

2019

**CHEMISTRY**

( Major )

Paper : 2.1

( **Physical Chemistry** )

Full Marks : 60

Time : 3 hours

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

1. Answer the following as directed : 1×7=7

(a) Name two gases for which the compressibility factor be never less than 1 at any temperature and pressure.

(b) State the principle of equipartition of energy.

(c) Define coefficient of viscosity.

(d) According to \_\_\_\_\_ law, relative lowering of vapour pressure is equal to mole fraction of the solute in solution.

(Fill in the blank)

(e) What is meant by abnormal colligative properties?

(f) At 298 K, the conductivity of 0.1 M KCl solution is  $1.286 \times 10^{-3} \text{ S cm}^{-1}$  and its resistance is 337.6 ohm, when conductivity is measured with a cell. Calculate the cell constant.

(g) Define buffer action.

2. Answer the following questions : 2×4=8

(a) Write the causes of deviations from ideal behaviour by the real gases.

(b) Define vapour pressure of a liquid. What are the highest and lowest limits of the variation of vapour pressure with temperature?

(c) State Henry's law. Give one limitation of the law.

(d) What is corrosion? Give two preventive measures of corrosion of metals.

3. Answer any *three* of the following questions :

5×3=15

(a) Explain how molar heat capacities at constant pressure and at constant volume of an ideal gas can be calculated using the principle of equipartition of energy.

(b) Give a general discussion on the structure of liquid water and ice.

(c) Using the concept of chemical potential, show that the elevation of boiling point of a dilute solution containing a non-volatile non-electrolyte solute is directly proportional to the molal concentration of the solute.

(d) What is battery? What are primary and secondary batteries? Give one example of each.

4. (a) Answer *either* [(i) and (ii)] or [(iii), (iv) and (v)] :

(i) Derive van der Waals' equation of state for  $n$  moles of a gas. Explain how van der Waals' equation explains the behaviour of real gases.

4+2=6

(ii) The van der Waals' constants for  $\text{HCl}(\text{g})$  are  $a=371.843 \text{ kPa dm}^6 \text{ mol}^{-2}$  and  $b=4.08 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ . Find the critical constants for  $\text{HCl}(\text{g})$ . 4

(iii) Explain what is meant by distribution of molecular speed. Deduce the expression for the root-mean-square speed of gas molecules from Maxwell distribution expression. 2+3=5

(iv) For  $\text{O}_2(\text{g})$  molecules, the root-mean-square velocity at temperature  $T_1$ , the average velocity at temperature  $T_2$  and most probable velocity at  $T_3$  are all equal to  $1.5 \times 10^3 \text{ m s}^{-1}$ . Find  $T_1$ ,  $T_2$  and  $T_3$ . 4

(v) For a gas, the van der Waals' constants are  $a=0$  and  $b=0$ . Explain whether the gas can be liquified or not. 1

(b) Answer either [(i), (ii) and (iii)] or [(iv) and (v)] :

(i) Write the virial equation of state of 1 mole of a gas. Explain the terms involved in it. 2

(ii) Deduce the expressions for critical constants  $P_c$ ,  $V_c$  and  $T_c$  in terms of the van der Waals' constants. 4

(iii) Using principle of equipartition of energy, calculate the energy of 1 mol  $\text{CO}_2(\text{g})$  at 298 K. 4

(iv) On the basis of kinetic theory, obtain an expression for coefficient of viscosity of a gas. 5

(v) Define vapour pressure of a liquid. Explain a method of determination of vapour pressure of a liquid. 1+4=5

(c) Answer either [(i), (ii) and (iii)] -or [(iv) and (v)] :

(i) Define mobility of ions in solution. Explain why mobility of  $\text{H}^+$  ion is highest in aqueous solution. 1+2=3

(ii) A moving boundary experiment was carried out with  $20 \text{ mol m}^{-3}$  NaCl solution in water. In the experiment,

a current of  $1.60 \times 10^{-3}$  A moved the boundary through a distance 0.06 m in 34 minutes and 30 seconds. Calculate the transport number of  $\text{Na}^+$  ion, if the radius of the tube used in the experiment is  $1.88 \times 10^{-3}$  m.

3

(iii) Explain the terms 'asymmetric effect' and 'electrophoretic effect' of the ions of strong electrolyte in solution.

4

(iv) Write Nernst equations for the potentials of Zn-electrode and Cu-electrode in the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell at any given temperature.

2+2=4

(v) For the reaction  $\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$ , standard electrode potential is  $-0.036$  V and the standard electrode potential for the reaction  $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$  is  $0.771$  V.

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Calculate the standard electrode potential for the reaction  $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$ . Predict whether the reaction  $\text{Fe} + 2\text{Fe}^{3+} \rightleftharpoons 3\text{Fe}^{2+}$  is spontaneous or not. 4+2=6

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**3 (Sem-2) CHM M 2**

**2019**

**CHEMISTRY**

**( Major )**

**Paper : 2.2**

**( Organic Chemistry )**

*Full Marks : 60*

*Time : 3 hours*

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

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

(a) Why do most of the carboxylic acids exist as dimer?

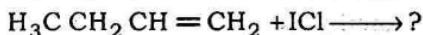
(b) Why are reductions with  $\text{LiAlH}_4$  carried out under anhydrous conditions?

(c) Bromination of olefins cannot be carried out in ethanol. Why?

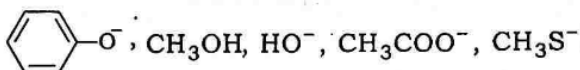
(d) Between benzoic acid and 2,6-dimethylbenzoic acid, which one is less acidic and why?

(e) Why are amines generally not prone to substitution reactions?

(f) Predict the major product :



- (g) Arrange the following in order of decreasing nucleophilicity :



- (h) Peroxide in ether can be detected using acidified aqueous KI solution. Explain.

2. Answer any four questions : 2×4=8

- (a) Can tertiary alkyl halides be used in coupling reactions with Gilman reagents? Explain.
- (b) What is the product of the reaction of acetamide with  $\text{OH}^-$ ? The  $\text{p}K_a$  of  $\text{NH}_3$  is 36; the  $\text{p}K_a$  of  $\text{H}_2\text{O}$  is 15.7.
- (c) Arrange the following carbonyl compounds in order of their decreasing reactivity towards nucleophiles and give a plausible explanation for the same :  
Cyclohexanone, Cyclopentanone, Cyclopropanone
- (d) Aniline on nitration under acidic conditions gives *m*-nitroaniline in good yield. Explain.
- (e) What are the topicities of hydrogen atom of the  $-\text{CH}_2$  group and the faces of the carbonyl group in benzyl methyl ketone?

3. Answer any two from (a), (b) and (c), and any one from (d) and (e) : 5×3=15

(a) (i) From the perspective of viewing down the  $C_2-C_3$  bond, draw the Newman projection of the most stable conformation of 2,3-dimethylbutane. 1

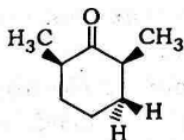
(ii) Draw and arrange the following conformers of butane in order of increasing energy : 2

Eclipsed, Gauche, Anti

(iii) Draw the chair conformer of *trans*-1-ethyl-2-methylcyclohexane and indicate the more stable conformer. 2

(b) Draw a potential energy diagram showing the conformers of cyclohexane as one chair conformer interconverts to the other. Explain the relative stabilities of all the conformers involved. 5

(c) (i) State whether the compound given below is chiral or achiral. Also indicate the topicities of the  $CH_3$ ,  $CH_3$  groups; H, H atoms and carbonyl faces : 3



(ii) State how you can establish the  
topicity of groups in a compound. 2

(d) In aromatic electrophilic substitution,  
halogens are deactivating but *o*-, *p*-  
directing. Explain, considering that  
such a substitution is kinetically  
controlled. 5

(e) Account for the following : 2+2+1=5

(i) In aromatic electrophilic substi-  
tution,  $\text{CF}_3$  is *meta*-directing.

(ii) 2,2-dimethylbiphenyl is more  
difficult to nitrate than biphenyl.

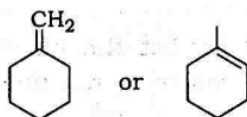
(iii) *t*-butylbenzene gives much less  
*ortho*-product on nitration as  
compared to toluene.

4. Answer either (a) or (b) and any two from  
(c), (d), (e) and (f) : 10×3=30

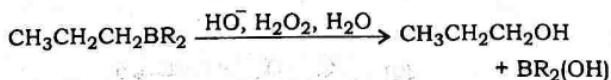
(a) (i) Write the major product obtained  
when *m*-nitrochlorobenzene is  
chlorinated. How can you explain  
the formation of the major product? 2

(ii) What factors govern the product  
ratios when a monosubstituted  
benzene ring containing an *ortho*-,  
*para*-directing group undergoes  
aromatic electrophilic substitution?  
Write in brief. 3

- (iii) What will happen when bromobenzene and 2-bromo-3-methylanisole are each allowed to react separately with  $\text{KNH}_2$  in liquid  $\text{NH}_3$ ? Propose a mechanism to justify the reactions. 5
- (b) (i) What is called cine-substitution? Give an example. 2
- (ii) Provide two evidences in support of  $\text{S}_{\text{N}}\text{Ar}$  mechanism. 2
- (iii) What happens when 2-chloropyridine reacts with phenol? Propose a mechanism for the reaction. 3
- (iv) How would you prepare  $\beta$ -naphthol from naphthalene? What happens when  $\beta$ -naphthol is treated with nitrous acid? 2+1=3
- (c) (i) To which of the following compounds is the addition of  $\text{HBr}$  more regioselective and why? 2



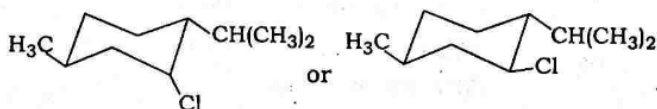
- (ii) Propose a mechanism for the following conversion : 2



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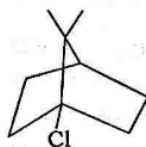
(iii) Suggest a method for conversion of butane-1-amine to but-1-ene. 2

(iv) Out of the following two compounds, which one undergoes E2 elimination faster and why? 2

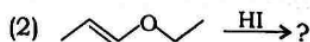
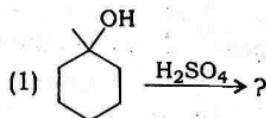


(v) Iodine does not react with ethane even though  $I_2$  is more easily cleaved homolytically than the other halogens. Explain. 2

(d) (i) Explain why the following alkyl halide does not undergo a substitution reaction, regardless of the condition under which the reaction is carried out : 3



(ii) Predict the major product for the following reactions : 2

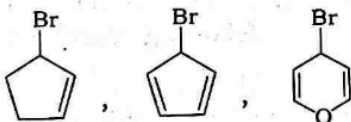


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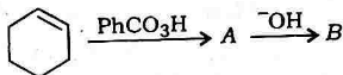
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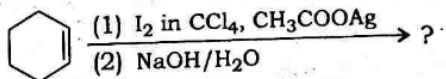
- (iii) Arrange the following compounds in order of decreasing  $S_N1$  reactivity and give a brief explanation : 3



- (iv) Identify A and B (including their stereochemistry) : 2



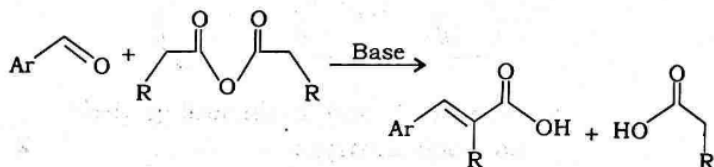
- (e) (i) What will happen when methyl vinyl ketone reacts with diethylmalonate in presence of sodium ethoxide? Propose a mechanism for the reaction. 1+2=3
- (ii) Predict the product for the given reaction and propose a mechanism : 3



- (iii) Explain why *p*-hydroxybenzaldehyde does not undergo Cannizzaro reaction. 2
- (iv) Distinguish between nitroethane and 2-nitropropane. 2

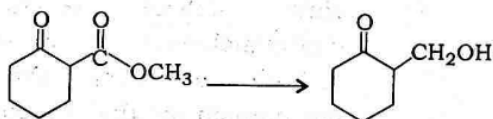
(f) (i) How can you distinguish between  $\beta$ -hydroxy acid and  $\gamma$ -hydroxy acid? 2

(ii) (1) Propose a mechanism for the following reaction : 1½



(2) How can naphthalene be prepared by Haworth synthesis? 1½

(iii) How can you carry out the following conversion? 2



(iv) What is chloromethylation? Give an example. 2

(v) Why do most higher ketones not give bisulphite adduct in appreciable amount? 1

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