

Enrolment No:



Course: CHEM-1008 (Chemistry)

(End Semester Examination May 2019)

Programme: B.Sc (H) Physics/Mathematics

Semester: II

Course Name: Chemical Energetics, Equilibria & Functional Group Organic Chemistry I

Time: 03 hrs.

Max. Marks:100

Instructions: Read all the below mentioned instructions carefully and follow them strictly:

- 1) Write your enrolment number on the top left of the question paper
- 2) Do not write anything on the question paper except your enrolment number
- 3) Attempt all part of a question at one place only
- 4) Internal choice is given for question number 9 and 11 only

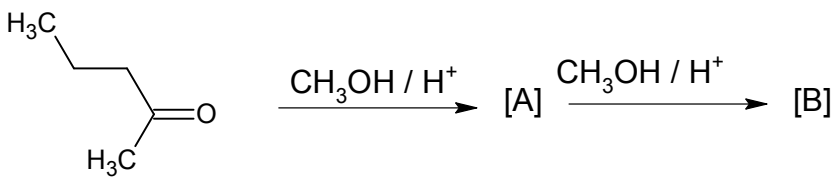
Section - A (Attempt all FIVE Questions)

1.	Calculate the pH of a solution obtained by mixing 30mL of $10^{-2}$ N HCl and 50mL of $10^{-6}$ N NaOH.	[4]	CO2
2.	The $K_a$ of propionic acid is $1.34 \times 10^{-5}$ . What is the pH of a solution containing 0.5M propionic acid and 0.5M sodium propionate? What happens to the pH of this solution when volume is doubled by the addition of water?	[4]	CO2
3.	For the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ , $K_p = 1.45 \times 10^{-5}$ at $500^\circ C$ . In an equilibrium mixture of the three gases at $500^\circ C$ the partial pressure of $H_2$ is 0.928 atm and that of $N_2$ is 0.432 atm. What is the partial pressure of $NH_3$ in this equilibrium mixture?	[4]	CO1
4.	Why is tertiary alkyl halide more prone to $S_N1$ reaction?	[4]	CO3
5.	Compare nucleophilic substitution reactions and elimination in alkyl halides.	[4]	CO3

SECTION-B

(Question No. 6, 7 and 8 are Compulsory); attempt any one from 9A & 9B

6.	Describe carnot cycle with suitable diagram. Derive expression for efficiency of Carnot engine.	[10]	CO1
7.	i) Discuss the characteristics of chemical equilibrium. ii) Why do aldehydes and ketones undergo nucleophilic addition reactions? Why are ketones less reactive than aldehydes?	[4+6]	CO1 CO3
8.	Complete the following reaction sequence:  <chem>c1ccccc1C=O</chem> $\xrightarrow{CH_3MgCl}$ [A] $\xrightarrow{PCC}$ [B] $\xrightarrow[\text{glycol, KOH}]{NH_2-NH_2}$ [C] $\xrightarrow{[D]}$ <chem>c1ccccc1C(=O)O</chem>	[10]	CO4

9A.	i) Explain Cannizzaro's reaction with example. ii) Why does dissociation of $\text{NH}_4\text{OH}$ decrease on addition of $\text{NH}_4\text{Cl}$ ? <p style="text-align: center;"><b>OR</b></p>	[6+4]	CO3 CO2								
9B.	i) Give three reagents, which can be used for oxidation of both primary and secondary alcohol. Why tertiary alcohols cannot be oxidized easily? ii) Why can we not consider hydrolysis of a salt of strong acid and strong base?	[6+4]	CO3 CO2								
<b>SECTION - C</b> <b>(Question No. 10 is Compulsory; Attempt any one from question numbers 11A &amp; 11B)</b>											
10.	i) Derive an expression of hydrolysis constant for salt of weak acid and strong base. Consider degree of hydrolysis to be "h". ii) Complete the reaction with mechanism  iii) With the help of suitable reaction explain Reimer Tiemann reaction. What is the electrophile in the reaction and how is it generated?	[8+8+4]	CO2 CO3 CO4								
11A.	i) Calculate the entropy change at 373 K for transformation $\text{H}_2\text{O} (\text{l}, 1.01325 \text{ bar}) = \text{H}_2\text{O} (\text{g}, 0.101325 \text{ bar})$ Given: $\Delta H_{\text{vap}} = 40.668 \text{ kJ/mole}$ ii) How does nitro group enhance the reactivity of chlorobenzene towards nucleophilic substitution reaction? Show with resonating structures. iii) Calculate the solubility, in grams per litre, of $\text{Al}(\text{OH})_3$ in water at $25^\circ\text{C}$ , if $K_s = 8.5 \times 10^{-32}$ . <p style="text-align: center;"><b>OR</b></p>	[8+8+4]	CO1 CO4 CO2								
11B.	i) Estimate the value of $\Delta H$ combustion for methane. Given the bond energies in kJ/mole, <table style="margin-left: auto; margin-right: auto;"> <tbody> <tr> <td>C-H</td> <td>413</td> <td>O=O</td> <td>498</td> </tr> <tr> <td>C=O</td> <td>803</td> <td>H-O</td> <td>463</td> </tr> </tbody> </table> ii) If you are provided with a set of primary, secondary and tertiary alcohols, suggest a test which can be used to distinguish them. Explain with reasoning. iii) A sample of hard water contains 0.005 mole of $\text{CaCl}_2$ per liter. What is the minimum concentration of $\text{Na}_2\text{SO}_4$ , which must be added for removing $\text{Ca}^{+2}$ ions from this water sample? $K_{\text{sp}}$ for $\text{CaSO}_4$ is $2.4 \times 10^{-5}$ .	C-H	413	O=O	498	C=O	803	H-O	463	[8+8+4]	CO1 CO4 CO2
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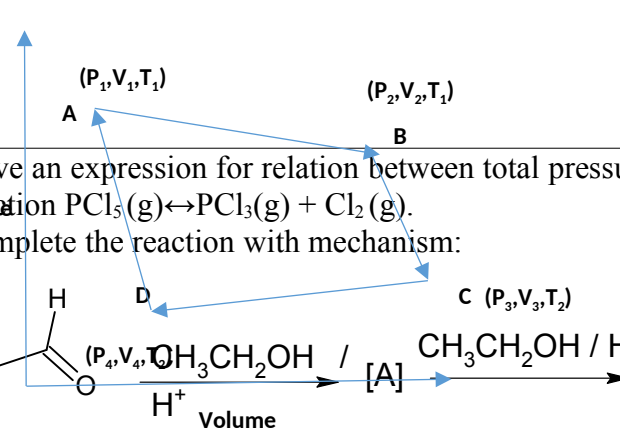
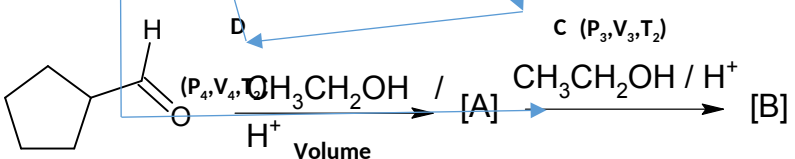
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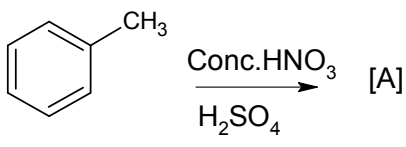
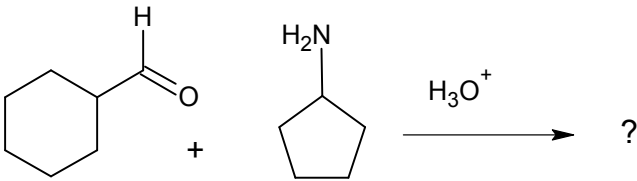
Section - A (Attempt all FIVE Questions)

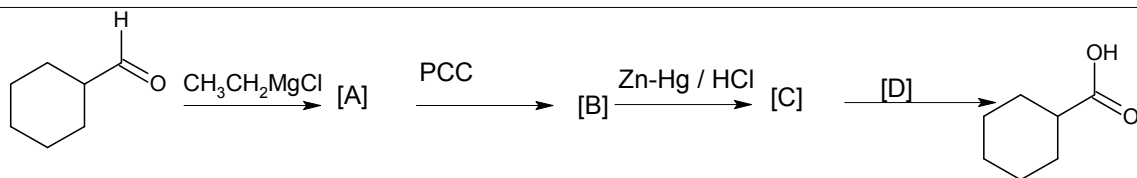
1.	Calculate the pH of a solution obtained by mixing 25 ml of 0.2 M HCl with 50 ml of 0.25 M NaOH.	[4]	CO2
2.	Calculate pH of following: (i) $10^{-3}$ N HNO <sub>3</sub> (ii) $10^{-3}$ M H <sub>2</sub> SO <sub>4</sub>	[4]	CO2
3.	$3A_{(g)} + B_{(g)} \leftrightarrow 2D_{(g)} + 60 \text{ Kcal}$ . Discuss the effect of temperature and concentration at equilibrium of given reaction.	[4]	CO1
4.	What happens when acetone is reacted with HCN ? Write reaction with mechanism.	[4]	CO3
5.	Explain Benzoin condensation with suitable reactions.	[4]	CO3

SECTION - B

(Question No. 6, 7 and 8 are Compulsory); attempt any one from 9A & 9B

6.	Calculate work done in the following cyclic process. 	[10]	CO1
7.	i) Derive an expression for relation between total pressure P and degree of dissociation $\alpha$ for reaction $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$ . ii) Complete the reaction with mechanism: 	[4+6]	CO1 CO3
8.	An organic compound A (C <sub>4</sub> H <sub>9</sub> Cl) on reaction with alcoholic KOH gives single product B. B on chlorination gives C which on treatment with excess KOH in water gives D. D in presence of protonic acid undergo rearrangement to give an aldehyde E. E reacts with	[10]	CO4

	phenyl hydrazine to give F. Identify the structures of compound A to F.		
9A.	<p>i) Explain Oppeneauer oxidation with example.</p> <p>ii) Calculate the percentage hydrolysis of sodium acetate in 0.1 M solution at 25°C assuming that the salt is completely dissociated. <math>K_a</math> of acetic acid at 25°C = <math>1.75 \times 10^{-5}</math>.</p> <p style="text-align: center;"><b>OR</b></p>	[6+4]	CO3 CO2
9B.	<p>i) Complete the reaction with mechanism:</p>  <p>ii) 25 ml of 0.01 M <math>\text{AgNO}_3</math> solution is mixed with 25 ml of 0.0005 M aqueous NaCl solution. Determine if the precipitate of AgCl will be formed or not. Given <math>K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10}</math></p>	[6+4]	CO3 CO2
<p><b>SECTION - C</b></p> <p><b>(Question No. 10 is Compulsory; Attempt any one from question numbers 11A &amp; 11B)</b></p>			
10.	<p>i) Derive an expression of pH for salt of weak base and strong acid.</p> <p>ii) Complete the reaction with mechanism:</p>  <p>iii) Explain Wittig reaction with suitable reaction.</p> <p style="text-align: center;"><b>OR</b></p>	[8+8+4]	CO2 CO3 CO4
11A.	<p>i) The molar heat of formation of <math>\text{NH}_4\text{NO}_3(\text{s})</math> is <math>-367.54 \text{ kJ}</math> and those of <math>\text{N}_2\text{O}(\text{g})</math> and <math>\text{H}_2\text{O}(\text{l})</math> are <math>+81.46 \text{ kJ}</math> and <math>-285.78 \text{ kJ}</math> respectively at 25°C and at 1atm pressure. Calculate <math>\Delta H</math> and <math>\Delta E</math> for the reaction <math>\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l})</math>.</p> <p>ii) Discuss benzyne mechanism with relevant example.</p> <p>iii) Given that the solubility product of <math>\text{BaSO}_4</math> is <math>1 \times 10^{-10}</math>. Will a precipitate be formed when equal volumes of <math>2 \times 10^{-3} \text{ M}</math> <math>\text{BaCl}_2</math> solution and <math>2 \times 10^{-4} \text{ M}</math> <math>\text{Na}_2\text{SO}_4</math> solution are mixed</p>	[8+8+4]	CO1 CO4 CO2
11B.	<p>i) Derive the following relation, thermodynamically.</p> $\Delta G^0 = -RT \ln K_p$ <p>ii) Complete the following reaction sequence:</p>	[8+8+4]	CO1 CO4 CO2



iii) Derive the equation for solubility product in terms of solubility of the corresponding ions for the following

- (i) AgCl
- (ii) BaF<sub>2</sub>
- (iii) Cu<sub>2</sub>S