Tutorial Sheet- CHEM-1001 (for session July 2017 – December 2017- Odd semester**)**

Unit-1 Fuels & Thermochemistry

1. Evaluate the standard enthalpy of combustion of propene, if standard enthalpies of combustion of propane and water are -2220KJ/mol and -286KJ/mol respectively. The standard enthalpy of hydrogenation of propene is -124KJ/mol.
2. Define the various characteristics of a good fuel.
3. Write short notes on Isomerization and its relation to petroleum industry.

4. (i) Describe the fractional distillation method for getting the various component of fuel from the petroleum.

   (ii) Compare the solid, liquid and gaseous fuel on the basis of their properties.

5. A sample of fuel oil analysis is as follows: 85% C, 6% H, 4.5% S, 2% O and 2.5% ash. This oil was employed for heating in a furnace with 30% excess air. Calculate the amount of air used per kg of fuel.
6. Why there is a need for various important reactions e.g. Isomerization, Dimerization, Aromatization, Cracking for petroleum industries? Discuss each one of the above giving an example.
7. A 0.500 g sample of Tri Nitro Toluene was burned in a bomb calorimeter containing 610 grams of water at an initial temperature of 293K. The heat capacity of the calorimeter is 400 grams and the HCV of TNT is 3.7 Kcal/gm. With these given data, find out the final temperature of the water and calorimeter after the completion of reaction.
8. What is the role of $CuSO_4$ and K_2SO_4 in the estimation of nitrogen content of any sample by Kjeldahl

method? A sample was digesting having the weight 0.9814 g by Kjeldahl method. The formed nitrogen was oxidized to NH_4^+, and then converted to NH_3 with NaOH, and the formed NH_3 was distilled into a collection flask contain 40.00 mL of 0.104 M HCl. The excess HCl was back titrated with 0.113 M NaOH, requiring 22.00 mL. What is the % of nitrogen content the sample?

9. (i) Calculate the weight and volume of air required for complete combustion of 1 kg of fuel containing 85% C, 2.5% H, 4% O, 2.5% S, 1% H_2O, 0.9% N and rest ash.

   (ii) Discuss the significance of isomerization reaction for petroleum industries.

   (b) Identify the pressure of oxygen over a sample of NiO(s) at 25 ^oC, if ΔG^o for the reaction is 211.7 kJ mol^{-1}. $NiO(s) \rightleftarrows Ni(s) + \frac{1}{2} O_2(g)$

10. 0.8 g sample of benzene is combusted in bomb calorimeter. The heat of formation of benzene, water and carbon dioxide are +11.72 KCal, -68.32 Kcal/mole and -94.05 Kcal/mole respectively at 25 ^{o}C. Calculate gross and net calorific value of benzene.

11. The determination of calorific value of a coal sample gives the following data-

Wt. of coal sample= 0.9 g
Water equivalent of calorimeter = 440 g
Wt. of water = 2500 g
Rise in temperature = 2.42 ^{O}C
Cooling correction = 0.052 ^{O}C
Fuse wire corrections = 10 Cal
Estimate the gross and net calorific value if the coal contains 6% hydrogen. Assume the latent heat of steam is 600 Cal/g.

12. Calculate the mass and volume of air required for the complete combustion of 5 Kg of coal containing 91% C, 5% hydrogen and rest is oxygen.

13. For the reaction: $CO(g) + Cl_2(g) = COCl_2$ (g) [ΔH° = -108 kJ]; The standard molar heats of combustion of C(graphite) and CO(g) are -393.5 and -285 Kj/ mol and respectively. Calculate the standard molar enthalpy of formation of $COCl_2$ (g).

14. 0.2475 g of an organic substance gave on combustion 0.4950 g of CO_2 and 0.2025 g of water. Calculate the % of carbon and hydrogen in it.

15. A sample of coal was analysed by taking exactly 1.40 g in a silica crucible. After heating for 1 hour at 110^{0}C, the residue weighed 1.125g. The crucible next was covered with a vented lid and strongly heated for exactly 7 minutes at 950±20^{0}C. The residue weighed 1.005 g. The crucible was then heated without cover, until a constant weight was obtained. The last residue was found to weigh 0.215 g. Analyze the percentage of fixed carbon content of the coal sample?

16. 1.5 g of a fuel sample was burnt with H_2SO_4 followed by KOH treatment, the formed ammonia gas was absorbed in 100mL of decinormal solution of H_2SO_4. The excess acid required 40 mL of N/20 NaOH. Estimate the % nitrogen present in fuel sample?

17. Illustrate the method of determination of carbon and hydrogen in coal sample.

18. Explain why- (i) Crucible is covered with lid for determination of volatile matter and

(ii) A minimum amount of moisture is required in a coal sample.

19. A coal sample 2.65 grams, was weighed in a silica crucible. After heating for an hour at 110 ^{0}C, the residue weighed 2.28 grams. The crucible next was covered with a vented lid and strongly heated to exactly 7 minutes at 950±20 ^{0}C. The residue weighed 1.728. The crucible was then heated without cover, until a constant weight was obtained. The last residue as found to weigh 0.275 g. Calculate the % moisture, volatile contents, ash and fixed carbon content in the sample.

20. The analysis of an organic compound gave the following data:

0.4020g gave 0.6098g CO_2 and 0.2080g H_2O.

0.1033 g of sample gave 0.2772 g $BaSO_4$

1.01g by Kjeldahl method produced ammonia which was neutralized by

23.2ml of N/2 HCl. Determine % of C, H, S and N contents in the sample.

21. Discuss any two important processes with reactions, used to enhance the quality of gasoline. Describe five important parameters for determination of efficiency of good fuel.

22. Calculate the heat of formation of naphthalene at 27 ^oC, if enthalpy of formation of CO_2 and H_2O are -393.5 and -285.8 kJ/mole respectively. Enthalpy of combustion of naphthalene at constant volume is -5100 kJ/ mole.

23. W g. benzene was completely burnt in tube furnace using excess amount of dry oxygen and exhaust gas was allowed to absorb in excess amount of conc. KOH solution. After the experiment an increment of 2.0 g was observed in weight of KOH solution. Calculate weight of benzene that was subjected to combustion.

24. 0.257 g of an organic substance was heated with conc. H_2SO_4 and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 ml of N/10 HCl, which required 23.2 ml of N/10 NaOH for neutralization at the end of the operation. Determine the % of nitrogen in the substance.

25. (i) The enthalpies of combustion of carbon, hydrogen and sucrose are -393.5, -286.2 and - 5644.2 $Kjmol^{-1}$ respectively. Evaluate the enthalpy of formation of sucrose.

(ii) On burning a 0.78g of a solid fuel in a bomb calorimeter the temperature of 2100g of water increased from 24.4 to 26.7 ^oC. The water equivalent of calorimeter is 234g. If the fuel contains 1.2% hydrogen and 79.7% carbon, assess the gross and net calorific value for this fuel.

26. 0.4 g of an organic compound was Kjeldahlised and ammonia evolved was absorbed into 50 ml of seminormal solution of H_2SO_4. The residual acid solution was diluted with distilled water and the volume was made upto 150 ml. 20 ml of this diluted solution required 31 ml of N/20 NaOH solution for complete neutralization. Calculate the % of nitrogen in the compound.

27. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3,500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 call g, respectively. If the fuel conations 0.7% hydrogen, calculate its gross and net calorific value.

28. A sample of coal contains: C = 93%, H = 6% and ash = 1%. The following data were obtained when the above coal was tested in a bomb calorimeter:

(i) Weight of cool burnt = 0.92 g

(ii) Weight of water taken = 550 g

(iii) Water equivalent of bomb and calorimeter = 2,200 g

(iv) Rise in temperature = 2.42 °C

(v) Fuse wire correction = 10.0 cal

(vi) Acid correction = 50.0 al.

Calculate the gross and net calorific value of cool, assuming that the latent heat of condensation of steam is 580 cal/g

29. A sample of coal was analyzed as follows:
Exactly 1.40 g was weighed in a silica crucible. After heating for one hour at 110°C, the residue weighed 1.10 g. The crucible next was covered with a vented lid and strongly heated for exactly 7 minutes at 950±20°C. The residue weighed 1 g. The crucible was then heated without cover, until a constant weight was obtained. The last residue was found to weigh 0.21g. Calculate the % results of the above analysis.

30. Calculate the heat of formation of one mole of CH_3CHO, using the data given below. Heat of vaporization of C(s), i.e. C(s) → C (g) = 170 kcal. Bond energies are C-C = 80 kcal, C-H = 98 kcal, H-H = 103 kcal, O=O = 118 kcal, and C=O = 173 kcal.

31. Standard heat of combustion of acetylene, ethane and hydrogen are -1301, -1561 and -286 kJ/mole respectively. Calculate the heat of hydrogenation of acetylene.

32. Calculate the enthalpy of formation of cynamide, CH_2N_2, if enthalpies of formation of CO_2 and H_2O are -93.97 kcal/mole and -68.32 kcal/mole respectively. Given: $CH_2N_2(s) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + H_2O$ (l) + N_2 (g), ΔH= -177.2 kcal/mole.

33. The standard heat of formation of $C_2H_5OH_{(l)}$, $CO_{2\ (g)}$ and $H_2O_{(l)}$ are -277, -393.5 and -285.5

Kj/mol respectively. Calculate the standard heat change for the reaction

$$C2H5OH\ (l) + 3O2\ (g) \longrightarrow 2CO2\ (g) + 3H2O\ (l)$$

34. Calculate the mass of air needed for complete combustion of 5 Kg of coal containing 80% carbon, 15% hydrogen and rest is oxygen.

35. From the following information, calculate the energy of C-H and C-C bonds. Energy absorbed in the dissociation of ethane into gaseous atoms is 584.6 kcal.

a. $C(s) + 2H_2(g) \rightarrow CH_4(g)$ ΔH = -22.4 kcal

b. $H_2(g) \rightarrow 2H(atom, g)$ ΔH = 103 kcal

c. $C(s) \rightarrow C(atom, g)$ ΔH = 125 kcal

36. Evaluate the standard enthalpy of formation for glucose using the following data: ($\Delta H°$Combustion of glucose = -2800.8 kJ/mol; $\Delta H°$formation of CO_2 = -393.5 kJ/mol and $\Delta H°$ formation of H_2O = -285.8 kJ/mol).

37. Determine the theoretical weight and volume of air required for the combustion of 4kg petrol sample containing 80% C, 4.5% H, 4% O, 1.5% S, 2% N, and rest ash. Also determine the actual weight of air if the sample requires 20% extra air for complete combustion.

UNIT-2 REACTION DYNAMICS

1. For the reaction, $2NOCl\,(g) \rightleftharpoons 2NO(g) + Cl_2\,(g)$

10.0 moles of NOCl were initially placed in a five liter flask. After the equilibrium the flask contains 3.30 moles of NOCl. Calculate the equilibrium constant at 25 ^{0}C for the reaction.

2. A first order reaction, $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ has rate constant of 2.2 x 10^{-5} sec^{-1} at 320 ^{o}C. What % of SO_2Cl_2 will be decomposed on heating this gas for 90 min?
3. In first order reaction 25% decomposition requires 40.4 minutes. Calculate the rate constant.
4. Calculate the value of rate constant (K_1) for the following reaction, assuming the initial concentration of [A]=a & [B]=0.

$$A \underset{K2}{\overset{K1}{\rightleftharpoons}} B$$

5. For the reaction: $CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$; the value of K at 552 ^{0}C is 0.137. If 5 moles of CO_2, 5 moles of H_2, 1 mole of CO and 1 mole of H_2O are initially present, what are the actual concentrations of all reactants and products at equilibrium?

6. The first order reaction has rate constant 1.5 x 10^{-6} sec^{-1} at 200 ^{o}C. If the reaction is allowed to run for 10 hours, identify the percentage of the initial concentration of the reactant which will be converted into the product. What is the half-life of the reaction?

7. Derive the rate constant equation (k_3) for 3rd order reactions of type, 3A → Products, mention its unit.

8. Draw an energy diagram for a reaction where ΔH = -40 kJ, the activation energy of the uncatalyzed reaction is +120 kJ, and the activation energy for a catalyzed reaction is + 80 kJ. Locate the position of the activated complex for both catalyzed and uncatalyzed reactions on the diagram?
9. A first order reaction is 25% completed in 30 minutes. Calculate (i) rate constant (ii) Half-life (iii) time required for 75 % conversion to be completed.
10. Following reaction takes place in a single step.

$$2NO(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

How many times the rate of above reaction changes if the volume of reaction vessel is decreased to one third of its original volume?

9. Given the following experimental data, find out the order of reaction w.r.to each reactant and overall order of reaction.

$$NO(g) + NO_2(g) + O_2(g) \longrightarrow N_2O_5(g)$$

Sl. No.	[NO]	[NO_2]	[O_2]	RATE (M/min)
1	0.10 M	0.10 M	0.10 M	2.1×10^{-2}
2	0.20 M	0.10 M	0.10 M	4.2×10^{-2}
3	0.20 M	0.30 M	0.20 M	1.26×10^{-1}
4	0.10 M	0.10 M	0.20 M	2.1×10^{-2}

10. 50 % of first order reaction is completed in 231 minutes. Calculate the time required to complete 90 % of the reaction.

11. In the vapour phase decomposition of ethylene oxide, $C_2H_4O \rightarrow CH_4 + CO$ at 414.5°C, the initial pressure and the pressure after 5 minute were 116.51 mm and 122.56 mm of Hg respectively. If the reaction follows first order kinetics, what must be the pressure after 12 minute?

12. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 15.2 - \left(\frac{12000}{T}\right)$$

Calculate the value of E_a for the above reaction and rate constant (k) if its half-life period will be 100 minutes. (Given: R= 8.314 $JK^{-1}mol^{-1}$).

13. Rate constant for first order reaction is 2.31×10^{-3} Minute. Calculate its half life time.

14. Derive a rate law expression for second order reaction of following type-

$2A \rightarrow$ Product

1. In an experiment at 490^0 C, the following equilibrium composition was obtained for the reaction $H_2 + I_2 \Leftrightarrow 2HI + heat$, [$H_2$] = 8.62×10^{-4} mol/lt, [I_2]= 2.63×10^{-3} mol/lt, [HI] = 1.02×10^{-2} mol/lt. Calculate equilibrium constant and calculate ΔG^0.

15. (i) For the reaction, $CO_{(g)} + \rightleftharpoons 2H_{2(g)}$ $CH_3OH_{(g)}$, hydrogen gas was introduced into a five litre flask at 327 ^{0}C containing 0.2 mole of $CO_{(g)}$ and a catalyst, until the pressure was 4.92 atm. At this point, 0.1 mole of $CH_3OH_{(g)}$ is formed. Calculate K_p and K_c.

(ii) For the given homogenous reaction, $NO_2 \rightleftharpoons 2NO$, derive the relationship between K_p and degree of dissociation.

16. A Ist order reaction is 50% complete in 30 minutes at 27 ^{0}C and in 10 minutes at 47 ^{0}C. Calculate the rate constant for reaction at 27 ^{0}C and 47 ^{0}C, and energy of activation for

reaction.

17. For the following reversible reaction:

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

Demonstrate the integrated rate expressions:

$$\ln \frac{x_{eq}}{x_{eq} - x} = k_f \frac{[A]_0}{x_{eq}} t$$

$$ln \frac{x_{eq}}{x_{eq} - x} = (k_f + k_b)t$$

18. Discuss, in brief, various methods for the determination of order. Describe the graphical method by taking example of second order reaction. How will you determine the rate constant from graph?

19. Illustrate the expression for Lindeman mechanism for unimolecular reaction in gaseous state. Correlate the effect of pressure and order of reaction.

20. For the reaction, $H_2 + Br_2 \rightarrow HBr$

Demonstrate that, $\frac{d[HBr]}{dt} = \frac{K'[Br_2]^{1/2}[H_2]}{1+K''\frac{[HBr]}{[Br_2]}}$

Where, $K' = 2k_2(\frac{k_1}{k_5})^{1/2}$ and $K'' = \frac{k_4}{k_3}$

Given that

$Br_2 \xrightarrow{k_1} 2Br$

$Br + H_2 \xrightarrow{k_2} HBr + H$

$H + Br_2 \xrightarrow{k_3} HBr + Br$

$H + HBr \xrightarrow{k_4} H_2 + Br$

$Br + Br \xrightarrow{k_5} Br_2$

21. The formation of phosgene from carbon monoxide and chlorine is occur as given below

$$CO + Cl_2 \longrightarrow COCl_2$$

A mechanism for the same is proposed as per below mentioned steps.

i. $Cl_2 \longrightarrow 2Cl\cdot$ (rate constant K_1)

ii. $2Cl\cdot \longrightarrow Cl_2$ (rate constant K_2)

iii. $CO + Cl\cdot \longrightarrow COCl\cdot$ (rate constant K_3)

iv. $COCl\cdot \longrightarrow CO + Cl\cdot$ (rate constant K_4)

v. $COCl\cdot + Cl_2 \longrightarrow COCl_2 + Cl\cdot$ (rate constant K_5)

Using suitable approximation determine rate of formation of $COCl_2$

22. For the reaction, $H_2 + NO_2 \rightarrow H_2O + NO$

The suggested mechanism is:

$H_2 + NO_2 \xrightarrow{k_1} H + HNO_2$

$H + NO_2 \xrightarrow{k_2} NO + OH$

$OH + H_2 \xrightarrow{k_3} H_2O + H$

$OH + NO_2 + M \xrightarrow{k_4} HNO_3 + M$

$OH + NO + M \xrightarrow{k_5} HNO_2 + M$

State the approximations at which the rate law would be given by:

$$\frac{-d[NO_2]}{dt} = \frac{k_1 k_3 [NO_2][H_2]^2}{k_4[NO_2][M] + k_5[NO][M]}$$

23. The following mechanism has been suggested for the thermal decomposition of NO_2

Overall reaction: $2NO_2 \longrightarrow 2NO + O_2$

Mechanism:

$$NO_2 + NO_2 \xrightarrow{K1} NO + NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{K2} NO_3 + NO$$

$$NO_3 + NO \xrightarrow{K_3} 2NO_2$$

$$NO_3 + NO_2 \xrightarrow{K_4} NO + NO_2 + O_2$$

Find the rate of reaction in terms of NO_2.

24. For the hydrolysis of ethyl acetate in aqueous solution, the following results were obtained:

Time(min.)	0	10	20
$[C_2H_5COOC_2H_5]$ (in mole/liter)	0.10	0.05	0.025

Show that it follows pseudo first order reaction, as the concentration of water remains constant.

25. The decomposition of aqueous hydrogen peroxide to gaseous oxygen and water is a first-order reaction. If it takes 6.5 hours for the concentration of H_2O_2 to decrease from 0.70 to 0.35M, how many hours are required for the concentration to decrease from 0.40 to 0.10 M?

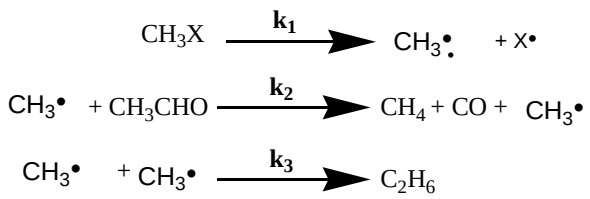
26. (i) Create a potential energy diagram that is represented by the following values of ΔH and E_a. You may make up appropriate values for the y-axis (potential energy). Is this an endothermic or exothermic reaction? Give appropriate justification(s).

$\Delta H = -100$ kJ and $E_a = 20$ kJ

(ii) Estimate the activation energy of a reaction whose rate constant doubles after 10^oC rise in temperature in the vicinity of 27^oC.

27. (i) In a study of the chemical reaction of methyl radicals with acetaldehyde vapour, CH_3X is used as a source of methyl radicals, which follows the first order

kinetics for its decomposition. A mechanism is proposed with the observed products as given below:



By applying the steady state approximation, derive an expression for the rate of formation of methane in terms of the concentrations of acetaldehyde and CH_3X.

UNIT-3 ELECTROCHEMISTRY AND CORROSION

1. Calculate the specific and molar conductance of a 0.0075M aqueous solution of KCl. Given: conductance is 1.49×10^{-3}S and cell constant is $1.05 cm^{-1}$.
2. A conductivity cell is filled with 0.05M KCl. Its specific conductance and observed resistance is $6.67 \times 10^{-3} \Omega^{-1} cm^{-1}$ and 243Ω, respectively. When the cell is filled with 0.01M NaOH, observed resistance is 681Ω. Calculate specific and molar conductance of 0.01M NaOH.
3. The resistance of a 0.1 N solution of an electrolyte occupying a volume between two platinum electrodes 1.55 cm apart having an area of 5.5 cm^2 is 52 ohm. Estimate the value of equivalent conductance of the solution.
4. At 25˚C, molar conductance of 0.01M aqueous solution of CH_3COOH is $16.32 \times 10^{-4} Sm^2 mol^{-1}$ and at infinite dilution is $390.72 \times 10^{-4} Sm^2 mol^{-1}$. Calculate degree of dissociation.
5. Calculate the equivalent conductance at infinite dilution of KOOC-COONa at 25 ^oC, if the ionic mobilities of Na^+, K^+ and $C_2O_4^{-2}$ are 0.00519, 0.000762 and $0.000768 cm^2 V^{-1} s^{-1}$, respectively.
6. The specific conductance of a decinormal solution of KCl at 18 ^0C is 1.12 Sm^{-1}. The resistance of a conductivity cell containing the solution at the same temperature was found to be 55 Ohm. Find out the value of cell constant.
7. Compute the value of equilibrium constant for the reaction at 25 ^oC.

   $Fe^{2+} + Ce^{4+} \leftrightarrow Fe^{3+} + Ce^{3+}$

   Given, $E^o_{Ce4+/Ce3+}$ = 1.44 V and $E^o_{Fe2+/Fe3+}$ = -0.68 V
8. A dilute solution of copper sulfate was electrolyzed between Pt electrodes. The amount of copper in the anodic solution was found to be 0.6350 g and 0.6236 g before and after electrolysis respectively. The weight of silver deposited in Ag-Coulometer, placed in series, was found to be 0.1351 g. Calculate transport number of copper and sulfate ions?

9. A person wants to buy an article. Same design is available in Zinc and Magnesium metal. As a chemist, which metal article would you suggest the person to buy and why? (Given that $E^o\ Mg^{2+}/Mg = -2.37V$, $E^o\ Zn^{2+}/Zn = -0.76V$)
10. On passing current through copper electrode dipped in copper sulfate solution, the total mass of copper deposited in a copper-voltammeter was observed 0.254 gm. The mass of copper sulfate around cathode solution, before and after electrolysis were 1.511 gm and 0.711 gm respectively. Applying the concept of Hittorf's rule, calculate the transport number of copper and sulfate ions? (Assume atomic weight of Copper=63.5 and Copper sulfate = 249.5)
11. Calculate the transport number of H^+ and Cl^- ions. Given that: Concentration of HCl solution = 0.1N
    Mass of Ag deposited in copper coulometer = 0.1209g, movement of boundary = 7.50cm and Cross-section of tube = $1.24cm^2$.
12. Calculate the moles of electrons passed through coulometer, transport number of H^+ and Cl^- from the following data obtained by Moving Boundary method using $CdCl_2$ as indicator electrolyte. Given that- [HCl] = 0.1 Mole/liter, movement of boundary (l) =7.50 cm, Cross sectional area of the tube (A) = 1.24 cm^2 and amount of silver (Ag, m.w. 108) deposited in Coulometer=0.2418gm
13. Differentiate the attackable and non-attackable electrodes for determination of transport number of electrolytes.
14. Examine the transport number of H^+ ion from the following data obtained by moving boundary method :
    Concentration of HCl solution = 0.10 N; weight of Ag deposited in the coulometer = 0. 12 g; distance moved by the boundary = 7.5 cm; diameter of the tube = 0.80 cm and equivalent weight of silver = 108
15. A decinormal solution of $AgNO_3$ was electrolyzed between platinum electrodes. After passing a small current for two hours, a fall of concentration of 0.0005124 gram equivalents occurred in the anodic solution. The mass of copper deposited in a copper coulometer placed in series was found to be 0.03879g. Calculate the transport numbers of Ag^+ and NO_3^- ions in $AgNO_3$.
16. Explain with reason:
    (a) Zinc container can be used to store a silver nitrate solution or not. Explain with suitable reason. Given, $E^o_{Ag+/Ag} = 0.80$ V and $E^o_{Zn^{2+}/Zn} = -0.76$ V.
17. What is the potential of zinc half-cell constructed by dipping metallic zinc wire in 0.10 M $ZnCl_2$ solution at 25°C, provided standard reduction potential of zinc is -0.76V. Concentration of employed $ZnCl_2$ solution drops to 0.09 M after few days as this salt is hygroscopic in nature. Calculate the modified value of EMF and suggest whether $ZnCl_2$ is suitable salt for cell construction.
18. Which of the following metals could provide cathodic protection to iron: Al, Zn, Ni, Cu
19. Wire mesh corrodes faster at the joints. Why?
20. What is differential aeration corrosion? Gives two examples of the same.

21. Explain the nature of different types of oxide layers formed on the metal surface in oxidation corrosion.

22. (a) (i) Describe the acid theory applicable to the rusting of iron.
(ii) Discuss the nature of metal oxide layer formed during oxidation reaction.

23. How does galvanic cell work and what is the role of salt bridge into it?
24. Explain the following:
    i. Iron nails undergo corrosion at the portion inside the wall
    ii. Grills in the windows always corrode at the joints.
    iii. Corrosion is a spontaneous process.
    iv. Two different ways of coating a surface to protect it from corrosion.
25. What is a sacrificial anode? Mention its role in corrosion control.
26. Deposition of dust and extraneous matter on metal furniture for a long period is undesirable.
27. If iron rod is dipped in pure degassed water, do you expect iron rod to be corroded? Explain with the help of given half-cell potential values:

$E^0 (Fe^{2+}/Fe) = -0.44$ V and $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$; $E^0 = -0.83$ V

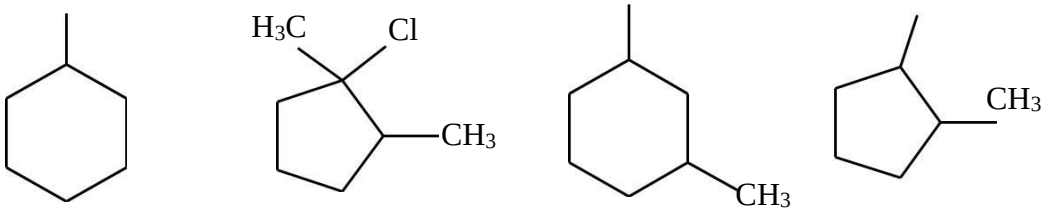
28. Determine the concentration of Cd^{2+} ions in the following electrochemical cell, $Fe, Fe^{2+}(0.1M) \| Cd^{2+}(x), Cd$

Given that EMF of the cell E = + 0.02 V and $E^0 = 0.04$ V

UNIT-4 ORGANIC CHEMISTRY

1. Give the mechanism of Wolf-Kischner and Clemmenson reduction.
2. Assuming only E_2 mechanism, write all the possible elimination products of:

$C(CH_3)_2Cl$ Br CH_2Cl

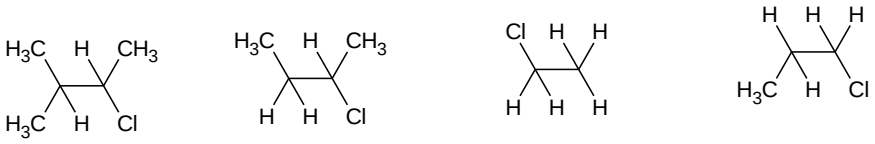


3. Discuss the geometry of carbocation with suitable diagram and correlate the geometry along with its stereochemistry, for the unimolecular nucleophilic substitution reactions.
4. Give an example where hydrolysis of alkyl halide may proceed according to SN_1 and one according to SN_2 mechanism.
5. Why is SN_2 displacement more difficult with 2-methyl-2-chlorobutane than with 2-methyl-1-chlorobutane?

6. (a) Examine the feasibility of nucleophilic substitution in vinyl chloride, allyl chloride, benzyl chloride and chlorobenzene with suitable reasoning.

(b) Arrange the following alkyl halide in increasing order of reactivity towards elimination reaction.

(6+2)



7. What distinguishes a nucleophile from a base? Identify stronger nucleophile each from the following three pairs: NH_2^- or NH_3; SH_2 or OH_2 and OH^- or CH_3^-
8. Arrange the following compounds in order of increasing acidity and explain your answer: $CH_3CH(Cl)CH_2COOH$, $CH_3CH_2CH(Cl)COOH$ and $CH_3CH_2CH_2COOH$.
9. Explain the following chlorides undergo solvolysis in the following order:

   a. $(C_6H_5)_3CCl > (C_6H_5)_2CHCl > C_6H_5CHClCH_3 > C_6H_5CH_2Cl$

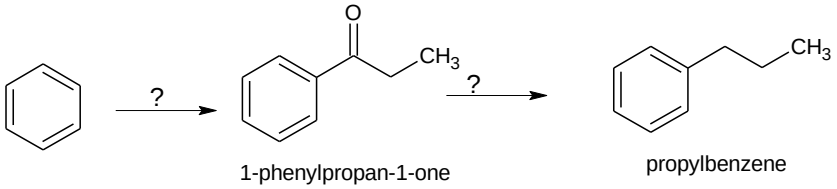
10. . Two Two elimination products are obtained from the following E_2 reaction:

$$CH_3\text{-}CH_2\text{-}CHD\text{-}CH_2Br \xrightarrow{OH^-/\Delta} A + B$$

(i) What are A and B? (ii) Which is obtained in greater yield and why?

11. Hydrocarbon A having molecular formula, C_4H_8 reacts with HI to yield B which on treatment with KOH in ethanol gives compound C. Compounds A and C are positional isomers and on reaction with bromine/CCl_4, yield a racemic mixture (D+E) and meso compound (F) respectively. Infer the compounds A-F and write the involved reaction sequence.

12. Complete the following two step synthesis of propyl benzene from benzene labeling suitable reagents, name of the reaction and type of the reaction involved.



13. Compound A with molecular formula C_4H_8 [exhibits geometrical isomerism] undergoes bromination to give a compound B with molecular formula $C_4H_8Br_2$ [exhibits optical isomerism] which on reaction with excess of alcoholic KOH with heating gives compound C with molecular formula C_4H_6. The compound C reacts with excess of BrOH to give compound D with molecular formula $C_4H_6Br_2O$. The compound D reacts with C_6H_5MgBr followed by H_2O to give compound E with molecular formula $C_{10}H_{12}Br_2O$. Interpret the above reactions giving the name of each compound.

14. Arrange the following compounds in decreasing order of reactivity for nucleophilic addition reaction: C_6H_5CHO; $C_6H_5COCH_3$; $C_6H_5COC_6H_5$; CH_3COCH_3; CH_3CHO.
15. Write down the mode of reaction in the following:

a. $CH_3Cl + KOH \rightarrow CH_3OH + KCl$

b. $C_6H_5CH_2Cl + KOH \rightarrow C_6H_5CH_2OH + KCl$

c. $(CH_3)_2CHCl + KOH \rightarrow (CH_3)_2CHOH + KCl$

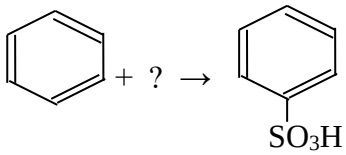
d. $(CH_3)_3CCl + KOH \rightarrow (CH_3)_3COH + KCl$

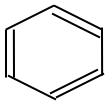
e. $(C_2H_5)_2CHCl + OH^- \xrightarrow{HCOOH} (C_2H_5)_2CHOH + Cl^-$

f. $(C_2H_5)_2CHCl + OH^- \xrightarrow{C_2H_5OH} (C_2H_5)_2CHOH + Cl^-$

16. Why is tertiary alkyl halide more prone to SN_1reaction?

17. State the missing in the following:

(i) 

(ii)  + $CH_3CH_2CH_2Cl \xrightarrow{AlCl_3}$?

(iii) 1-bromopentane + sodium ethoxide → ?

(iv) 1-bromopentane + potassium tert. Butoxide → ?

18. Discuss the role of □-hydrogens in E_2 elimination reaction giving an example.

19. Write a note on isomerization on alkanes.

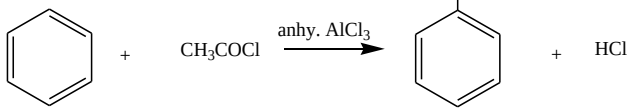
20. Write step 1 of the mechanism (generation of electrophile) for nitration, halogenation and sulphonation of benzene with proper reagents used and species formed

21. What is Fisher-Troph's synthesis? Discuss its applicability.

22. Explain why racemic mixture is obtained when cis but-2-ene undergoes addition reaction with bromine molecule in CCl_4?

23. Identify the type of reaction and mention the type of mechanism (electrophilic/ nucleophilic).

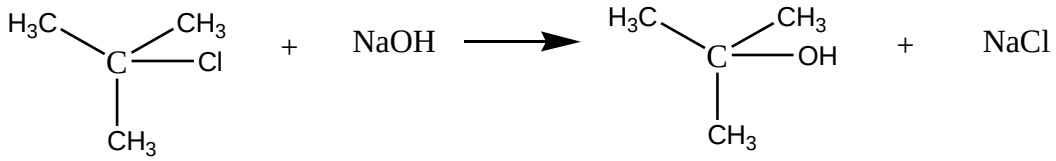
a. $CH_3CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CHBr - CH_2Br$

b. 

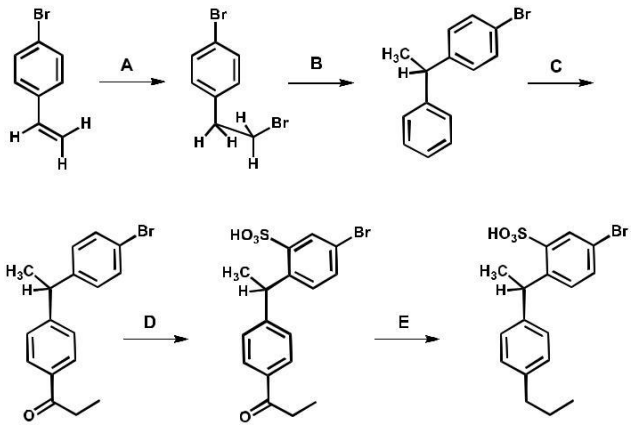
c.

$$CH_3CHO \quad + \quad HCN \quad \rightarrow CH_3CH(OH)CN$$

d.



24. Solve the reaction sequence with suitable reagents and name each of the transformation-



25. i) A compound 'A' with molecular formula C_8H_9Br reacts with aqueous NaOH to form 'B', which in turn reacts with conc. H_2SO_4 to give 'C'. 'C' on reaction with HBr forms 'D', an isomer of 'A'. Infer the structures of 'A', 'B', 'C' and 'D' to complete the reaction sequence and probable mechanism of the conversion A to B.

UNIT- 5 POLYMERS

1. Give Reasons:
    a. PVC is used for making electrical fittings.
    b. PMMA is a good substitute for glass.
    c. PP is used for making hospital accessories.
    d. Plasticizers are added to PVC.
    e. HDPE is used for storage applications.
    f. Melting point of polyurethanes is lesser than polyamides.
2. With structure give the monomers of:
    a. Nylon 6, 6
    b. PMMA
    c. PAN
    d. Polyester
3. Gives the mechanism of cationic polymerization giving a suitable example.
    4.Describe different types of polymers based on mode of reaction involved.
5. One gram of polymer sample contains a mixture of three polymers having molecular weights of 2500; 8000; and 13,000 g/mol in a ratio of 0.25:0.25:0.50. Find out the Mn and Mw of the sample.

    6. (a) Apply the concept of vulcanization of natural rubber with the help of chemical reactions?
    (b) A polymer has considered to be made of following molecules as per given below-

No. of moles	5	10	10	10
Molecular mass	3000	6000	9000	12,000

7. Find out the value of $\overline{Mn}$ and $\overline{Mw}$ of the polymer.
8. In a polymer sample, 30 % of the molecules have a molecular mass 20000; 40 % have 30000 and the rest have 60000. Finds out the number average (Mn), Weight average (Mw) molecular mass of the polymeric mixture.
9. Discuss the various types of plastic material with special reference to their monomers, types the polymerization, uses in our daily life and possible hazards.
10. Explain a suitable polymerization technique that you will suggest for polymerization of water insoluble monomer.
11. Write short notes on tacticity of polymers and vulcanization.

12. State the disadvantages of the solution polymerization technique. Explain the technique in which polymer is obtained in the form of beads.
13. Discuss the advantages and disadvantages of plastic use in daily life.
14. Write a note on vulcanization.
15. Give base catalyzed mechanism for the formation of phenol formaldehyde resin.
16. Compare isotactic, syndiotactic and atactic polymers with examples.
17. Give the applications of biopolymers.
18. The number average molecular weight of polystyrene is 10^6g/mol. Find the number average degree of polymerization.
19. Find weight average molecular weight of polyethylene, given its degree of polymerization as 10,000.
20. One gram of polymer sample contains a mixture of three polymers having molecular weights of 2500; 8000; and 13,000 g/mol in a ratio of 0.25:0.25:0.50. Find out the Mn, Mw, Mz and PDI of the sample.
21. In a polymer there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10000. Find number average molecular weight (M_n), weight average molecular weight (M_w) and poly dispersity index (PDI).

<u>UNIT- 6</u> NANO CHEMISTRY

1. What are nanomaterials in two dimensions? Explain with two examples.
2. Write different application areas of nanomaterials specifying their properties responsible for those applications with examples.
3. Explain microemulsion synthesis method for nanoparticles.
4. The properties of nanoparticles change drastically when they are being formed from macro size. Why? Explain the surface properties of nanoparticles in detail.
5. What are nanomaterials? Classify them with suitable examples.
6. Describe sol-gel synthesis for producing nanomaterials? Explain the same with the help of diagram.
7. The first order diffraction of X-rays from a certain set of crystal planes occurs at an angle of 11.8^o from the planes. If the planes are 0.281 nm apart, predict the wavelength of the X-rays used?
8. In Bragg's reflection of x-ray, a reflection was found at 300 with lattice plane of spacing 1.87 Å. If this is second order reflection, calculate the wavelength.

9. The distance between the layers in a NaCl crystal is 282 pm. X-rays are diffracted from these layers at an angle of 48^o. Assuming first order diffraction, predict the wave length of X-rays in nm.

10. In a system, the cubic crystals were present, with each having the volume of 27 cm^3. If the volume of each crystal is decreased to 1 cm^3, evaluate the extent to which surface area per unit volume will be affected with respect to the initial value?

11. Fill the value of the inter planner distance (d) obtained through XRD analysis of a nano particle having third order reflection in both cases.

Sample	**Lambda(in nm)**	**2theta values**	**d(in nm)**
A	18	30	?
B	36	40	?