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Your Roll No. : 2019

Sl. No. of Q. Paper : **2199** **IC**

Unique Paper Code : 32171201

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Organic Chemistry - I

Semester : II

Time : 3 Hours ***Maximum Marks : 75***

Instructions for Candidates :

(a) Write your Roll No. on the top immediately on receipt of this question paper.

(b) Attempt any **six** questions in **all**.

(c) Question **No.1** is compulsory.

1. Attempt any **five** questions : 3×5=15

(a) *cis*- but-2-ene on treating with carbene gives 100% *cis* – 1,2 – dimethylcyclopropane, sometimes its gives mixture of 50% *cis* and 50% *trans*-1,2 – dimethylcyclopropane. Explain this observation.

(b) Discuss the stereochemical implications of S_{N1} and S_{N2} reaction.

P.T.O.

(c) Phenol is more acidic than an alkyl alcohol. Explain.

(d) Write down all the possible conformational isomer of Ethylene glycol. Which conformation is most stable and why ?

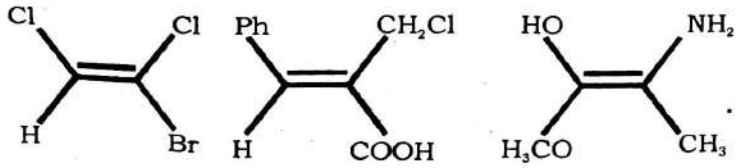
(e) Write the structure formula of (S) (E)-2-Bromo-3-heptene.

(f) Explain the order of stability of the following carbocations :

$3°>2°>1°>CH_3^+$

2. (a) Write down all the possible stereoisomer of 1,3-dibromo-2-methylbutane. Assign R/S configuration to each and every chiral center present in each possible stereoisomer. 6

(b) Assign priorities and give E/Z notations to following : 6



3. (a) How many products we will get on dehydration of 3,3-Dimethylbutan-2-ol? Explain with mechanism. 4

(b) 1,3-butadiene on treating with HBr gives 3-Bromobut-1-ene at low temperature whereas at high temperature gives 1-Bromobut-2-ene. Explain this observation. 4

(c) (i) Convert Propane to 2,3-Dimethylbutane.

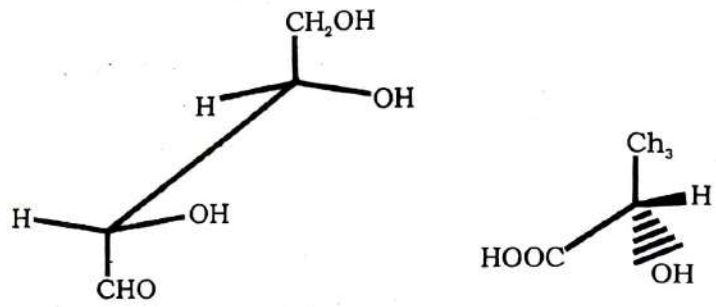
(ii) How is it proved that the chlorination of methane occurs via free radical mechanism ? 4

4. (a) Friedel Craft Alkylation of benzene with 1-chlorobutane gives mixture of product. Explain with mechanism. 3

(b) Convert Benzene to 1-chloro-1-phenylethane. 3

(c) Define Huckel's rule and give one example of each with explanationfor : Aromatic, Anti-aromatic and Alicyclic compounds. 3

(d) Write down the standard Fischer Projection for the following : 3



5. (a) Write down all the possible conformational isomers of 1-methylcyclohexane. Which conformer is more stable and why ? 3

(b) *cis*-1,4-but-2-ene-dioic acid (maleic acid) on treatment with $KMnO_4$ (cold) gives a product. Explain the reaction with mechanism. Also give the stereochemistry of the product. 3

(c) Convert benzene into m-nitrobenzoic acid. 3

(d) What are the limitations of Wurtz's reaction? How Corey-House synthesis overcomes these limitations. 3

6. Complete the following and give stereochemistry wherever necessary : 12

(a) $CH_3CH{=}CH_2 \xrightarrow{BH_3} ? \xrightarrow{H_2O_2/O\bar{H}} ?$

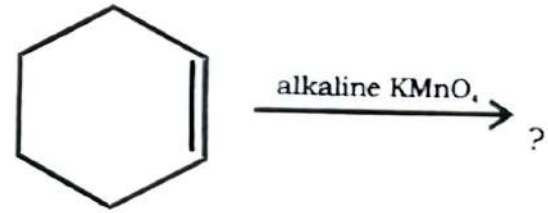
(b) $(CH_3)_2C{=}CHCH{=}C(CH_3)_2 \xrightarrow{O_3} ? + ?$

(c) but-1yne $\xrightarrow[H_2SO_4]{HgSO_4} ?$

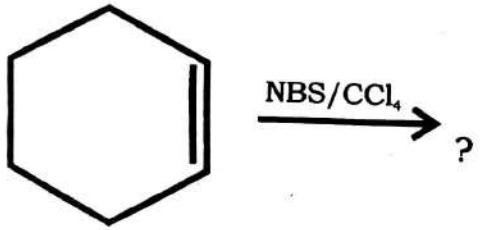
(d) $CH_3CH{=}CH_2 + HOCl \longrightarrow ?$

(e) but-2yne + $Na/NH_3 \longrightarrow ?$

(f) 1,3 butadiene + Maleic acid $\longrightarrow ?$

(g) 

(h) $(C_2H_5)_4N^+O\bar{H} \xrightarrow{\text{heat}} ?$

(i) 

(j) cis-but-2-ene $\xrightarrow{CH_2(singlet)}$?

7. (a) Propene on bromination at low temperature gives different product than reacting at 500°C . Explain. 4

(b) Explain the following terms : 4

(i) 1,3 diaxial interaction

(ii) Torsional strain

(c) How will you distinguish between : 4

(i) 1-heptyne and 2-heptyne

(ii) But-1-ene and Butane

8. Write a short note on any **three** : 4×3=12

(a) Saytzeff elimination Vs. Hoffmann elimination

(b) Hydrogen Bonding

(c) Types of Elimination reactions

(d) *Oxymercuration*-Demercuration reaction

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Your Roll No. : .....

2019

Sl. No. of Q. Paper : **2200** **IC**

Unique Paper Code : 32171202

Name of the Course : **B.Sc. (Hons.) Chemistry**

Name of the Paper : Physical Chemistry - II

Semester : II

Time : 3 Hours ***Maximum Marks : 75***

Instructions for Candidates :

(a) Write your Roll No. on the top immediately on receipt of this question paper.

(b) Answer any **six** questions.

(c) Question No. **1** is compulsory.

(d) Use of scientific calculator is allowed.

$R = 8.314\ JK^{-1}\ mol^{-1}$, $N = 6.0231023\ mol^{-1}$

1. Attempt any **five** : 5×3

(a) The magnitude of the boiling point elevation is less than that of the freezing point depression for a solution of the same concentration : Explain the statement in terms of chemical potential along with diagram.

P.T.O.

(b) Equilibrium constant K_p is a dimensionless quantity. Explain.

(c) Is the Joule Thomson experiment reversible ? Explain by describing how one could or could not, restore the gas to its initial state by the same path.

(d) Reversible processes are ideal process and cannot be carried out in practice. Comment.

(e) Why standard solutions are prepared in volumetric flask rather than a beaker ?

(f) Why ΔG is used more compared to ΔA to express the condition of spontaneity of the reaction ?

2. (a) An imaginary gas has the equation of state $PV^2=n^2KT$ (where K is a constant) and its heat capacity C_v is independent of temperature and pressure. For this gas U depends only on T, as for an ideal gas.

(i) Obtain an equation that relate the initial and final pressure to the initial and final temperature in a reversible adiabatic expansion of the gas.

(ii) Find $\overline{C_p} - \overline{C_v}$ for this gas in terms of P, T and K. 6

(b) 0.1 M solution of *NaCl* is found to be isotonic with 1.1% solution of urea. Calculate the apparent degree of dissociation of *NaCl*. 4

(c) A useful reaction has a positive value of ΔG. Can the reaction be made to proceed ? Explain with example. 2

3. (a) For the solute (2) in dilute solution in a certain solvent the partial molal volume is given by $\bar{V}_2 = a + bm$, where m is the molality of the solution and a, b are constants. Express the partial molal volume $\bar{V}_1$ in terms of a, b, m and quantities characteristics of the solvent. 5

(b) The bond dissociation enthalpies of H_2 (g) and N_2 (g) are + 435.95 $kJmol^{-1}$ and + 941.8 $kJmol^{-1}$ and the enthalpy of formation of NH_3 (g) is − 46.024 $kJmol^{-1}$.

(i) What is the enthalpy of atomisation of NH_3 (g) ? 2

(ii) What is the average bond enthalpy of N-H bond ? 2

(c) Why in the use of entropy as a criterion for spontaneity do we have to consider ΔS_{total}, but in the case of the Gibbs free energy we have to consider only ΔG_{system} not ΔG_{total} ? 3

4. (a) $dU = xy^2dx + x^2y\,dy$ and $dw = \text{Sin}(y)\,dx + \text{Sin}(x)\,dy$

(i) Ascertain whether dU and dw are exact or inexact differentials. 3

(ii) For each differential that is exact find the function of which it is differential by integrating over a suitable path. Show in a diagram the path that you choose. 3

(b) Calculate the standard enthalpy of formation of ethane at 350 K. Given that its value at 298 K is -84.68 kJ mol^{-1} and $\overline{C_p}$ / (JK^{-1} mol^{-1}) for H_2 *(g)* is $27.28 + 3.26\times10^{-3}$ T, *C (s)* is $16.86+4.77\times10^{-3}$ T and C_2H_6 is $14.72+ 0.1272$ T. 4

(c) Distinguish between bond enthalpy and bond dissociation enthalpy. 2

5. (a) One mole of hydrogen and nine moles of nitrogen are mixed at 298 K and 1 atm pressure. Assuming ideal behaviour for the gases, calculate the entropy of mixing per mole of the mixture formed. Would it make any difference if under similar conditions one mole of hydrogen is mixed with nine moles of oxygen ? 4

(b) Show that chemical potential μ can also be written as $\left(\frac{\partial U}{\partial n_i}\right)_{v,s,nj}$ Is this a partial molar quantity ? Give reason. 4

(c) Derive a relation between osmotic pressure and elevation in boiling point. 4

6. (a) A 25 g mass of ice at 273 K is added to 150 g of liquid water at 360 K at constant *P*. What is the final state of system? Calculate ΔS for the process. Given : $\Delta H_{fus}(H_2O) = 6.0095$ kJ mol^{-1}, $\overline{C_p}$ (H_2O, l) = 75.29 JK^{-1} mol^{-1} and Tm (H_2O, s) = 273K. 4

(b) Which of the following processes are spontaneous ? Give reason. 4

(i) Reversible isothermal expansion of an ideal gas

(ii) Vaporization of superheated water at 102 °C and 1 bar.

(iii) The constant P melting of ice at its normal freezing point by addition of infinitesimal amount of heat.

(iv) Adiabatic expansion of a gas into vacuum.

(c) Derive the relation $\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V$ 4

7. (a) Starting from the definition of G and using thermal equation of state dG= -SdT+VdP. Derive the following relation

$$\left(\frac{\partial(\Delta G/T)}{\partial(1/T)}\right)_P = \Delta H \quad .$$ 4

(b) 1 mole of an ideal gas at 25 °C and 1 atm is subjected to following changes successively

(i) Heated to 50 °C at constant volume

(ii) Expanded isothermally reversibly till P is 0.5 atm.

(iii) Cooled to 25 °C at constant P.

Calculate q, w, ΔU and ΔH if $C_v = \frac{3}{2}R$.

6

(c) Van't Hoff factor, i, for aqueous solution of both $NaCl$ and CH_3COOH depends on the concentration of the solution. Explain.

2

8. (a) Heat capacity of metal X is 3.053 $J°C^{-1}{}_1 mol^{-1}$ at 20 K. Calculate the standard absolute entropy of this substance in JK^{-1} mol^{-1} at 20 K.

4

(b) Derive the relation $\Delta S = C_p I_n \frac{T_f}{T_i} - \alpha V\left(P_f - P_i\right)$ starting from dH = TdS + VdP. 4

(c) At 480 K and a total pressure of 1 atm, a mixture consisting of nitrogen and hydrogen in the mole ratio of 1:3 contains 16% ammonia at equilibrium. Calculate K_p for the reaction. 4

3563 (19) SET II

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Unique Paper code :217201

Name of the Paper: CHHT -203: Physical Chemistry I

Name of the course : B.Sc (H) Chemistry

Semester: II

Duration: 3 Hours Maximum Marks: 75

(Write your roll no on the top immediately on receipt of the question paper)

Instructions for candidates

1. Answer six questions
2. Question No.1 is compulsory
3. Use of Scientific calculator and log tables is permitted

$R = 8.314\ JK^{-1}mol^{-1}$; $N_A = 6.023 \times 10^{23}\ mol^{-1}K$; $k = 1.38 \times 10^{-23}\ JK^{-1}$

Q.1 Attempt any Five of the following: (3 x 5 = 15)

(a) Show that the van der Waals constant b for real gas is four times its molecular volume.

(b) K^+ and Cl^- are indistinguishable by x ray diffraction method

(c) Calculate the miller indices of the crystal plane which cuts through the crystal axis at: (2a, 3b, c); (2a, -3b, -3c).

(d) What is the effect of temperature on viscosity of liquid?

(e) Solubility of AgCl will decrease if some $AgNO_3$ is added to its saturated solution.

(f) pH of neutral water at 110^0C is less than 7 but it is not acidic in nature.

(4, 4,4)

Q.2 (a) Derive the van der Waals equation with correction of pressure and volumes. Explain its limitation and give the units of van der Waals constant.

(b) Define the terms collision diameter and collision frequency. Derive the expression for number of collision per unit time and per unit volume Z_{11}.

(c) Define degree of ionization. Derive the exact expression to calculate $[H_3O^+]$ for weak monoprotic acid.

(4, 4, 4)

Q.3 (a) An indicator HIn has ionization constant of 9×10^{-9} M. The acid colour of indicator is yellow and alkaline colour is red. The yellow colour is visible when the ratio of yellow to red form is 30 to 1 and the red form is visible when the ratio of red to yellow form is 2 to 1. What is the pH range of indicator?

(b) Describe the methods used to determine the viscosity of liquid.

(c) Describe all the symmetry elements of cube.

(4, 4, 4)

Q.4 (a) A solution is 0.1 M in Cl^{-1}, 0.1 M Br^{-1} and I^{-1} in I^-. Solid $AgNO_3$ is gradually added to this solution. Assuming that the addition of $AgNO_3$ does not change the volume answer the following:

(i) What concentration of Ag^+ ions will be required to start precipitation of each of the three ions?

(ii) Which ion will be precipitated first?

Given : ksp (AgCl) = 1.7×10^{-10} M^2, ksp (AgBr) = 5.0×10^{-13} M^2, ksp = 8.5×10^{-17} M^2

(b) What is meant by salt hydrolysis? Derive the expression for hydrolysis constant, degree of hydrolysis and pH of a salt of weak acid and strong base in terms of dissociation constant of weak acid and ionic product of water.

(c) 50ml of 0.1 M HCl is being titrated with 0.1 M NaOH. Determine the pH when (i) 15 ml and (ii) 25 ml of NaOH has been added.

(4, 4, 4)

Q.5 (a) Derive a, b, and R in terms of P_c, V_c, and T_c.

(b) State Troutons Rule. Calculate the boiling point for Benzene given that

$$\Delta_{vap}H = 30.72 \text{ kJ mol}^{-1}.$$

(c) What do you understand by the term critical phenomenon? Draw the isotherm of CO_2 at different temperature to explain it?

(4, 4, 4)

Q.6 (a) Derive the following relationship:

$$P_r = \frac{8T_r}{3V_r} - \frac{3}{V_r}$$

Where symbols have their usual meanings

(b) (i) Derive the expression for Boyle's Temperature.

(ii) Evaluate Boyle's temperature of gas.

Given that: a = 17.7 kPa dm^6 mol^{-2} and b = 0.02 dm^3 mol^{-1}

(c) At 60^0C, the ionic product of water is 9.6 X 10^{-14} M^2. Evaluate the pH at this temperature.

(4, 4, 4)

Q.7 (a) Derive an expression for kinetic gas equation.

(b) Derive the Bragg's equation.

(c) Show that the ratio of molar heat capacity at constant pressure $C_{p,m}$ to molar heat capacity at constant volume $C_{v,m}$ for a monoatomic gas is 1.67.

(4, 4, 4)

Q.8 (a) Describe the methods commonly employed for measurement of vapour pressure of a liquid.

(b) Explain screw axis and glide plane.

(c) An element crystallizing in cubic form gives first five diffraction lines at 19.08^0, 22.17^0, 32.26^0, 38.74^0 and 40.82^0, when using x ray with λ = 154 pm. What is the type of cubic crystal formed from elements?

(4, 4, 4)

Q.9 Write short notes on any three of the following:

(a) Cleansing action of soap

(b) Law of crystallography

(c) Theory of acid-base indicators

(d) Activation energy of viscous flow

(3 x 4 = 12)

(20)

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S. No. of Question Paper : 3564

Unique Paper Code : 217203

Name of the Paper : **Analytical Methods in Chemical analysis** T

Name of the Course : **B. Sc. (H). Chemistry**

Semester : ~~VI~~ IV

Duration : 3 Hours Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper)

Attempt *five* questions in all.

Question 1 is compulsory

Use of scientific calculator/log table is allowed

1*(a)*. Differentiate the followings (any *three*): (2 x 3 = 6)

(i) Absolute uncertainty and relative uncertainty

(ii) Qualitative and quantitative analysis

(iii) Potentiometer and conductometer

(iv) Calomel and glass electrode

(v) Analytical molarity and equilibrium molarity

1*(b)*. Complete the following : (1 x 5 = 5)

(i) Difference between the experimental mean value and a true value is_____

(ii) _____chromatography involves the analytical separation of a chemical mixture based on the interaction of the adsorbate with the adsorbent

(iii) Partial removal of a substance from a solution or mixture by dissolving it in another, immiscible solvent in which it is more solubleis called_____

(iv) Point at which chemically equivalent quantities of bases and acids are mixed_____

(v) Wavelength of maximum absorbance is known as _____

1(c). Explain the mechanism of ion-exchange chromatography with suitable examples? (4)

2(a). Explain the principle of thermogravimetric analyzer (TGA). Sketch the flow diagram of instrument. (5)

2(b). A 0.6025 g sample was dissolved and the Mg^{2+} and Ca^{2+} ions present were precipitated as $MgC_2O_4.H_2O$ and $CaC_2O_4.H_2O$. The oxalates were then heated in a thermogravimetric apparatus leaving a residue that weighed 0.5713 g in the range of 320°C to 400°C and 0.4673 g in the range of 580°C to 620°C. Calculate the % mg and Ca in the sample? (5)

2(c). What do you mean by column efficiency and plate height? Explain. (5)

3(a). What do you understand by the term 'Accuracy and Precision'? Explain them by suitable examples? (3)

3(b). What are the sources of systematic errors and how can they be removed? (3)

3(c). What do you understand by term stationary and mobile phase? Give the stationary phase in case of paper and column chromatography? (3)

3(d). Give the emission wavelength observed for Ca, K and Mg in flame photometry? (3)

3(e). Analytical chemistry is a unique experimental science? Comment. (3)

4(a). What is the operational definition of pH? List the several sources of uncertainty in pH measurements with a glass reference electrode system? (5)

4(b). What do you mean by error in data? What are the sources of determinate errors? (5)

4(c). In solvent extraction of Uranium with 8-hydroxyquinoline in chloroform the volumes of the aqueous and organic phase were 25 ml when the % extraction was 99.8%. Calculate the distribution ratio.

5. Substance A and B have retention times of 16.40 and 17.63 min respectively on a 30 cm column. An unretained species passes through the column in 1.30 min. The peak widths (at base) for A and B are 1.11 and 1.2 min, respectively. Calculate. (3 x 5 = 15)

(i) Column resolution

(ii) Plate height

(iii) The average number of plates in column

(iv) The length of column required to achieve resolution of 1.5

(v) The time required to elute sample B on the column which gives an R_s value of 1.5

(5)

6*(a)*. Draw a schematic of a single beam flame atomic absorption spectrophotometer (5)

6*(b)*. Calculate (2 x 5 = 10)

(i) Average deviation

(ii) Standard deviation

(iii) Rejection of results

(iv) 90% confidence limit

(v) t-distribution

values are: 7.146, 7.098,, 6.942, 7.256 and 6.593 (n = 5)

7*(a)*. What is the principle of solvent extraction? Explain the mechanism of metal extraction by chelation. (5)

7*(b)*. What is standard electrode potential? What is the correlation between current and cell potential? (5)

7*(c)*. Potentiometric technique can be used in variety of titrations. Comment and justify by giving examples. (5)