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**UNIVERSITY OF PETROLEUM
AND ENERGY STUDIES**



End Semester Examination – May 2016

Program/course: B.Tech. (CS-OSS, CS-TI, CS-Mainframe, CS-O&G, CS-CCVT, ADE, APE-Gas, APE-UP, AE, ASE, Chemical, FSE, MSNT)

Subject: CHEMISTRY

Code : CHEM-107

No. of page/s: 3

Semester– IInd

Max. Marks: 100

Duration: 3 Hrs

Instructions - Read all the below mentioned instruction carefully and follow them strictly

- 1) Mention Roll No. at the top of the question paper
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- 4) All questions are compulsory.
- 5) Internal choice is given for question number 8-10 and 12.

SECTION-A

(4 x 5= 20 Marks)

1. 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	λ (in nm)	2θ	d(in nm)
A	18	30	?
B	36	40	?

2. A first order reaction, $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$ has rate constant of $2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What % of SO_2Cl_2 will be decomposed on heating this gas for 90 min?
3. Discuss the role of β -hydrogens in E_2 elimination reaction giving an example.
4. What is differential aeration corrosion? Gives two examples of the same.
5. Write a short note on activation energy for a first order reaction giving suitable diagram of the same.

SECTION- B

(8 x 5= 40 Marks)

6. Write different application areas of nanomaterials specifying their properties responsible for those applications with examples.
7. (a) 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 .
(b) 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.
8. Classify polymers on the basis of thermal response, tacticity and final utility giving suitable example of each one. **OR**
Discuss the role of surfactant in emulsion and suspension polymerization. Explain why CMC is important in emulsion polymerization.

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



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

- i. $\text{Cl}_2 \longrightarrow 2\text{Cl}^\cdot$ (rate constant K_1)
- ii. $2\text{Cl}^\cdot \longrightarrow \text{Cl}_2$ (rate constant K_2)
- iii. $\text{CO} + \text{Cl}^\cdot \longrightarrow \text{COCl}^\cdot$ (rate constant K_3)
- iv. $\text{COCl}^\cdot \longrightarrow \text{CO} + \text{Cl}^\cdot$ (rate constant K_4)
- v. $\text{COCl}^\cdot + \text{Cl}_2 \longrightarrow \text{COCl}_2 + \text{Cl}^\cdot$ (rate constant K_5)

Using suitable approximation determine rate of formation of COCl_2 .

OR

The equilibrium constant K_c for the reaction is 0.235 at 573 K and 2 atmospheric pressure. Calculate K_p and K_x . ($R = 0.0821 \text{ dm}^3 \text{ K}^{-1} \text{ mole}^{-1}$)



10. (a) Using bond energy data given below, estimate the heat of formation of gaseous isoprene $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2]$:

Bond energy of C-H bond-	98.8 kcal/mol
Bond energy of C-C bond-	83.1 kcal/mol
Bond energy of C=C bond-	147.0 kcal/mol
Heat of sublimation of carbon-	171.7 kcal/mol
Heat of dissociation of $\text{H}_{2(\text{g})}$ -	104.2 kcal/mol

OR

A sample of coal contains 92% C, 7% H and 1% ash. Following data was obtained when the above coal sample was tested in bomb calorimeter:

Amount of coal burnt	=	0.80g
Amount of water taken	=	650g
Water equivalent of bomb and calorimeter	=	2,100g
Rise in temperature	=	2.5°C
Fuse wire correction	=	12 cal

Estimate the gross and net calorific value of coal, assuming the latent heat of condensation of steam as 580 cal/g.

- (b) On an average, a person requires 2870 Kcal of energy for leading normal life. How many grams of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) must be consumed if all the required energy has to be derived from the combustion of cane sugar? The heats of formation of cane sugar_(s), carbon dioxide_(g) and water_(l) are -530.3, -94.0 and -68.3 Kcal per mole respectively.

OR

Analyze the efficiency of a coal sample when its 2.8g was weighed in a silica crucible. After heating for 1hr at 110°C, the residue weighed 2.615 g. Next the crucible was covered with a lid and strongly heated for exactly 7 min. at 950°C. The

residue weighed 1.87 g. Finally the crucible was heated without lid until a constant weight was obtained. The last residue weighed 0.47g.

SECTION- C

(20 x 2= 40 Marks)

11. (a) (i) For the cell: $\text{Mg}_{(s)}/\text{Mg}_{(aq)}^{+2} // \text{Ag}_{(aq)}^{+}/\text{Ag}_{(s)}$; calculate the equilibrium constant at 25°C and the maximum work done that can be obtained during operation of cell using Nernst equation. Given, $E^0 \text{Mg}/\text{Mg}^{+2} = 2.37 \text{ V}$ and $E^0 \text{Ag}^{+}/\text{Ag} = 0.80 \text{ V}$. Assume $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$.
 - (ii) Discuss in detail the effect of dilution on conductance of strong electrolyte.
 - (b) (i) Explain the direction of film growth in oxidation corrosion, when we take oxides of Fe and Cd giving suitable diagram.
 - (ii) Applying Hittorf methodology, deduce the expression for transport number for non-attackable electrode.
12. (a) Discuss the geometry of carbocation with suitable diagram and correlate the geometry along with its stereochemistry, for the unimolecular nucleophilic substitution reactions.

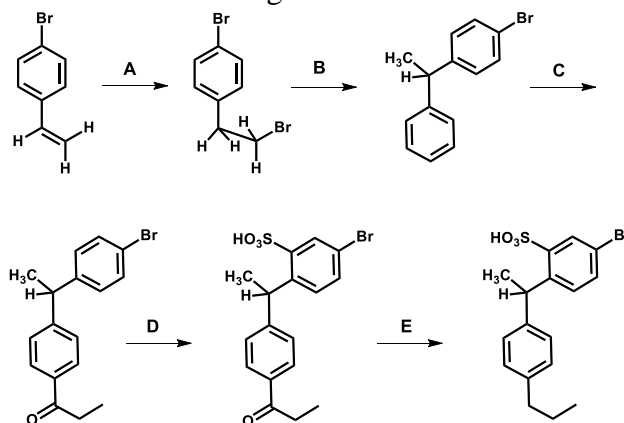
OR

- (i) 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^-
- (ii) Arrange the following compounds in order of increasing acidity and explain your answer: $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.

(b) 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.

OR

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



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SECTION-A

(4 x 5= 20 Marks)

1. Calculate the wavelength of X-rays which produces a diffraction angle 2θ equal to 16.80° for a nano crystal. Assume first order diffraction with inter particle distance in crystal of 0.2 nm.
2. In the vapour phase decomposition of ethylene oxide, $C_2H_4O \rightarrow CH_4 + CO$ at $414.5^\circ C$, 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?
3. Discuss the effect of polarity of solvents on stereochemistry of products in SN^1 reaction
4. 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)
5. Explain kinetics of hydrolysis of an ester in presence of an acid.

SECTION- B

(8 x 5= 40 Marks)

6. Explain synthesis of metal oxide nanoparticles using sol-gel method. Discuss about the applications of nanomaterials in various fields by giving examples.
7. A gaseous fuel has the following composition by volume: $H_2 = 20\%$, $CH_4 = 5\%$, $CO = 20\%$, $CO_2 = 5\%$, $N_2 = 50\%$. If 50% excess air is used, estimate the weight as well as volume of the air actually supplied per m^3 of this gas.

8. Discuss the role of surfactant in suspension and emulsion polymerization. Explain the importance of CMC in emulsion polymerization.

OR

Classify polymers on the basis of thermal response, tacticity and final utility giving suitable example of each one.

9. (a) A second order reaction, where initial concentrations of both reactants are equal, is 25% completed in 400 seconds. How long will it take for the reaction to go to 75% completion?

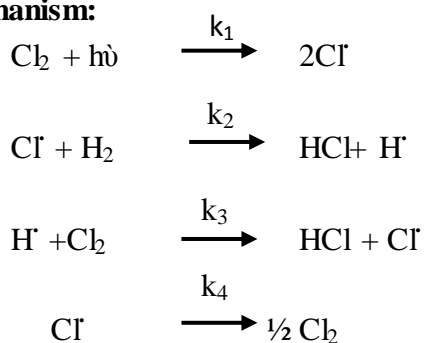
OR

How much ester would be formed when 0.5 mole of ethyl alcohol is mixed with 1.0 mole of acetic acid? (Given $K_c = 4$ at 25°C)

- (b) The following mechanism has been suggested for the formation of HCl

Overall reaction: $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}(\text{g})$

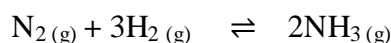
Proposed Mechanism:



Formulate the rate of reaction in terms of HCl.

OR

The equilibrium constant K_c for the reaction is 0.495 at 673 K and 2 atmospheric pressure. Calculate K_p and K_x . Given that $R = 0.0821 \text{ dm}^3 \text{ K}^{-1} \text{ mole}^{-1}$.



10. An organic compound contains 69.4% C, 5.8% H. A sample of 0.30 g of this compound was analysed for nitrogen by Kjeldahl method. The ammonia evolved was absorbed in 50 ml of 0.05M H_2SO_4 . The excess acid required 25 ml of 0.1M NaOH for neutralization. Deduce the molecular formula of the compound, it has molecular weight is 121.

OR

Standard heat of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -76.2, -394.8 & -241.6 KJ/mole respectively. Calculate the amount of heat evolved by burning one m^3 of $\text{CH}_4(\text{g})$ measured under normal conditions.

SECTION- C

(20 x 2= 40 Marks)

11. (a) (i) Explain the direction of film growth in oxidation corrosion, when we take oxides of Fe and Cd giving suitable diagram.
(ii) What is differential aeration corrosion? Give two examples of the same.
(b) Discuss the basic principle, method and limitations of moving boundary method in determining transport number of an electrolyte. Give necessary diagrams and electrode reactions.
12. (a) When bromobenzene is monochlorinated, two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of molecular formula $C_6H_3ClBr_2$, while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A), however (D) is totally different from any of the isomeric compounds obtained from the bromination of (A). Infer the structures of A to D and all the isomeric monobrominated products of (A).

OR

An alkyl halide C_8H_9Cl (A) reacts with alcoholic KOH to give an alkene (B), which reacts with bromine to form (C). Compound (C) on reaction with aqueous KOH, forms D (Major) and E (Minor). D on reaction with benzene in presence of $FeBr_3$ forms an alcohol F. Identify the structures of A to F, nature of the alcohol and write down the reactions involved in the above reaction.

(b) **Discuss the**

- i. mechanism for conversion of Benzene to n-propyl benzene
- ii. mechanism for conversion of 1-butene to n-butyl chloride
- iii. stereochemistry of addition of Br_2 to trans-2-butene
- iv. role of inductive effect on further electrophilic substitution in mono substituted benzene

OR

- i. Arrange the following compounds in order of increasing reactivity towards nucleophilic addition reactions and justify your answer:
 $HCHO$, CH_3CHO , CH_3COCH_3 , $C_6H_5COCH_3$ and $C_6H_5COC_6H_5$
- ii. Arrange the following compounds in order of increasing reactivity towards electrophilic substitution reactions giving suitable driving force for the same-
 C_6H_5OH , $C_6H_5OCH_3$, C_6H_6 , $C_6H_5NO_2$, $C_6H_5CH_3$, $C_6H_5NH_2$,
 C_6H_5COOH