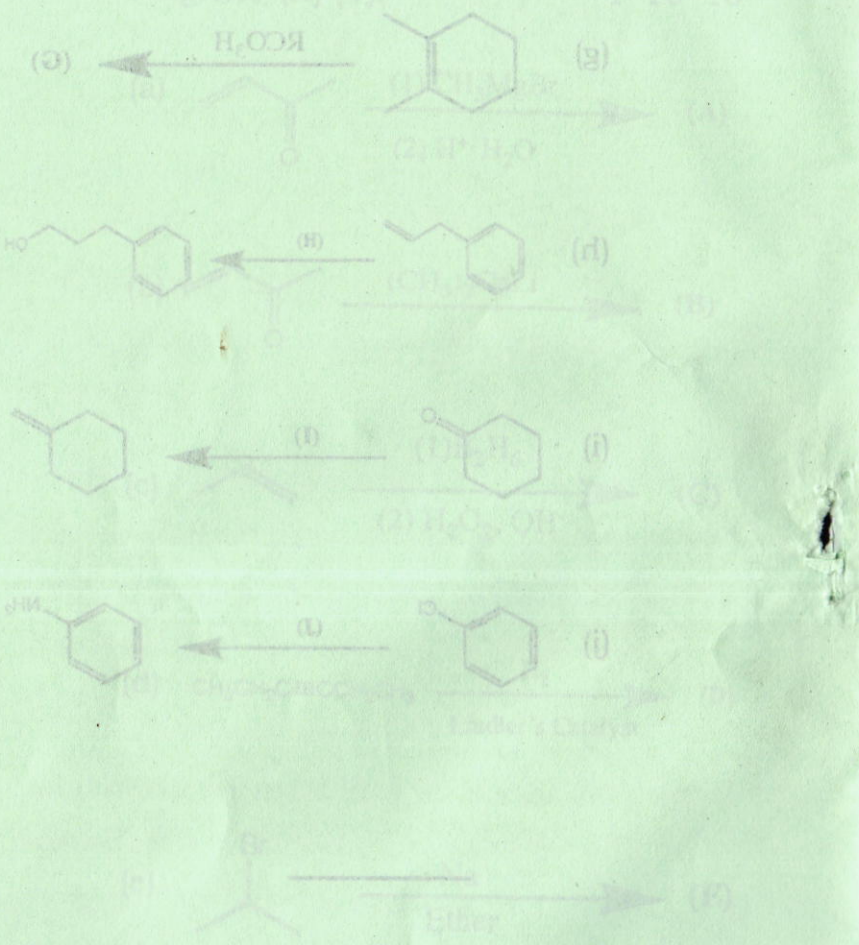


2022

CHEMISTRY

(Honours)

Paper : CHE–HC–2016

(Organic Chemistry–I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer ***any seven*** questions : 1×7=7

(a) Out of the following, which one exhibits positive inductive (+*I*) effect ?

(i) $-CH_3$

(ii) $-OH$

(iii) $-F$

(iv) $-C_6H_5$

(b) BCl_3 is a planar molecule whereas NCl_3 is pyramidal. Why ?

(c) Find the optically active compound among the following :

(i) Glycerine

(ii) Acetaldehyde

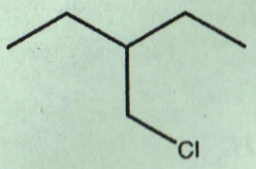
(iii) Glyceraldehyde

(iv) Acetone

(d) Are the following molecules enantiomers, diastereomers or same ?

(R,R)-Tartaric Acid and (R,S)-Tartaric Acid

(e) Write the IUPAC name of the following compound :



(f) Write the name of the reaction when alkyl halide is allowed to react with metallic sodium in presence of dry ether.

(g) Name the products formed when propene is subjected to ozonolysis.

(h) What are products obtained when alkenes are subjected to hydroxylation ?

(i) Define angle strain.

(j) Explain why are alkynes more acidic than alkenes and alkanes.

2. Answer ***any four*** questions from the following : 2×4=8

(a) Explain why $(CH_3)_4N^+$ is neither an electrophile nor a nucleophile.

(b) Draw all the possible geometrical isomers of

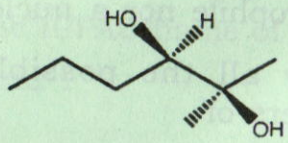
$CH_3-CH=CH-CH=CH-C_2H_5$.

(c) What are the similarities and differences between achiral and meso compounds ?

(d) Peroxides are good initiators for radical reactions. Given the peroxide RO-OR, draw the initiation and propagation step of the peroxide radical to create bromine radical with HBr.

(e) With proper stereochemistry, write the products obtained when 1,2-dimethylcyclopentene is reacted with Br_2.

(f) Give a reaction scheme starting with alkene and required reagents to produce the following compound :



(g) Draw the most stable conformations of *cis*-and *trans*-1,2-dimethylcyclohexane.

(h) Draw the Newman projection formula of the eclipsed and staggered conformers of 1,2-dichloroethane.

3. Answer ***any three*** questions : 5×3=15

(a) State the differences between substitution and elimination reaction. What are the factors that determine whether a reaction will follow substitution mechanism or elimination mechanism ? 2+3=5

(b) What are carbenes ? Give *one* method of preparation of carbene. Write the structures of singlet and triplet methylene. 1+2+2=5

(c) With the help of examples, explain 2.5×2=5

(i) conformation and

(ii) configuration

(d) A tertiary alkyl halide **A** of formula $C_6H_{13}Br$ on treatment with potassium *t*-butoxide gives two isomeric alkenes **B** and **C** having the formula C_6H_{12}. Both of these alkenes on hydrogenation give 2,3-Dimethylbutane **D**. Predict the products and write the reactions involved.

(e) Write the E1cB mechanism of elimination reaction. How does it differ from E1 mechanism ? 3+2=5

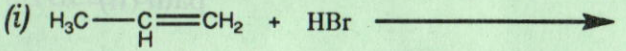
(f) Hydrogenation of Hex-3-yne produces cis-and trans-Hex-3-ene under different reaction conditions. Write the reactions involved. How can you convert Hex-3-ene back to Hex-3-yne ? 1.5×2+2=5

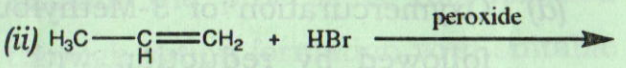
(g) What is 1,3-diaxial interaction in cyclohexanes ? How does it affect the stability of the molecule ? Draw the most stable and most unstable conformers of 1,3-disubstituted cyclohexane. 1+2+2=5

(h) What do you understand by ortho-and para-directing effects of substituent groups ? Give examples for each. Explain the terms activating and deactivating group. 2+1+2=5

4. Answer ***any three*** questions from the following : 10×3=30

(a) What are different pathways via which an addition reaction can proceed ? Predict the product and propose mechanism for the following reactions : 2+4×2=10

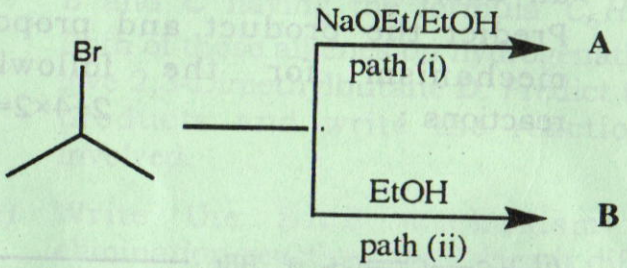
(i) 

(ii) 

(b) Draw the Fischer projections for (2R, 3S)-2-Bromo-3-chlorobutane and (2S,3R)-2-Bromo-3-chlorobutane, with the carbon chain on the vertical line. Label each structure as (2R, 3S) or (2S, 3R). Assume that you have a mixture of equal amount of each of the above compounds. What is this mixture called ? Can they be separated into two containers based on their physical properties ? Explain. 3+3+1+3=10

(c) Predict the products **A** and **B** and write mechanism for their formation.

1+4+1+4=10



(d) Oxymercuration of 3-Methylbut-1-ene followed by reduction with sodium borohydride leads to the formation of 3-Methylbutan-2-ol via Markovnikov's addition. Draw the mercurinium ion intermediate and rationalize the formation of the Markovnikov's product. Can 3-Methylbutan-1-ol also be obtained from 3-Methylbut-1-ene ? How ? Is there any stereochemical control in the oxymercuration-demercuration process ?

1+4+1+2+2=10

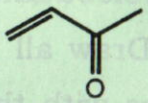
(e) *Trans*-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-Dimethylcyclobutane. Explain this observation. Draw all the different structures with the formula C_6H_{12} with only one ring and name them. Also, draw the energy profile diagram and label the position of the structures. 2+4+4=10

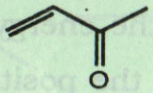
(f) Explain the process of racemization through cation formation with suitable examples. How would you resolve optically active alcohols from a racemic mixture ? 5+5=10

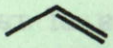
(g) Discuss SNAr and Benzyne mechanism for aromatic nucleophilic substitution reaction. Discuss effect of leaving group and attacking nucleophile on aromatic nucleophilic substitution reaction.

3+3+2+2=10

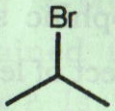
(h) Write the structure of products and reagents **(A)-(J)**. 1×10=10

(a)  $\xrightarrow[(2)\ H^+,\ H_2O]{(1)\ CH_3MgBr}$ **(A)**

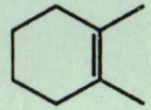
(b)  $\xrightarrow{(CH_3)_2CuLi}$ **(B)**

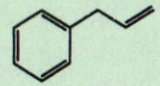
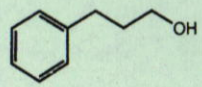
(c)  $\xrightarrow[(2)\ H_2O_2,\ OH^-]{(1)B_2H_6}$ **(C)**

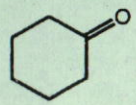
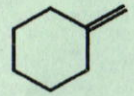
(d) $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{Lindler's Catalyst}]{H_2}$ **(D)**

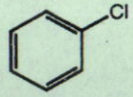
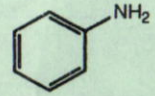
(e)  $\xrightarrow[\text{Ether}]{Na}$ **(E)**

(f)  $\xrightarrow[H_2S]{OsO_4}$ **(F)**

(g)  $\xrightarrow{RCO_3H}$ **(G)**

(h)  $\xrightarrow{(H)}$ 

(i)  $\xrightarrow{(I)}$ 

(j)  $\xrightarrow{(J)}$ 

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3 (Sem–2/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–2026

(Physical Chemistry – II)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer ***any seven*** of the following questions : 1×7=7

   (a) Give the SI unit of energy.

   (b) Define specific heat of a system.

Contd.

(c) The variation of enthalpy of a reaction with temperature is given by

(i) Hess's law

(ii) Kirchhoff's equation,

(iii) Henry's law,

(iv) Raoult's law

(Choose the correct option)

(d) A process is carried out at constant pressure and temperature. It will be spontaneous if

(i) $\Delta G < 0$

(ii) $\Delta H < 0$

(iii) $\Delta U < 0$

(iv) $\Delta S < 0$

(Choose the correct option)

(e) A solution is a

(i) homogeneous mixture of only two components

(ii) homogeneous mixture of any number of components

(iii) heterogeneous mixture

(iv) anything mixed with water

(Choose the correct option)

(f) What is excess thermodynamic function ?

(g) Name a colligative property that is used to determine the molar mass of a protein.

(h) Equimolar solutions of glucose and sodium chloride are not isotonic. Justify.

(i) Find the value of work done when 2 moles of an ideal gas is allowed to expand from 1 L to 10 L against vacuum at 298K.

(j) Name the thermodynamic property that measures the disorderliness of a system.

2. Answer ***any four*** of the following questions : 2×4=8

(a) Define intensive property. Give *one* example.

(b) State Zeroth law of thermodynamics.

(c) Define explosion temperature and adiabatic maximum flame temperature.

(d) What do you mean by network ? Briefly explain.

(e) Explain residual entropy.

(f) Define fugacity function.

(g) An ideal gas undergoes a single step expansion a constant external pressure P from (P_1, T, V_1) to (P, T, V_2). What is the magnitude of work done by the system ?

(h) Find ΔH of the reaction :

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given :

$\Delta H_{H-H} = 435.1$, $\Delta H_{Br-Br} = 192.5$,

$\Delta H_{H-Br} = 368.2\ kJ/mol$.

3. Answer ***any three*** of the following questions : 5×3=15

(a) (i) State Path function with suitable example. 2

(ii) Show that in an isothermal expansion, the work is done at the expense of the heat absorbed. 3

(b) Derive the Gibbs – Helmholtz equation.

(c) (i) Write short note on the third law of thermodynamics. 3

(ii) Explain briefly how absolute entropy of a molecule can be determined from heat capacity measurement. 2

(d) Give the criteria of spontaneity and thermodynamic equilibrium in terms of enthalpy, entropy, Helmholtz free energy and Gibbs free energy. 5

(e) (i) Calculate K_c for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g)+O_2(g)$ for which $K_p=3{\cdot}5 \times 10^{-23}$ *atm* at 27°C. 3

(ii) How molar mass can be determined from freezing point depression ? 2

(f) (i) 0.5*g* of a non-volatile solute of molar mass 60*g* mol^{-1} is dissolved in 100*g* of ethyl acetate at 20°C. What would be the vapour pressure of this solution at 20°C ? The vapour pressure of ethyl acetate at 20°C is 72.8 *Torr.* 3

(ii) Explain briefly *any one* method for measurement of vapour pressure lowering. 2

(g) What is osmotic pressure ? Give detailed thermodynamic derivation of osmotic pressure of a solution having non-volatile solute.

(h) What are colligative properties ? Explain *two* practical applications of colligative properties.

4. Answer ***any three*** of the following questions : 10×3=30

(a) (i) State and explain first law of thermodynamics. Show that for isochoric process, $q=\Delta U$. 3+2=5

(ii) Derive the integrated Kirchhoff equation. 5

(b) (i) Define heat capacity of a system. Show that $C_p - C_v = R$ for 1*mole* of an ideal gas. 1+3=4

(ii) State and explain Raoult's law for vapour pressure of binary solution of volatile liquid. What is an ideal solution ? 5+1=6

(c) (i) Calculate q, w, ΔU and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 27°C from a volume of 10 dm^3 to a volume of $20\,dm^3$. 4

(ii) Explain that the entropy of the universe is increasing continuously. 2

(iii) Explain briefly the vapour pressure *vs.* composition diagram of a binary liquid mixtures having positive deviation. 4

(d) (i) Explain that the thermodynamic isothermal reversible work of expansion is the maximum work. 3

(ii) Give the thermodynamic derivation of the relation between Gibb's free energy of a reaction and its reaction quotient. 5

(iii) Give *two* limitations of first law of thermodynamics. 2

(e) (i) Define enthalpy of neutralization. 1

(ii) The enthalpy of combustion of glucose $C_6H_{12}O_6(S)$ is $-2816\ kJ\,mol^{-1}$ at 25°C. Calculate ΔH_f^o of $C_6H_{12}O_6(S)$. The ΔH_f^o values for $CO_2(g)$ and $H_2O(l)$ are -393.5 and $-286.2\,kJ\,mol^{-1}$ respectively. 3

(iii) Give a brief account of coupling of exoergic and endoergic reactions. 3

(iv) State and explain van't Hoff theory of dilute solution as applied to osmotic pressure. 3

(f) (i) Discuss about the molecular and statistical interpretation of entropy. 2½×2=5

(ii) Show that :

$\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$ 5

(g) (i) Prove that : $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ 5

(ii) Explain the variation of chemical potential with temperature. 3

(iii) Calculate the pressure of CO_2 gas at $700K$ in the heterogeneous equilibrium reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ if ΔG^o for this reaction is $130.2\ kJmol^{-1}$. 2

(h) (i) Show that :

$K_p = K_x(P)^{\Delta n_g} = K_c(RT)^{\Delta n_g}$

under what conditions,

$K_p = K_x = K_c$? 5+1=6

(ii) State and explain *Le* Chatelier's principle taking *any one* example. 4