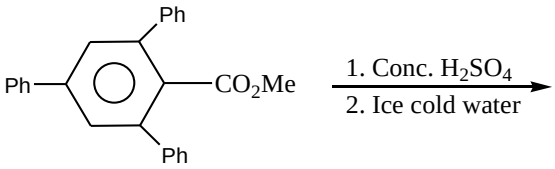
1. a) Predict the product of the following reaction and give explanation by FMO approach: [3]



b) Identify A, B and C with proper explanation. [3]

(i) 

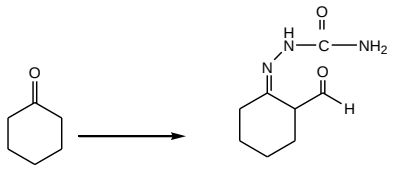
c) Predict the product of the following reaction with plausible mechanism. [3]



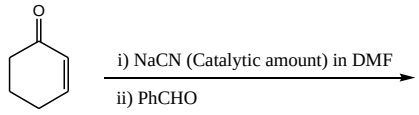
d) p-nitrobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde, the condensation does occur. Explain. [2]

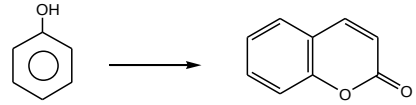
e) Use of excess active methylene compound is not recommended in knoevenagel reaction.- Explain. [2]

f) Convert: [2]

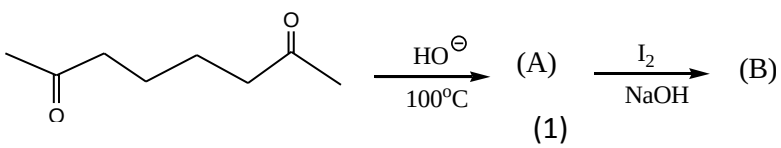


2. a) Write the product of the following reactions with explanation. [2+2]

(i) 

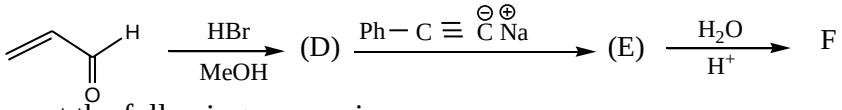
(ii) 

b) Write the structure of (A) to (F) in the following reactions: [6]

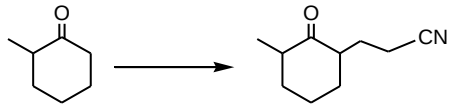
(i) 

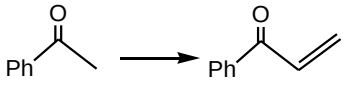
(1)

(ii) CH_3CHO (1 eq) + HCHO (4 eq) $\xrightarrow{HO^{\ominus}}$ C

(iii) 

c) Carry out the following conversions: [2½ × 2]

(i) 

(ii) 

Unit-II [12 marks]

3. a) We have L cc of water containing x_0 gms of a certain solute. This is to be washed with 'nV' cc of an organic solvent (immiscible with water). It can be done either by n successive extractions, each time with an amount V cc of solvent or by a single addition of nV cc of it. Derive the expression for x_n (the amount of solute which remains in water after the extraction is over for both the cases) in terms of x_0 and explain which of the above paths you would prefer if you want to get the water rid of maximum amount of organic solute. [3+2]

b) Starting with a suitable mathematical form for chemical potential derive the formula : $\left(\frac{\partial u_i}{\partial p}\right)_{T,N} = \bar{V}_i$, where all the symbols have their usual meaning. [2]

c) For the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ the standard Gibb's free energy of the reaction (ΔG^o) is -3.1 K cal_h at 25°C consider the transformation : where the partial pressure of H_2, I_2 and HI are 1 atmosphere each to a state where the partial pressure for H_2 is 0.1 atm, I_2 is 0.1 atm and HI is 2.8 atm. Is such a transformation spontaneous (if the temperature is maintained at 25°C throughout.) in the forward reaction? [3]

d) In the gaseous reaction $2A + B = A_2B, K_p = 3.35$. What total pressure could be necessary to produce a 60 % conversion (degree of conversion = 0.6) of B into A_2B when a mixture of A and B in the mole ration 2:1 be used. [2]

4. a) For Ozone at 25C, ΔG_f^0 = 163.2 kj/mol

i) Compute the equilibrium constant for the reaction : $3O_2(g) \rightleftharpoons 2O_3(g)$

ii) assuming that the advancement at equilibrium ξ is much smaller than unity show

$\xi = 1.5(P.K_p)^{1/2}$ the initial number of moles of O_2 be 3 and of O_3 be 0. [4]

b) Mention whether the quantities ξ and K_p in the above reaction change if (i) a different standard state is chosen (ii) pressure is measured in a different unit. [2]

c) For the reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ the value for K_c is 3.75×10^{-6} at 1069 K. Calculate K_p for this reaction at the same temperature. [2]

d) Determine, using suitable justification, how the equilibrium is affected for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ on addition of an inert gas to the reaction system, maintaining a constant system pressure. [2]

e) Depict, graphically, the variation of Gibbs free energy of a system, maintained at constant temperature and pressure, with the advancement of reaction under going in the system. [2]

Unit-III [13 marks]

5. a) A particle is confined to move in a two dimensional rectangular box having dimension $L_x = 2L_y$. Give the expression for the 1st three energy levels and the corresponding wave function. Comment on the degeneracy for ψ_{21} and ψ_{12}. [3+1]

b) A system is represented by a function ψ

$$\psi = \frac{1}{\sqrt{3}}\varphi_1 + \sqrt{\frac{2}{3}}\varphi_2$$

where φ_1 and φ_2 are orthonormal. What is the probability of getting the energy E_1 as the eigenvalue of φ_1 if a single measurement is made? [3]

c) Justify using the Heisenberg uncertainly principle that an electron $\left(m_e = 9.11\times10^{-31} kg\right)$ cannot be confined in the nucleus of an atom (assume size of a nuclei $\sim 10^{-15} m$). [2]

d) Prove that the set of function $\psi_n(x) = (2a)^{-1/2}\ e^{i\pi nx/a}$ for $n = 0, \pm1, \pm2$ are orthonormal over the interval $-a \le x \le a$. [2]

e) What was the units, if any, for the wave function of particle in a one-dimensional box. Justify your answer in brief. [2]

6. a) Determine whether the following operators are linear or not :

$(i)\ \hat{A}f(x) = \left(f(x)\right)^{-1/2}$; $\hat{A}f(x) = x^2 f(x)$. [2]

b) Determine the average position of a particle confined in a square of edge length 'a'. [2]

c) (i) Show that if the two linear operations $\hat{A}$ and $\hat{B}$ have the same complete set of eigen function, [A,B] = 0 [2]

(ii) Find $\left[\hat{H}, \hat{P}_x\right]$ for particle is one dimensional box with v(x) = constant. [2]

d) A certain system is describe by the operator

$$\hat{A} = -\frac{d^2}{dx^2} + x^2$$

(i) Show that $\psi = Cxe^{-x^2/2}$ is eigenfunction of $\hat{A}$,

(ii) Using normalization condition, find out C. [3]

e) Calculate the width of the spectral line resulting when an atom in an excited state of life time 10^{-10}S returns to the ground state. [2]

———— × ————