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[This question paper contains 8 printed pages.]

Your Roll No. ....

Sr. No. of Question Paper : 2907

Unique Paper Code : 32171201

Name of the Paper : Organic Chemistry-I : Basics and Hydrocarbons I

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

Semester : II

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

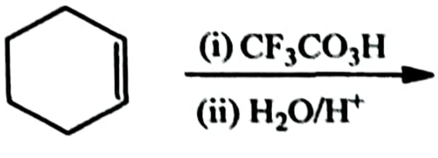
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **six** questions in all.
3. **All** questions carry equal marks.

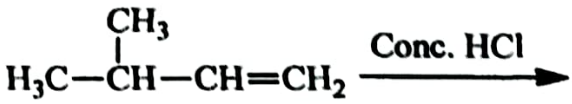
1. (a) An organic compound A (molecular formula C_6H_{10}) upon hydroboration-oxidation, mercuration-demercuration and acid catalyzed hydration gives same compound B . (molecular formula $C_6H_{12}O$).

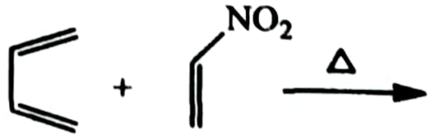
P.T.O.

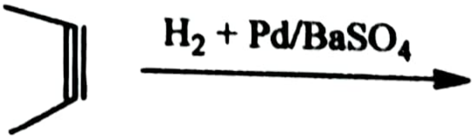
The reductive ozonolysis of A yields a dicarboxaldehyde C (molecular formula $C_6H_{10}O_2$). Write the structures of A, B and C. Also write the mechanism of ozonolysis reaction to obtain compound C from compound A.

(b) Complete the following reaction with product(s) including stereochemistry wherever applicable.

(i) 

(ii) 
$H_3C-\overset{CH_3}{\overset{|}{C}H}-CH=CH_2 \xrightarrow{\text{Conc. HCl}}$

(iii) 

(iv) 

(6,5,6)

2. Give reasons for the following statements :

   (i) The chair conformer of cyclohexane is more stable than its boat conformer.

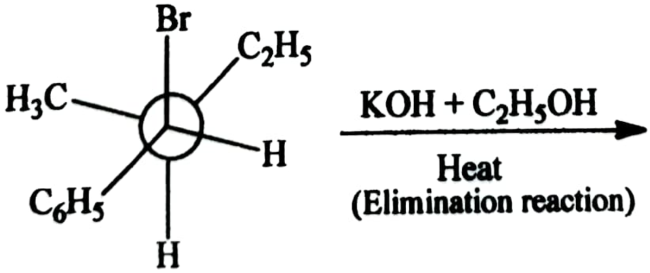
   (ii) Stability of alkanes increases with branching.

   (iii) Benzyl carbocation is more stable than isopropyl carbocation.

   (iv) Toluene undergoes electrophilic substitution reactions more easily than nitrobenzene.

   (v) *Ortho*-nitrophenol is more volatile than *para*-nitrophenol. (2.5×5)

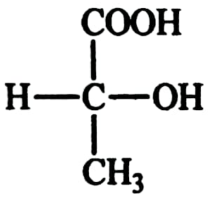
3. (a) Write the structure of product, assign E/Z configuration and state the type of elimination reaction in the following.



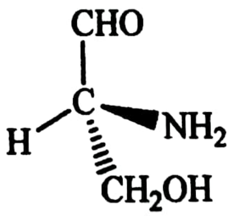
(b) Draw structures of all the mono-chloro derivatives of 3,4-dimethylhexane.

(c) When benzene reacts with n-propylchloride in the presence of anhydrous $AlCl_3$ it gives *iso*-propylbenzene (cumene) as major product. Write the mechanism. (4.5,4,4)

4. (a) Assigning priorities determine the configuration (R/S or E/Z) for the following compounds.



(i)



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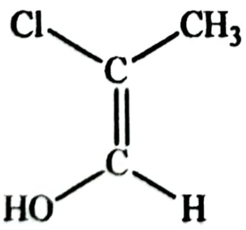

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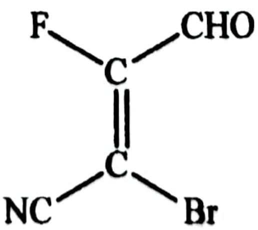
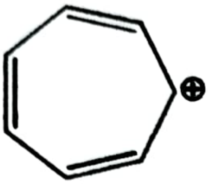
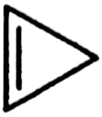
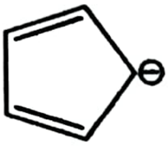


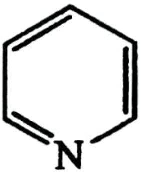
(iv)

(b) Classify with reason the aromatic and non aromatic compounds from the following.

(i) 

(ii) 

(iii) 

(iv) 

(6.5,6)

5. (a) How can you chemically differentiate between the following?

   (i) But-l-yne and But-2-yne

   (ii) Benzene and Toluene

(b) Write the products obtained on ozonolysis of 1,2-Dimethylbenzene.

(c) How can you convert the following?

   (i) 1-Bromopropane to 2-Bromopropane

   (ii) Bromoethane to Butane

   (iii) Propene to 3-Bromopropene (4,4,4.5)

6. (a) Arrange the following alkenes in increasing order of stability, also give suitable reason for your answer.

Isobutene, *Cis*-Butene, *Trans*-Butene, 1-Butene

(b) How can you differentiate between the cis- and trans-isomers on the basis of their physical properties?

(c) Discuss the order of stability of 1^0, 2^0 and 3^0 free radicals.

(d) Arrange the following compounds in increasing order of their acidic behavior. Also give plausible reason of your answer.

(i) $CH_3CH_2CH(Cl)COOH$

(ii) $ClCH_2CH_2CH_2COOH$

(iii) $CH_3CH(Cl)CH_2COOH$

(e) Draw Newmann projection of all conformers of 1,2-Dibromoethane. (2.5×5)

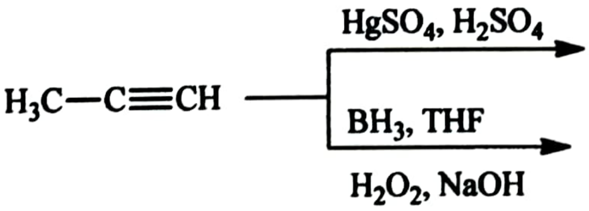
7. (a) A solution of organic compound (2.5 g) dissolved in acetone (100 mL) was taken in a polarimeter tube of length 10 cm and its optical rotation at 25°C was observed at +1.4°. Calculate the specific optical rotation.

(b) Write the mechanism of electrophilic aromatic substitution (ArES) reaction on arene.

(c) Define enantiomers and diastereoisomers with suitable example. (4.5,4,4)

8. (a) Complete the reaction by writing structure of product(s).

(i)



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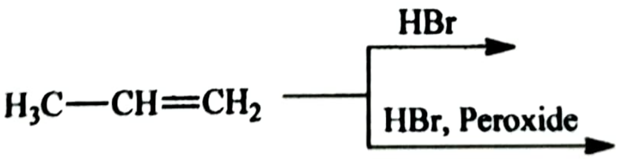
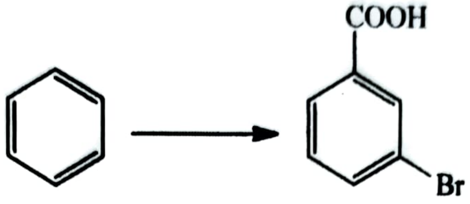
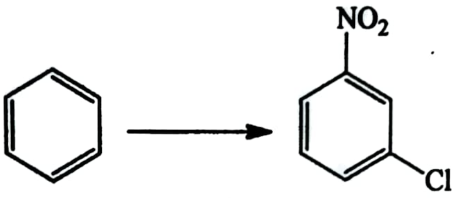
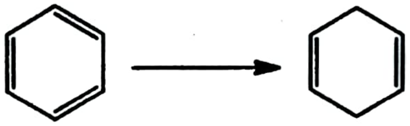


(b) Carry out the following conversions :

(i) 

(ii) 

(iii) 

(2.5×5

⑨ 30/5/24

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Your Roll No. ....

Sr. No. of Question Paper : 2961

Unique Paper Code : 32171202

Name of the Paper : Physical Chemistry II : Chemical Thermodynamics and its Applications

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

Semester : II

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. Question number **1** is compulsory.
4. Use of scientific calculators is allowed.

1. Explain, giving reason, any **five** of the following :

   (a) Enthalpy of neutralization of MgO(s) with HCl(aq) is very much higher than the accepted value $-57.32\ \text{kJ mol}^{-1}$.

(b) Why gases cool on expansion?

(c) Define the standard enthalpy of formation. Compare the values of standard enthalpy of formation for graphite and diamond.

(d) Why nitric oxide does not possess zero entropy at 0 K.

(e) Define Reaction Potential. Also write its expression.

(f) The thermal compressibility, α is equal to the reciprocal of temperature for a perfect gas.

(g) Can a process be spontaneous if there is decrease in the entropy of the system? Explain giving one example. (5×3)

2. (a) Five moles of an ideal gas at 293 K are expanded arc expanded-isothermally from an initial pressure of 0.4053 MPa to a final pressure of 0.1013 MPa against a constant external pressure of 0.101 MPa. Calculate q, w ΔU and ΔH.

(b) Show that the work involved in a reversible adiabatic expansion of an ideal gas from P_1 & V_1 to P_2 & V_2 is given by $w = nC_vT_1\left[\left(\frac{P_2}{P_1}\right)^{R/nC_P} - 1\right]$.

(c) Prove that the ratio of thermal compressibility (α) and compressibility factor (β) is $\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V$.

(4,4,4)

3. (a) For an Ideal gas $C_{p,m} = 5/2R$. Calculate the change in entropy for 3 mol of the gas on being heated from 300 K to 600 K at

(i) constant pressure and

(ii) constant volume.

(b) Give the Kelvin-Plank and Clausius statement of second law of thermodynamics. Also write one importance of second law over the first law of thermodynamics.

(c) Describe the Joule-Thomson experiment. Show that the expansion in this experiment is an Isenthalpic process. (4,4,4)

4. (a) Calculate $\Delta_r H^\circ_{373K}$ for the reaction

$$1/2N_{2(g)} + O_2(g) \rightarrow NO_{2(g)} \quad \Delta_r H^0_{373K} = -33.18 \text{ kJ mol}^{-1}$$

Given :

$C_{p,m}(NO_2, g) = 37.20 \text{ J K}^{-1} \text{ mol}^{-1}$

$C_{p,m}(O_2, g) = 29.36 \text{ J K}^{-1} \text{ mol}^{-1}$

$C_{p,m}(N_2, g) = 29.13 \text{ JK}^{-1} \text{ mol}^{-1}$

(b) Explain why Differential enthalpies (solution and dilution) are also called as Partial Molar Enthalpies.

(c) Enthalpy of neutralization of HCl by NaOH is -13.66 kcal mol^{-1}, HCl by NH_4OH is 12.03 kcal mol^{-1} and CH_3COOH by NaOH is 12.50 kcal mol^{-1}. Calculate the enthalpy of neutralization of CH_3COOH by NH_4OH and also calculate the enthalpy of dissociation of NH_4OH. (4,4,4)

5. (a) Prove that change in Gibbs free energy is non-PV work at constant temperature and pressure

(b) Starting with A = U – TS, prove

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V .$$

Also write one importance of this equation.

(c) Prove that the quantity $\left(\frac{\partial U}{\partial V}\right)_T$ is equal to the internal pressure for Van der Waal gas equation.

(4,4,4)

6. (a) Prove $\left(\frac{\partial\left({}^{\Delta A}\!/_{T}\right)}{\partial\, {}^{1}\!/_{T}}\right)_V = \Delta U$.

(b) Calculate the $\Delta_{mix}G$, $\Delta_{mix}H$ and $\Delta_{mix}S$ when 10 mol of gas A is mixed with 10 mol of gas B at 298 K and 1 bar pressure.

(c) Prove $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P}$. (4,4,4)

7. (a) Why chemical potential is also known as escaping tendency?

(b) Prove $\mu = \mu^0 + RT\ln(p)$ of an ideal gas, where μ^0 is the chemical potential when the initial pressure of the gas is 1 bar.

(c) What is Additivity rule. Write the Additivity rule for free energy, entropy and enthalpy.

(4,4,4)

8. (a) Write the Gibbs Helmholtz equation and derive the relation :

$$\left(\frac{d(\ln K_p)}{dT}\right)_p = \frac{\Delta H}{RT^2}$$

(b) The equilibrium reaction $N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g)$ was studied at 25°C with initial amount of N_2O_3 equal to 1.0 mol. At equilibrium the extent of reaction is found to be 0.3 mol for a total pressure of 1 bar. Calculate K^0_p and $\Delta_r G^0$ for the reaction.

(c) Differentiate between Q^0_p and K^0_p. (4,4,4)

9. (a) When 0.1 M aqueous solution of $K_4[Fe(CN)_6]$ is separated from 0.1 M $FeCl_3$ solution by a semipermeable membrane predict whether the blue color will appear in either of the compartments as a result of the reaction between $K_4[Fe(CN)_6]$ and $FeCl_3$ due to osmosis. Give reason in support of your answer.

(b) Explain by use of phase diagram why the normal boiling point of water is raised by addition of a non-volatile solute while the freezing point is lowered. Label all pertinent points explicitly

(c) Derive thermodynamically :

$$\Delta T_f = \frac{RT_0^2}{\Delta H_m} M_1 m_2$$

(4,4,4)

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This question paper contains 8 printed pages.] 03/6/24

Your Roll No...............

S. No. of Question Paper : 4113

Unique Paper Code : 2172011202

Title of the Paper : Haloalkanes, Arenes, Haloarenes, Alcohols, Phenols, Ethers and Epoxides

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

Semester : II

Duration : 2 Hours

Maximum Marks : 60

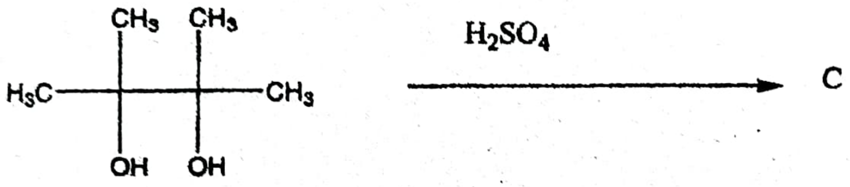
Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt all parts of a question together.
3. Attempt any **four** questions in all.
4. Question no. **1** is compulsory.
5. Each question carries **15** marks.

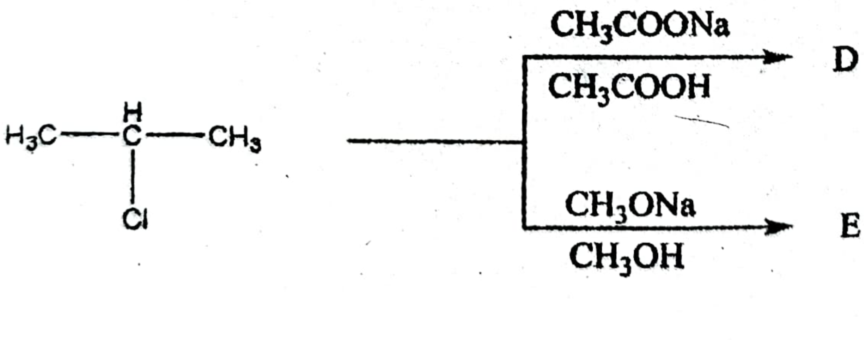
P.T.O.

1. (a) Complete the following reaction as indicated, identify and write their names-

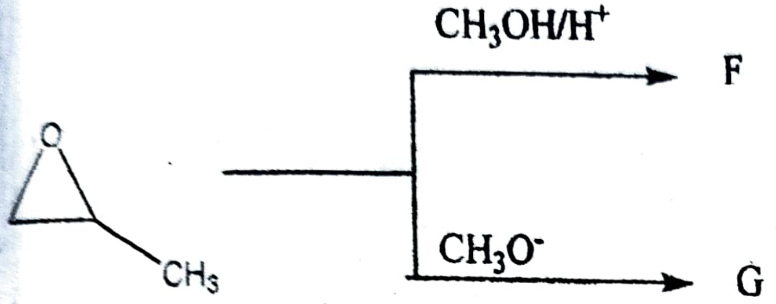
(i) $\text{Aniline} \xrightarrow[0\text{-}5^{\circ}C]{NaNO_2 + HCl} A \xrightarrow{CuBr/HBr} B$

(ii) 

(b) Write products of the following reactions and identify the mechanism involved-



(c) Write various steps in the reaction of given epoxide in the given conditions :



(5×3=15)

tify the given statements **(any three)**

Ethyl bromide reacts differently with KNO_2 and $AgNO_2$.

Aryl halides have very low reactivity towards Nucleophilic substitution reaction as compared to Alkyl halides and Benzyl halides.

Di-tertiary Butyl ether cannot be prepared by Williamson's ether synthesis.

Cleavage of phenyl alkyl ether with HI gives phenol and alkyl iodide. (5×3=15)

P.T.O.

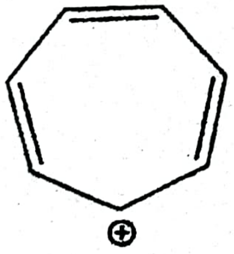
3. (a) Giving reasons arrange the following compounds as mentioned in parentheses

(i) t-butanol, n-butanol and isopropanol (towards lucas test)

(ii) o-methyl phenol, p-methyl phenol and m-methyl phenol (increasing order of acidity)

(b) Define aromaticity. Classify the following as aromatic or antiaromatic giving suitable explanation –

(i)



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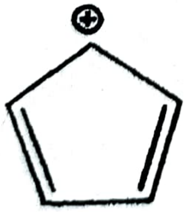
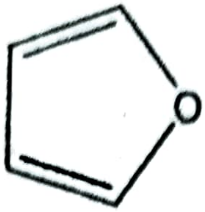
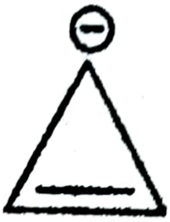


(iii) 

(iv) 

(c) Carry out the following conversions (Give complete chemical equations)

(i) Benzene to m-Dinitrobenzene

(ii) Methyl chloride to Ethanoic acid

(5×3=15)

Write reaction mechanism for the given reactions (any three)

(a) Cumene is oxidized in air and the resulting compound undergoes rearrangement in presence of an acid catalyst. Why is this method an industrial method of preparation?

(b) Esterification of ethyl alcohol with acetic acid in acidic medium.

(c) Reaction of ortho-bromotoluene with $NaNH_2$ in liq. NH_3.

(d) A compound 'A' reacts with CH_3MgBr to give Ethanol which upon oxidation with PCC gets converted to 'B'. Identify A and B. Write all the steps involved in the given reaction.

(5×3=15)

5. (a) What happens when 2-Butanol is treated with Thionyl chloride in presence and in absence of Pyridine?

(b) Out of $C_6H_5CH_2Cl$ and $(C_6H_5)_2CHCl$ which is more easily hydrolyzed by aqueous sodium hydroxide under S_N1 and S_N2 conditions and why?

(c) What are the limitations of reaction of benzene with CH_3Cl? Why these limitations are not there in reaction of benzene and CH_3COCl?

(5×3=15)

6. (a) Explain why Halogens in haloarenes are (i) weakly deactivating (ii) ortho/para directing.

(b) Taking Nitrobenzene as an example explain how a Nitro group deactivates the benzene ring towards electrophilic substitution reaction but at the same time it activates the ring towards Nucleophilic substitution reaction

(c) What happens when phenyl acetate is treated with $AlCl_3$ in presence of aq. HCl? Name the reaction and give mechanistic details. (5×3=15)

⑪ June 2024

[This question paper contains 8 printed pages.]

Your Roll No...............

Sr. No. of Question Paper : 4151

Unique Paper Code : 2172011203

Name of the Paper : CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS

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

Semester : II

Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. **Q. 1** is compulsory.
4. Use of scientific calculators is allowed.

1. Attempt any **five** :

   (a) Why is the Helmholtz free energy called as work function?

(b) Freezing occurs spontaneously below the freezing point although it leads to a more ordered state. Explain.

(c) Two liquids A and B are mixed in the ratio 1:2 in one solution and in the ratio 1: 3 in the second solution. Will the partial molar volume of A be same or different in the two solutions? Explain qualitatively.

(d) Efficiency of Carnot engine cannot be one or more than one. Why? Explain the implication of this in terms of second law of thermodynamics.

(e) Endothermic reactions are entropy driven processes. Explain.

(f) Is Hess's Law valid for heat exchanged 'q' in a process? Is it valid for entropy change 'ΔS'? Give reason for your answer.

(g) Why do gases diffuse spontaneously to form a homogeneous mixture? (5×3=15)

2. (a) Derive the relation $C_P - C_V = \left\{V - \left(\frac{\partial H}{\partial P}\right)_T\right\}\left(\frac{\partial P}{\partial T}\right)_V$ starting from the relation H = U + PV.

(b) Show that the magnitude of work involved in a reversible adiabatic expansion of an ideal gas is less than in isothermal expansion when the expansion is carried out between same initial and final volumes.

(c) An ideal gas at 30 Pa and 298K is expanded reversibly and adiabatically from a volume of 1.43dm^3 to 2.86dm^3. If $C_{P,m}$ = 29.1JK^{-1} mol^{-1}, calculate the final T and P of the gas and q, w and ΔU for the process. (5,5,5)

3. (a) Using an indicator diagram show that more work has to be done by the surroundings in compressing a gas in an irreversible process than in a reversible process.

(b) Prove that the criterion of $\Delta G < 0$ for predicting the spontaneous nature of a process is completely equivalent with that of $\Delta S_{total} > 0$.

(c) Define enthalpy of combustion.

Calculate the enthalpy of formation of methane from the given data :

Enthalpy of combustion of methane = –890.36 kJ mol^{-1}, enthalpies of formation of carbon dioxide and water = –393.13 kJ mol^{-1} and –285.58 kJ mol^{-1} respectively. (5,5,5)

4. (a) For an isothermal reversible expansion of a van der Waals gas show that

$$w = -nRT\ln\frac{V_2 - nb}{V_1 - nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

(b) Describe the Joule-Thomson experiment. Show that the expansion in this experiment is an isenthalpic process. Define Joule Thomson coefficient.

(c) Using the given data, calculate the enthalpy of formation of acetic acid :

(i) Enthalpy of sublimation of graphite = 718.39 kJ mol^{-1},

(ii) Enthalpy of dissociation of hydrogen gas = 435.97 kJ mol^{-1}

(iii) Enthalpy of dissociation of oxygen gas = 495.04 kJ mol^{-1}

(iv) $\varepsilon_{C\text{-}H}$ = 413.38 kJ mol^{-1}, $\varepsilon_{C\text{-}C}$ = 347.69 kJ mol^{-1}, $\varepsilon_{C=O}$ = 728.02 kJ mol^{-1}, $\varepsilon_{C\text{-}O}$ = 351.46 kJ mol^{-1}, $\varepsilon_{O\text{-}H}$ = 462.75 kJ mol^{-1}.

(5,5,5)

6.

5. (a) Show that ΔG_{mix} has minimum value and ΔS_{mix} has maximum value for a binary mixture of ideal gases when the mixture is equimolar.

(b) Predict if ΔS_{sys} is positive, negative or zero in each of the following giving reason

(i) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(ii) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

(iii) Reversible adiabatic expansion of an ideal gas

(iv) Reversible isothermal expansion of ideal gas

(v) Stretching of a rubber band

(c) Calculate ΔS for the transformation H_2O (s, 0°C, 1bar) $\rightarrow$ H_2O (g, 100°C, 1bar) if $T_m = 0°C$, $\Delta_{fus}H = 6.01 kJmol^{-1}$, $T_b = 100°C$, $C_p(H_2O, l) = 75.24 JK^{-1} mol^{-1}$ and $\Delta H_{vap} = 40.65 kJmol^{-1}$. (5,5,5)

6. (a) Show that for an isothermal change in an ideal gas

$$\Delta G = nRT \ln \frac{p_2}{p_1} = nRT \ln \frac{V_1}{V_2}.$$

Glucose is oxidized to CO_2 and water according to the equation:

$$C_6H_{12}O_6\ (s) + 6O_2(g) \rightarrow 6\ CO_2(g) + 6H_2O\ (l)$$

In this process $\Delta U = -2810\ kJmol^{-1}$ and $\Delta S = 182.4\ JK^{-1}$ at 25°C. How much of this energy change can be extracted as (a) heat (b) work?

(b) The enthalpy of neutralization of HCl with NaOH is $-57.3\ kJmol^{-1}$; enthalpy of neutralization of CH_3COOH with NaOH is $-49.86\ kJmol^{-1}$ and enthalpy of neutralization of NH_4OH with HCl is $-51.34\ kJmol^{-1}$.

(i) How much heat will be evolved when 50mL of 1N HCl is mixed with 50mL 0.9N NaOH?

(ii) Calculate enthalpy of ionization of CH_3COOH and of NH_4OH.

(iii) What is the enthalpy of neutralization of NH_4OH with CH_3COOH?

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(c) Derive the relationship between $\Delta_r G^\circ$ and $\Delta_r A^\circ$ for a chemical reaction. At 298K ΔG for the reaction $C_6H_6(l) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ is -9.26 kJmol^{-1}. Find ΔA for the same reaction at 298K. (5,5,5)

7. (a) Derive the relation $\left\{\frac{\partial\left(\frac{\Delta_r G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right\}_p = \Delta_r H.$

(b) The free energy change of a reaction, $\Delta_r G$ is positive. Is there any way by which this reaction can be made to proceed? Explain with examples.

(c) Calculate $\Delta_f H^\circ$ at 373K for the reaction

$\frac{1}{2} N_2(g) + O_2(g) \rightarrow NO_2(g)$ Given that $\Delta_f H^0$ at 298K $= -33.18$ kJ mol^{-1}

$C_{p,m}(NO_2, g)/J\,K^{-1}\,mol^{-1} = 27.78 + 30.85 \times 10^{-3}(T/K)$

$C_{p,m}(N_2, g)/J\,K^{-1}\,mol^{-1} = 28.46 + 2.26 \times 10^{-3}(T/K)$

$C_{p,m}(O_2, g)/J\,K^{-1}\,mol^{-1} = 26.85 + 8.49 \times 10^{-3}(T/K)$

(5,5,5)

8. (a) Derive the relation $\Delta S = C_v \ln\frac{T_f}{T_i} + \frac{\alpha}{\kappa}(V_f - V_i)$ starting from dU = dq + dw.

(b) How are extremely low temperatures achieved? Why is it not possible to attain absolute zero in a finite number of steps?

(c) A solution of 60 mole% ethanol in water has to be prepared. The partial molar volumes of ethanol and water in this solution are 57 cm^3 mol^{-1} & 16 cm^3 mol^{-1} respectively. The molar volumes for pure water and ethanol are 18.0 and 58 cm^{3}mol^{-1} respectively. Calculate the volumes of ethanol and water that should be mixed to get 3 m^3 of this solution. (5,5,5)

(2000)