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 General Certificate of Education (Adv. Level) Examination, August 2019

Grade 13 - 1st Term Test
 28th Nov. 2018

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 Chemistry

02 E I

පැය දෙකසි
 Two hours

This paper consists of 09 pages.

- Answer all the questions.
- Use of calculators is not allowed.
- Write your Index Number in the space provided in the answer sheet.
- Follow the instructions given on the back of the answer sheet carefully.
- In each of the questions 1 to 50, pick one of the alternatives from (1), (2), (3), (4), (5) which is correct or most appropriate and mark your response on the answer sheet with a cross (X) in accordance with the instructions given on the back of the answer sheet.

$$\text{Universal gas constant} \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Avogadro constant} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Planck's constant} \quad h = 6.626 \times 10^{-34} \text{ J s}$$

$$\text{Velocity of light} \quad C = 3 \times 10^8 \text{ m s}^{-1}$$

1. Which of the following is the best oxidant?
 1) F 2) Cl 3) O 4) Na 5) K
2. Which of the following species has the strongest bond between any two atoms.
 1) NH₃ 2) HNO₂ 3) HNO₃ 4) HCN 5) NO₂
3. In which of the following nuclear reactions the product X is not neutron.
 1) $^{27}_{13}Al + ^4_2He \longrightarrow ^{30}_{15}P + X$ 2) $^{12}_6C + ^1_1H \longrightarrow ^{12}_7N + X$
 3) $^{31}_{15}P \longrightarrow ^{30}_{14}Si + X$ 4) $^{241}_{96}Cm + ^4_2He \longrightarrow ^{244}_{98}Cf + X$
 5) $^{238}_{92}U \longrightarrow ^{236}_{92}U + 2X$
4. The IUPAC name of the following compound is,

$$\begin{array}{c} \text{O} & \text{O} & \text{Br} \\ || & || & | \\ \text{CH}_3-\text{C}-\text{CH}=\text{C}-\text{C}-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ & & \text{Br} \end{array}$$
 - 1) 2-bromopropyl 2-bromo-2-ene-4-oxopentanoate
 - 2) 2-bromopropyl 2-ene-2-bromo-4-oxopentanoate
 - 3) 2-bromopropyl 2-bromo-4-oxopent-2-enoate
 - 4) 2-bromopropyl 4-oxo-2-ene-2-bromopentanoate
 - 5) 2-bromopropyl 4-oxo-2-ene-2-bromopent-2-enoate

5. Which of the following statements is true regarding the Mn^{2+} ion,

- 1) Mn^{2+} can easily be oxidized to MnO_4^{2-} in acidic medium by strong oxidizing agents.
- 2) Mn^{2+} does not readily react with oxygen as it has stable electron configuration.
- 3) Mn^{2+} readily reacts with oxygen in acidic medium.
- 4) Mn^{2+} readily reacts with oxygen in basic medium.
- 5) Mn^{2+} , evolves Cl_2 when react with HCl.

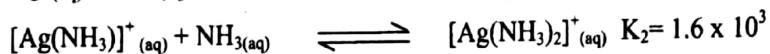
6. Consider the following Gibbs free energy changes at 1000 K.



Among the following reactions what is the most feasible reaction at 1000 K?

- 1) $ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$
- 2) $2 ZnO(s) + C(s) \longrightarrow 2 Zn(s) + CO_2(g)$
- 3) $Zn(s) + CO_2(g) \longrightarrow ZnO(s) + CO(g)$
- 4) $Zn(s) + CO(g) \longrightarrow ZnO(s) + C(s)$
- 5) $2 Zn(s) + CO_2(g) \longrightarrow 2 ZnO(s) + C(s)$

7. Given that



The value of equilibrium constant of $Ag^+_{(aq)} + 2 NH_3_{(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)}$ is,

- 1) 6.8×10^6
- 2) 1.08×10^5
- 3) 1.08×10^6
- 4) 6.8×10^5
- 5) 7.08×10^5

8. The activation energies for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2 AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. In the presence of catalyst, the activation energy of both forward and reverse reactions, lower by 100 kJ mol^{-1} . The enthalpy change for the given reaction in the presence of the catalyst will be,

- 1) 300 kJ mol^{-1}
- 2) 120 kJ mol^{-1}
- 3) 80 kJ mol^{-1}
- 4) -20 kJ mol^{-1}
- 5) -180 kJ mol^{-1}

9. $V \text{ cm}^3$ of HCl solution which has 29.2% W/W composition and density 1.25 g cm^{-3} was diluted up to 200 cm^3 . 25 cm^3 of that solution was treated with excess of $AgNO_3$. The dry mass of the precipitate was 1.435 g. What is the value of V used to prepare the dilute HCl solution. ($Ag - 108$, $Cl - 35.5$)

- 1) 80
- 2) 8
- 3) 2
- 4) 0.8
- 5) 0.2

10. For the redox reaction

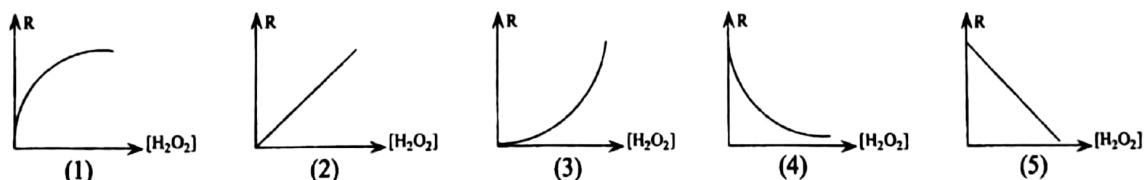


the coefficients x , y and z respectively are.

- 1) 8, 3, 5
- 2) 5, 3, 8
- 3) 5, 3, 4
- 4) 10, 3, 4
- 5) 10, 3, 8

11. The major product of the reaction between $\text{CH}_3\text{-CH=CH}-\text{C}_6\text{H}_4\text{-OH}$ and HBr is,
- 1) $\text{CH}_3\text{-CHBr-CH}_2\text{-C}_6\text{H}_4\text{-OH}$
 - 2) $\text{CH}_3\text{-CH}_2\text{-CHBr-C}_6\text{H}_4\text{-OH}$
 - 3) $\text{CH}_3\text{-CHBr-CH}_2\text{-C}_6\text{H}_4\text{-Br}$
 - 4) $\text{CH}_3\text{-CH=CH-C}_6\text{H}_4\text{-Br}$
 - 5) $\text{CH}_3\text{-CH}_2\text{-CHBr-C}_6\text{H}_4\text{-OH}^{\text{Br}}$
12. A rigid vessel contains a mixture of gases of CO_2 , CO and O_2 . Total amount of CO was completely converted into CO_2 using an electric arc. 50% of O_2 has been consumed in this conversion and 10% reduction of the pressure was observed (all pressures have been measured at 25°C) What is the $\text{CO}_2 : \text{CO}$ mole ratio in the initial gas mixture.
- 1) 1 : 1
 - 2) 2 : 1
 - 3) 1 : 3
 - 4) 3 : 1
 - 5) 5 : 2
13. Which of the following set consists of the complexes with the same colour?
- 1) $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
 - 2) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ $[\text{Cu}(\text{NH}_3)_6]^{3+}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
 - 3) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $[\text{CuCl}_4]^{2-}$
 - 4) $[\text{FeCl}_4]^{2-}$ $[\text{CuCl}_4]^{2-}$ $[\text{CoCl}_4]^{2-}$
 - 5) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $[\text{CoCl}_4]^{2-}$
14. 10.0 cm^3 of 0.10 mol dm^{-3} FeSO_4 is titrated against $0.025 \text{ mol dm}^{-3}$ KMnO_4 in the presence of an excess of hydrogen ions it was found that exactly 10.0 cm^3 of the KMnO_4 solution was required to reach the end point. What is the oxidation number of the manganese at the end point.
- 1) +2
 - 2) +3
 - 3) +4
 - 4) +5
 - 5) +6

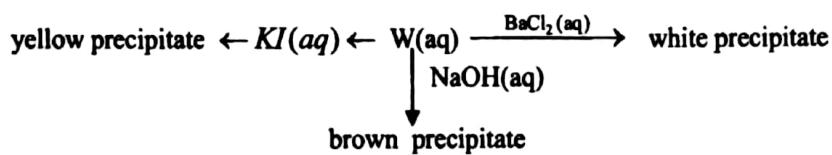
15. Which one of the following graphs would show that the de-composition of hydrogen peroxide is first order? (R – rate of decomposition of H_2O_2)



16. Which one of the following does not have a permanent dipole moment?

- 1) $\text{C}_2\text{H}_5\text{Cl}$
- 2) CF_2Cl_2
- 3) C_2Cl_2
- 4) CHCl_3
- 5) CH_3OCH_3

17. Some reactions of the compound W are shown below,



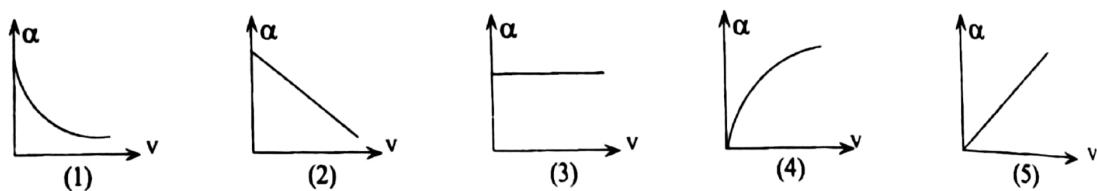
What would the compound "W" be,

- 1) AgNO_3
- 2) Ag_2SO_4
- 3) CaCrO_4
- 4) $\text{Pb}(\text{NO}_3)_2$
- 5) PbSO_4

18. When a vapor at the atmospheric pressure was gradually heated from 25°C , its color was deepened at first and then faded as the temperature raised above 160°C . At a certain temperature vapor was almost colorless but its colour deepened when the pressure was raised at high temperature. Which one of the following could have been the vapour / gas.

- 1) pure bromine.
- 2) pure hydrogen iodide
- 3) pure nitrogen dioxide
- 4) a mixture of hydrogen and bromine.
- 5) a mixture of nitrogen dioxide and dinitrogen tetraoxide

19. When 1 mol of ethanoic acid is diluted at constant temperature to a volume V, which one of the following diagrams represents the variation of degree of dissociation (α) of the acid with V?



20. Which one of the following compounds is most acidic?

- 1) $\text{CH}_3\text{CH}_2\text{OH}$
- 2) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- 3) ClCH_2COOH
- 4) CH_3COCH_3
- 5) H_2CO_3

21. For the reaction,



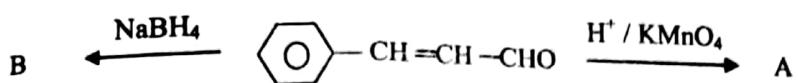
The value of K_p is 3.16×10^{-3} atm at 298K and is 1.48 atm. 500 K Which one of the following statement is correct?

- 1) The value of ΔH for the forward reaction is negligible.
- 2) The yield of carbondioxide will increase at high pressure.
- 3) The yield of carbondioxide is independent of temperature.
- 4) The forward reaction is endothermic.
- 5) The value of K_p depends on the amount of Ag_2CO_3 used.

22. The correct increasing order of polarity of the species A, B and C is?.

- | | | | | |
|--|--------------------------------------|-------------------------------------|--------------|--------------|
| A) $\text{CH}_3\text{CH}_2\text{CH}_3$ | B) $\text{CH}_3\text{CH}_2\text{OH}$ | C) $\text{CH}_3\text{CH}_2\text{F}$ | | |
| 1) A < B < C | 2) C < B < A | 3) A < C < B | 4) C < A < B | 5) B < C < A |

23. What would be the products A and B of the following reaction respectively,

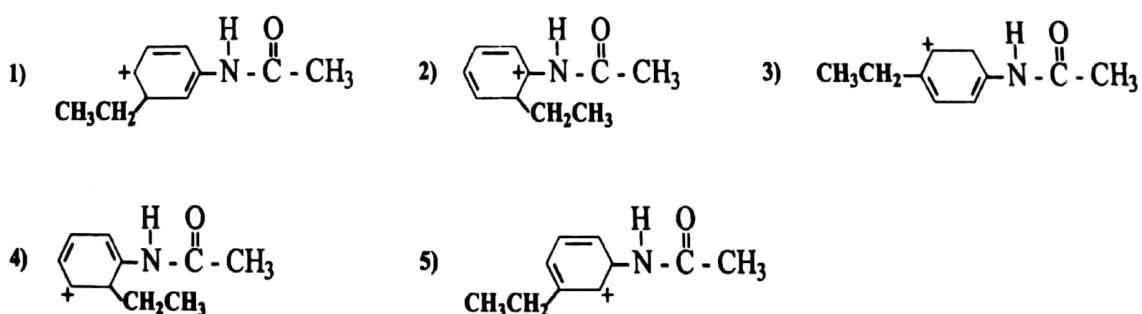


- | | |
|--|---|
| 1)  | ,  |
| 2)  | ,  |
| 3)  | ,  |
| 4)  | ,  |
| 5)  | ,  |

24. Which one of the following is true regarding the isomers of 1-chloro-2-butene-1-ol.

- 1) It exhibits the diasteromerism.
- 2) It exhibits the enantiomerism.
- 3) It has two chiral centers.
- 4) It exhibits both diastereomerism and enantiomerism.
- 5) It exhibits neither diasteromerism nor enantiomerism.

25. One of the intermediate product of the reaction between  and $\text{CH}_3\text{CH}_2\text{Cl} / \text{Anhy. AlCl}_3$



26. Compound X shows the following observations.

- Brown colored gas evolves when conc. H_2SO_4 is added.
- The gas evolved when X is heated passed through FeSO_4 solution, the solution gradually turned yellow – brown.
- KI was added to X and then starch was added. No color change was observed.
The compound X would be?

1) NaBr

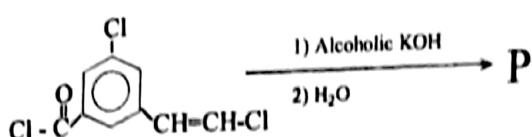
2) NaNO_2

3) NaNO_3

4) NaI

5) NaNH_2

27. The structure of the product P in the following reaction is?



- 1)
- 2)
- 3)
- 4)
- 5)

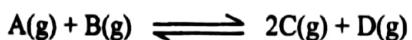
28. The oxide of metal M dissolves in conc. HCl giving clear solution Z. Then Z was diluted with excess of water then the solution became turbid. Another portion of diluted solution of Z was treated with Na_2S a black precipitate was formed.

- 1) Pb 2) Sb 3) Cu 4) Hg 5) Bi

29. 0.0050 mol of $\text{Na}_2\text{C}_2\text{O}_4$ and 1.6 g of NaOH were required to completely react with two different samples of 1.68 g of the organic compound X. The molecular formula of X is $\text{C}_8\text{H}_8\text{O}_4$. What is the structural formula of X.

- 1)
- 2)
- 3)
- 4)
- 5)

30. 1 mol of A(g) and 2 mol of B were placed in a rigid vessel of volume V at temperature T. Then the temperature of the container raised to 2T and allowed the system to attain to equilibrium according to the following equation.



If the equilibrium constant for the above reaction at 2T is K_p and the degree of dissociation of A is α what is the correct expression for K_p .

- 1) $K_p = \frac{4\alpha^3 RT}{(1-\alpha)^2 V}$
- 2) $K_p = \frac{2\alpha^3 RT}{(1-\alpha)^2 V}$
- 3) $K_p = \frac{2\alpha^3 RT}{3(1-\alpha)^2 V}$
- 4) $K_p = \frac{8\alpha^3 RT}{(1-\alpha)(2-\alpha)V}$
- 5) $K_p = \frac{4\alpha^3 RT}{(1-\alpha)(2-\alpha)V}$

- For each of the questions 31 to 40, one or more responses out of the four responses (a), (b), (c) and (d) given is/are correct. Select the correct response/responses. In accordance with the instructions given on your answer sheet, mark

- If only (a) and (b) are correct
- If only (b) and (c) are correct
- If only (c) and (d) are correct
- If only (d) and (a) are correct
- If any other number or combination of responses is/are correct.

Summary of above instructions				
1	2	3	4	5
Only (a) and (b) correct	Only (b) and (c) correct	Only (c) and (d) correct	Only (d) and (a) correct	Any other response or combination of responses correct

31. Which of the following statements about the catalysts is true.
- A catalyst accelerates the rate of a reaction by decreasing the activation energy.
 - A catalyst does not participate in reaction mechanism.
 - A catalyst makes the reaction more feasible by making ΔG more negative.
 - A catalyst makes equilibrium constant more favorable for the forward reaction.
32. For the following reversible reaction (first order in both directions), if equilibrium constant greater than unity,
- $$A \xrightleftharpoons[k_2]{k_1} P$$
- Rate of the forward reaction is always greater than the rate of backward reaction.
 - Amount of product of equilibrium is greater than the amount of reactant.
 - Activation energy for the forward reaction is greater than the activation energy for backward reaction.
 - Addition of a catalyst will increase both k_1 and k_2 by same factor.
33. Which of the following statement/s is/are not true regarding s – block element lithium?
- Lithium is the strongest oxidizing agent among alkali metals family as it is the smallest in size.
 - Lithium hydrogencarbonate is the only hydrogen carbonate which can be solidified in aqueous medium among hydrogen carbonates of alkali metals.
 - Lithium gets dissolved in liquid ammonia to form Li_3N .
 - Solubility of lithium carbonate in water is low due to low hydration enthalpy of cation as it has the smallest radius.

34. Consider the dissociations of a weak acid and a weak base with has the dissociation constants K_a and K_b respectively. Initial concentrations of each $C \text{ mol dm}^{-3}$. Which of the following relationships are correct at 25°C .
- $\text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$ (for weak acid)
 - $\text{pH} = 14 - \frac{1}{2} \text{p}K_b + \frac{1}{2} \log C$ (for weak base)
 - $\text{pH} = 14 - \frac{1}{2} K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$ (salt of weak acid)
 - $\text{pH} = \text{p}K_a - \log \left[\frac{\text{salt}}{\text{acid}} \right]$ (for weak acid and weak base)
35. Consider the diprotic weak acid H_2A . The solution S has been prepared by mixing 100 cm^3 of 0.2 mol dm^{-3} Na_2A solution and 100 cm^3 of 0.3 mol dm^{-3} HCl solution. Which of the following statement/s is/are true regarding S.
- It can act as a buffer
 - pH is approximately equal to 10
 - $[\text{HA}^-] = [\text{A}^{2-}]$
 - HA^- is more basic than A^{2-}
36. Which of the following reaction evolve NH_3 ?
- $\text{NH}_4\text{Cl} + \text{Na}_2\text{CO}_3 \longrightarrow$
 - $\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow$
 - $\text{R}-\text{CONH}_2 + \text{NaOH} \xrightarrow{\Delta} \longrightarrow$
 - $\text{R}-\text{NH}_2 + \text{NaOH} \xrightarrow{\Delta} \longrightarrow$
37. Which of the following statements is/are wrong?
- Solid silver halides dissolve in excess of $\text{Na}_2\text{S}_2\text{O}_3$ solution due to formation of complexes.
 - AgI dissolves in excess of conc. NH_3 .
 - Solubility of AgBr in dilute NH_3 is less due to formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex.
 - Solubility of AgI even in conc. NH_3 is extremely low because of the formation of complex does not reduce $[\text{Ag}^+]$ low enough to cause AgI to dissolve.
38. The following two equilibria can be found at temperature T when $\text{AB}_2(\text{g})$ and $\text{B}_2\text{C}(\text{g})$ gases are allowed to react in a closed system.
- $$\text{AB}_2(\text{g}) + \text{B}_2\text{C}(\text{g}) \rightleftharpoons \text{AB}_3(\text{g}) + \text{BC}(\text{g})$$
- $$\text{BC}(\text{g}) + \text{B}_2\text{C}(\text{g}) \rightleftharpoons \text{B}_3\text{C}_2(\text{g})$$
- only $\text{B}_2\text{C}(\text{g})$ and $\text{AB}_2(\text{g})$ were placed in a rigid vessel and allow to attain equilibrium at temperature T. Which of the following must necessarily be fulfill to occur above equilibria.
- $[\text{AB}_3(\text{g})] = [\text{BC}(\text{g})]$
 - $[\text{AB}_2(\text{g})] = [\text{B}_2\text{C}(\text{g})]$
 - $[\text{AB}_3(\text{g})] > [\text{B}_3\text{C}_2(\text{g})]$
 - $[\text{AB}_3(\text{g})] > [\text{BC}(\text{g})]$
39. Which of the following is/are correct regarding the chemistry of carbon?
- CO_3^{2-} is the conjugate base of HCO_3^{2-}
 - Dry ice ($\text{CO}_2(\text{s})$) is formed when liquid CO_2 eject to atmosphere
 - Carbon suboxide (C_3O_2) is a linear molecule.
 - CO is isoelectronic with $\text{O}_2(\text{g})$

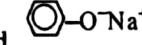
40. Which of the following statement/s out of the followings are wrong?

- a) The attractive forces among non-polar molecules in their liquid state are dispersion forces.
- b) In CS_2 the carbon atom is sp^2 hybridized.
- c) There are some differences of chemical properties of D_2O and H_2O .
- d) Ionic compounds are generally ductile

• In question no. 41 to 50, two statements are given in respect of each question.

From the table given below, select the response out of the responses (1), (2), (3), (4) and (5) that best fits the two statements and mark appropriately on your answer sheet.

Response	first statement	second statement
(1)	True	true and correctly explain the first statement
(2)	True	true, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

	First Statement	Second Statement
41.	$\text{CH}_3\text{CH}_2\text{OH}$ and  react with Na forming $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+$ and  respectively and both of these salts are basic.	$\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+$ and  are stable in aqueous medium.
42.	Solubility of CaF_2 is greater than that of CaCl_2	CaF_2 is more ionic than CaCl_2
43.	Fraction of molecules with maximum probable speed of a given gas sample at 1000 K is less than that of at 500 K.	Maximum probable speed of a gas sample increase with temperature.
44.	When the temperature of the system of the reaction $\text{A(g)} \rightleftharpoons \text{B(g)}$ $\Delta H < 0$ increases both the rate and the yield of the reaction increase.	In general rate of a reaction increases with temperature.
45.	Catalyst increase the rate of a reaction primarily due to change in mechanism of the reaction.	Activation energy of a reaction under given temperature cannot be changed without changing the mechanism.
46.	pH of weak acid independent of the concentration at constant temperature.	K_a of a weak acid depends on temperature.
47.	Chemical properties of isomers are the same.	Chemical properties of enantiomers are same.
48.	AgNO_3 forms precipitate upon addition of $\text{NaOH}_{(\text{aq})}$ and turns black when NH_4OH is added.	AgOH is unstable, it is decomposed to Ag_2O .
49.	When $\text{CH}_3\text{CH}_2\text{ONa}$ is added into a cold solution containing the precipitate  , the precipitate dissolves.	$\text{CH}_3\text{CH}_2\text{O}^-$ is a stronger base than $\text{C}_6\text{H}_5\text{COO}^-$
50.	pH of the 1 dm^3 solution prepared by mixing 1 mol of the HCl and 1 mole of CH_3ONa at 60°C is less than 7.	K_w at 60°C is greater than $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

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 Chemistry II

02

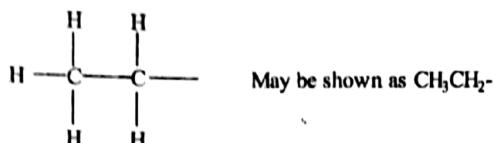
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 Three hours

Name Class: Ind No:

- A Periodic table and logarithm table are provided separately
- Use of calculators is not allowed.
- Universal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
- Plank's constant $h = 6.626 \times 10^{-34} \text{ J s}$
- Speed of light $C = 3 \times 10^8 \text{ m s}^{-1}$
- In answering this paper, you may represent alkyl groups in a condensed manner.



- Part A – Structured Essay (pages 2 – 9)**
- Answer all the questions on the question paper itself.
- Write your answer in the space provided for each question. Please note that the space provided is sufficient for the answer and that extensive answers are not expected.
- Part B and C Essay (pages 10 – 16)**
- Answer four questions only. Two questions from each Part B and Part C. Use the papers supplied for this purpose.
- At the end of the time allotted for this paper, tie the answers to the Parts A and B together so that Part A is on top and hand them over to the Supervisor.
- You are permitted to remove only Part B of the question paper from the Examination Hall.

For Examiner's Use Only

Part	Question No.	Marks
A	1	
	2	
	3	
	4	
B	5	
	6	
C	7	
	8	
	9	
Total		
Percentage		

Final Mark

In Numbers	
In Letters	

Marking Examiner 1	
Marking Examiner 2	
Checked by :	
Supervised by:	

Part A – Structured Essay

Answer all four questions on this paper itself. (Each question carries 10 marks.)

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I) a) Arrange the following in the increasing order of the property indicated in parentheses,

i) F, Cl, Fe, Na (oxidation property)

.....
ii) CHCl₃, CH₂Cl₂, CH₃Cl, SF₆, (dipole moment)

.....
iii) SO₂, S₂O₃²⁻, SO₂Cl₂, SO₃ ($\hat{O-S-O}$ bond angle)

.....
iv) B³⁺, Be²⁺, Na⁺, Cs⁺, (Polarizing Power)

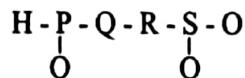
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v) Na, Al, Si, S. (Second ionization energy)

.....
vi) CH₃Cl, CCl₄, CH₄, CBr₄ (London dispersion force)

b) i) Draw the most acceptable Lewis structures for the following species.

PO ₃ S ³⁻	SO ₃ Cl ⁻	FCON ₂ ⁺
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ii) A is a uni-negative ion. The skeleton of A is given below.



Consider the following statements regarding A.

- ❖ Only P, Q, R, and S are unknown elements to be identified.
- ❖ The principal quantum number “n” of all atoms are same except hydrogen.
- ❖ Electro negativity of S is greater than that of Q (S > Q)
- ❖ P, Q, R, and S may be same or different.

- ❖ Number or VSEPR pairs and the geometry around atoms are as follow.

Atom	P	Q	R	S
Number of VSEPR pairs	3	3	2	3
Shape around atom	(Trigonal) planer	bent	Linear	Trigonal planer.

- I) Identify the actual chemical elements appropriate for P, Q, R and S.

P..... Q..... R..... S.....

- II) Draw the most acceptable Lewis structure for the ion A using. Actual chemical elements for P, Q, R and S

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- III) Identify the hybridization of each atom P, Q, R and S

P..... Q..... R..... S.....

- IV) Draw four resonance structures for the ion A drawn in part (ii) above

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- c) State whether the following statements are true or false and briefly explain your answer.

- i) The first electron gaining enthalpy of oxygen is numerically greater than that of sulfur.

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- ii) Magnesium does not show a specific color in flame test while sodium gives a color.

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- 2) a) The following procedure was carried out to determine the $\text{CaCO}_3 : \text{MgCO}_3$ mole ratio in a pure dolomite sample. 9.36 g of dolomite was reacted with excess of dilute HCl solution and evolved gas was collected at $t^\circ\text{C}$ under atmospheric pressure. The volume of the gas collected was 2.4 dm^3 . The molar volume of the gas under same condition is $24 \text{ dm}^3 \text{ mol}^{-1}$.

- i) Write down the balanced chemical equations for the reaction / reactions taking place in this procedure.

.....
.....

- ii) Calculate the number of moles of gas collected.

.....

- iii) Calculate the $\text{Ca CO}_3 : \text{Mg CO}_3$ mole ratio in given dolomite sample

- iv) State one important use of that gas and one environmental impact of that gas

usage impact :

- b) Set of quantum numbers of the Last electron of the element A is $(5, 0, 0, \pm 1/2)$. A reacts with excess of oxygen forming white solid B. B forms a white precipitate "C" and an aqueous solution of D, when reacts with dilute H_2SO_4 . D reacts with green color solution containing E^{3+} ions in basic medium turning the solution in to yellow. This yellow colored solution F was turned in to orange colored solution "G" on addition of dilute H_2SO_4 .

- i) Identify element / compound / ion denoted by A, B ,C, D, E, F and G.

A..... D..... G.....

B **E**

C F

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- ii) Write down the balanced chemical equation for the reaction between B and Dil. H_2SO_4 .

.....

- iii) Explain why the method explained in the above paragraph is a good method to prepare an aqueous solution of D in laboratory

.....

- iv) Write down the complete electron can figuration of the gaseous isolated ion E^{3+} .

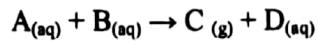
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- v) Write down the balance chemical equation for the reaction taking place between D and d E^{3+} ion in basic medium.

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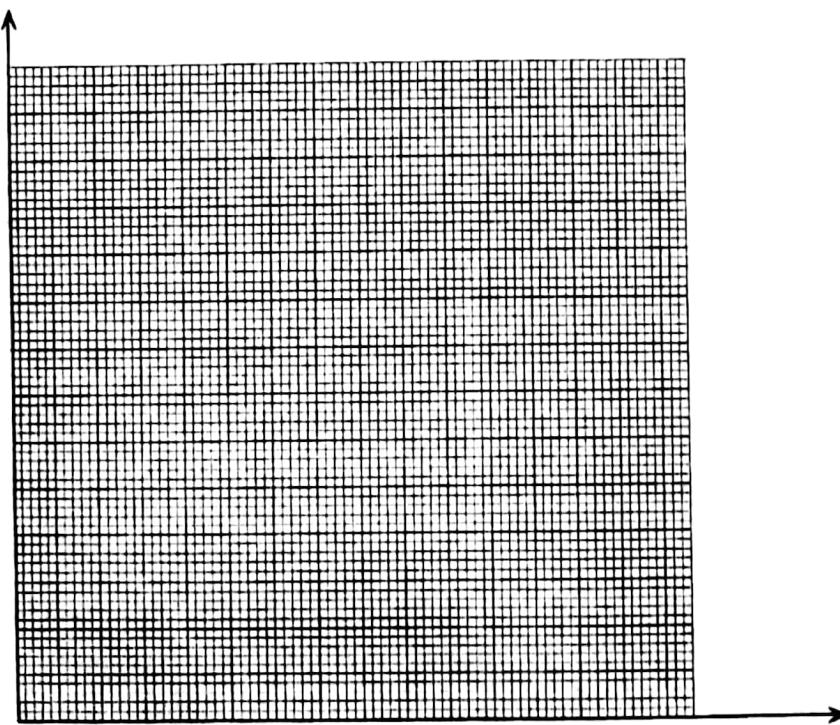
- 3) a) A group of students investigated the rate of reaction between $A_{(aq)}$ and $B_{(aq)}$ which evolves gas $C_{(g)}$ as a product. A freshly prepared solutions of equal concentration $A_{(aq)}$ was mixed with largely excess of $B_{(aq)}$. The following *elementary reaction* is taking place between A and B in aqueous medium.



The *total volume* of gas liberated was recorded every minute and tabulated as follow after 7 min no more A $_{(aq)}$ in the reaction vessel was remained.

Time / min	0	1	2	3	4	5	6	7
Total volume of gas / cm^3	0	23.0	36.5	46.0	51.0	54.5	57.0	58.5

- i) Plot the experimental results on the grid given bellow.



- ii) If the overall order of the reaction is x , state the value of x that you would expect to obtain in this experiment x .
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- iii) Explain why the experimental results indicate that the overall order is the value you mention above (x).
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- iv) Calculate the half life of the reaction (or state the half life of the reaction with the explanation).
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- v) The relationship between initial concentration $[A]_0$ and the concentration at time t $[A]_t$ of a reaction which has the overall order x (x – the value you stated in (ii) above) is given by the following equation.

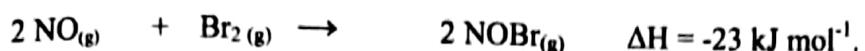
$$2.303 \log [A]_t = -Kt + 2.303 \log [A]_0 \quad K - \text{the rate constant of the reaction.}$$

- I. Show that the $t_{1/2}$ of this reaction independent from the initial concentration of the reactant.
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- II. Calculate the Rate constant K of the reaction.
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- b) The following reaction is an elementary reaction



The activation energy of the reaction is $+5.4 \text{ kJ mol}^{-1}$.

- i) Write the rate equation for the reaction and state the units of the rate constant

.....
.....

- ii) Sketch and label a reaction pathway for the reaction showing all the energy change

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- 4) (a) A, B, C and D are isomers with the molecular formula $\text{C}_6\text{H}_{10}\text{O}_2$. All four isomers exhibit optical isomerism when reacted with H_2/Pt A and B give the same compound E, and E exhibit optical isomerism (enantiomerism). A exhibit geometrical isomerism while B, C and D do not exhibit geometrical isomerism. Only A, B and C are liberated CO_2 when reacted with NaHCO_3 . C reacts with H_2/Pt giving compound F. F does not exhibit optical isomerism. D gives yellow, orange precipitate with 2,4-DNP and D does not give a silver mirror in the silver mirror test. D gives a turbid solution rapidly when treated with Lucas reagent (Anhydrous ZnCl_2 / conc. HCl)

- i) Draw the structures of A, B, C, D, E and F.

A

B

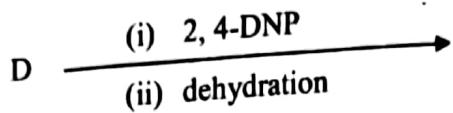
C

D

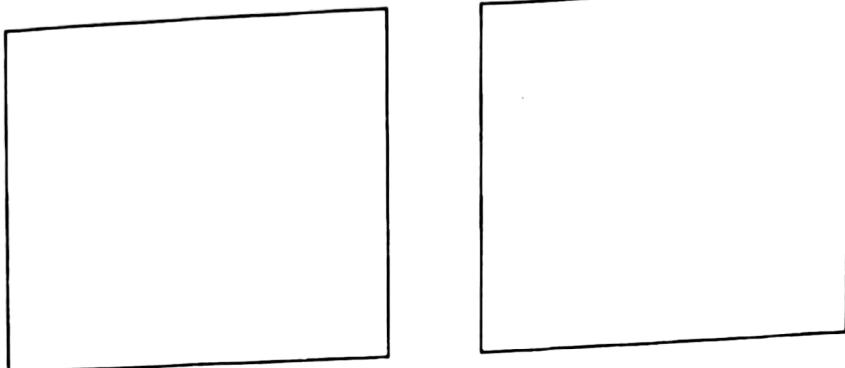
E

F

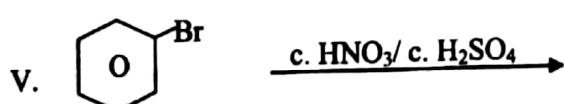
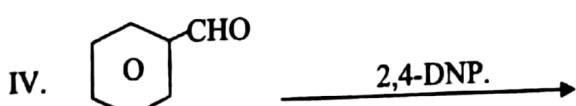
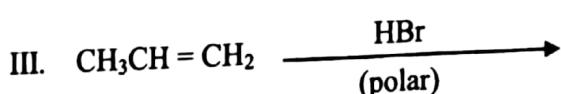
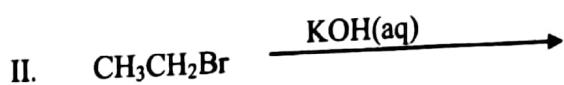
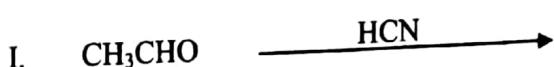
ii) Draw the structure of the product of the following reaction.



iii) Draw the structures of diasteromers of A



b) i) Draw the structures of the major organic product in each of the following reactions.



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- ii) Identify the mechanism type of the above reactions I, II, III, IV and V and write the mechanism type and the electrophiles in electrophilic reactions and the nucleophiles in nucleophilic reactions in appropriate cages in the following tale.

Mechanisms are abbreviated as,

Electrophilic Addition (A_E)

Nucleophilic Addition (A_N)

Acid – Base reaction (AB)

Any other reaction (M_O)

Electrophilic Substitution (S_E)

Nucleophilic substitution (S_N)

Elimination reaction (E)

Reaction	Mechanism	Active Species	
		Electrophile	Nucleophile
I.			
II.			
III.			
IV.			
V.			

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- 28.11.2018 (7.20 am – 10.30 am) -



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Chemistry II

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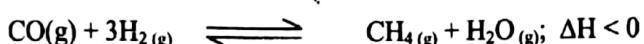
- * Universal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- * Plank's constant $h = 6.626 \times 10^{-34} \text{ J s}$

- Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
- Speed of light $C = 3 \times 10^8 \text{ m s}^{-1}$

PART B – ESSAY

Answer two questions only. (Each question carries 15 marks)

- (5) a) The following equilibrium occurs at high temperatures (above 400 K). A rigid vessel of 20 dm^3 contains 1 mol of CO gas and 1 mol of H₂ gas. The temperature of the system was increased to T₁ ($T_1 > 400 \text{ K}$)



At the equilibrium, it was observed that the pressure was reduced by 20% (When compared to the initial pressure before the reaction starts at T₁)

Calculate

- Equilibrium moles of CO_(g), H_{2(g)}, CH_{4(g)} and H_{2O(g)} at T₁.
- Equilibrium concentration CO_(g), H_{2(g)}, CH_{4(g)} and H_{2O(g)} at T₁.
- Equilibrium constant K_c at T₁.
- It was observed that the system has taken 4 minutes to reach the above equilibrium, at T₁. The system at the equilibrium at T₁ was left for another 2 minutes and then 0.16 moles of H_{2O(g)} and 0.24 moles of He were injected to the system at T₁. This new system reached the equilibrium after 4 minutes of the above change. The equilibrium mixture contained 0.46 mol of H_{2O(g)} at T₁.

I) Calculate the equilibrium concentrations of CO_(g), H_{2(g)}, CH_{4(g)} and H_{2O(g)}.

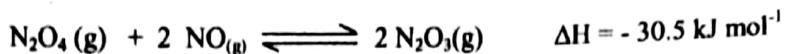
II) Explain qualitatively the effect of change in temperature of the system at the equilibrium, below 300K.

- b) 40 g sample of solid ammonium carbonate is placed in a closed vessel of 3.0 dm^3 flask and heated to 400 K. It decomposes to produce ammonia gas, water vapor and carbon dioxide gas.



- Write the expression of K_p for the above equilibrium system. Hence show that K_p = K_c(RT)⁴
- The value of the equilibrium constant K_p for the above equilibrium at 400 K is 0.25 atm⁴
Calculate the partial pressure of NH_{3(g)} at 400K.
- Calculate the total pressure inside the flask at equilibrium.
- Calculate the mass of solid ammonium carbonate preset in the flask at the equilibrium.

- c) Consider the following reaction



The above equilibrium is achieved when 5 mol of $\text{N}_2\text{O}_{4(\text{g})}$ and 7 mol of $\text{NO}_{(\text{g})}$ heated in a 2.0 dm^3 rigid vessel. Temperature of the vessel was kept at 500°C at the equilibrium. At the equilibrium mixture contained 2.30 mol of $\text{NO}_{(\text{g})}$ and the equilibrium achieved in 2 minutes. After another two minutes, temperature was increased. Assuming that the system takes another two minutes to reach the equilibrium, sketch on the same axis how the concentration of the three gas will change during the first eight minutes.

- 6) a) i) Write down an expression for the dissociation constant K_a of the weak acid HA. Show that

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

using the above expression.
ii) Consider the hydrolysis of A^- which is the conjugate base of HA. Write an expression for the dissociation constant K_b for A^- .

iii) Using above expressions show that $K_a \times K_b = K_w$ (K_w = dissociation constant of water)

- b) HA is a weak acid. pH of 0.1 mol dm^{-3} HA acid solution at 25°C is 3.3. A solution containing HA and NaA, acts as a buffer solution. 25 cm^3 of above HA solution was transferred in to a titration flask and titrated against 0.1 mol dm^{-3} NaOH solution in the presence of a suitable indicator.

$$(K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-3} \text{ at } 25^\circ\text{C})$$

i) Calculate the H^+ concentration of the above HA solution at 25°C .

ii) Calculate the K_a of HA.

iii) Calculate the pH at the end point of the titration.

iv) Choose a suitable indicator for the titration from the following table.

Indicator	pH range
Methyl Red	4.2 - 6.3
Bromo thymole blue	6.0 - 7.6
Pinolphthalene	8.3 - 10.0

- v) In the above titration 50 cm^3 of NaOH was added drop wise to the titration flask while mixing the solution. Sketch a graph (only the shape of the expected graph) of pH vs NaOH volume.

- vi) Mark the following pH values on the pH axis of the above drawn graph.

I) Initial pH of the flask.

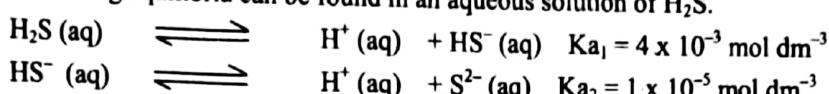
II) $pH = 7$

III) pH at the end point of the titration.

IV) pH at the end of the titration (at 50 cm^3 of NaOH)

- vii) What do you understand the term "buffer solution"
 viii) Briefly explain, whether the solution in titration flask is a buffer at the end point of the titration using the graph drawn draw in (v) above.
 ix) What is the approximate pH range of the HA and NaA mixture which shows the buffer action?
 x) Explain that, this solution shows buffer action within the given pH range using the graph drawn in (V) above.

- c) Following equilibria can be found in an aqueous solution of H_2S .



- i) Calculate the S^{2-} concentration of 0.1 mol dm^{-3} H_2S solutions.
 ii) In a mixture containing H_2S and HCl . The concentration of H_2S and HCl are 0.1 mol dm^{-3} and 0.3 mol dm^{-3} respectively. Calculate the S^{2-} and HS^- concentrations in this solution.

- 7) a) Equal volumes of 0.06 mol dm^{-3} CoI_2 and 0.16 mol dm^{-3} NH_3 Solutions were mixed together. Then the formed compound "A" which has an octahedral geometry was completely removed and the remaining solution was labeled as "B". A portion of "A" was then reacted with excess of KI and formed compound was Labeled as "C" A, B and C were analyzed as follow

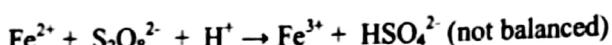
- A - Excess of Cl_2 gas was bubbled through 20 cm^3 of 0.15 mol dm^{-3} solution of A and then the resultant solution was titrated with 0.2 mol dm^{-3} $\text{Na}_2\text{S}_2\text{O}_3$ solution burette reading at the endpoint was 30 cm^3
- B - H_2S was bubbled through a portion of aqueous solution of "B" There was no appreciable change in the solution.
 20 cm^3 of $0.025 \text{ mol dm}^{-3}$ HCl required to reach the endpoint in the titration between 25 cm^3 of solution B and HCl .
- C - 40 cm^3 of 0.1 mol dm^{-3} of C was treated with excess of $\text{Pb}(\text{CH}_3\text{COO})_2$. Then the mass of the resultant precipitate was 0.922 g . (molar mass of the compound in precipitate is 461 g mol^{-1})

- i) Answer the following questions based on analysis of A and B.
- I) Show that all ligands present in the co-ordination sphere of A are neutral.
 - II) Find the number of neutral Ligands present in the co-ordination sphere of A (with the help of Analysis - B)
 - III) Deduce the structural formular of A
 - IV) Write down the IUPAC name of A
- ii) Answer the following questions based an analysis – C
- I) Identify the precipitate of C with the color.
 - II) What is the charge of the co-ordination sphere of C.
 - III) Deduce the structural formular of C.
- b) $\text{Na}_2\text{S}_2\text{O}_8$ is used as an initiating reagent in the production polymers. A sample of $\text{Na}_2\text{S}_2\text{O}_8$ is contaminated, with Na_2SO_4 and water Soluble inert substance. The mixture was analyzed as flows to determine the percentage composition of $\text{Na}_2\text{S}_2\text{O}_8$ and Na_2SO_4 by mass.

5 g of above sample was completely dissolved in water and diluted up to 250 cm³ and Labeled as P. 1.568g of (NH₄)₂Fe(SO₄)₂. 6 H₂O was added to 25 cm³ of P and mixed well. Then the solution was titrated with 0.025 mol dm⁻³ acidified KMnO₄ solution, 20 cm³ of KMnO₄ was required to reached the endpoint. Another 25 cm³ portion of P was treated with excess of BaCl₂. The mass of the precipitate was 0.466 g (Ba - 137, Fe - 56, S - 32, O - 16, N - 14, H - 1)

Molar mass of (NH₄)₂ Fe(SO₄)₂. 6 H₂O = 392 g mol⁻¹.

The following reaction is taking place between Fe²⁺ and S₂O₈²⁻

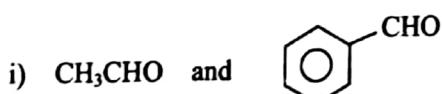


- i) Draw the appreciable Lewis structure for the S₂O₈²⁻ (Peroxodisulfate ion)
- ii) Write down the balanced chemical equation for the reaction between Fe²⁺ and S₂O₈²⁻.
- iii) Calculate the mass percentages of Na₂S₂O₈ and Na₂SO₄ in the mixture.
- iv) State any assumption you made in the calculations.

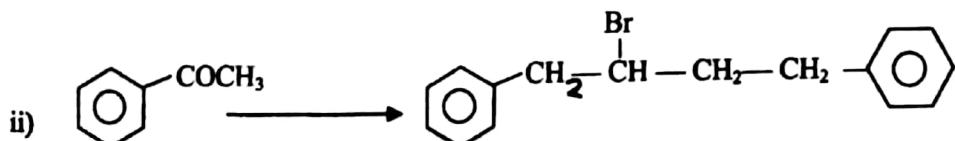
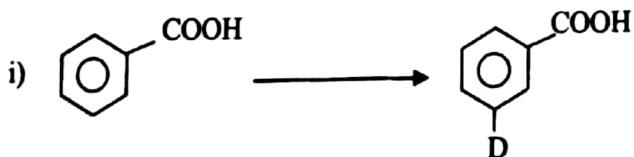
PART C – ESSAY

Answer two questions only. (Each question carries 15 marks)

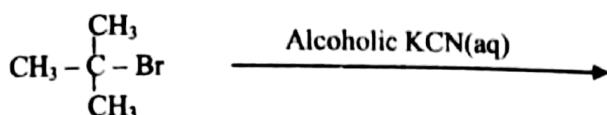
- 8) a) Show that how do you chemically distinguish each chemical species in the following pairs.



- b) Show how you would carry out the following conversion using the given starting compound as the only organic compound.



- c) i) Write down the mechanism for the following reaction.



- ii) Explain why KCN is used in both alcoholic and aqueous media.
 iii) What are the competitive reactions of alkyl halides.
 iv) One of the products of the reaction between $\text{CH}_3\text{CH}_2\text{Br}$ and $\text{CH}_3\text{C}\equiv\text{CNa}$ is $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$. Write down another organic product / products and the mechanism for the formation of that product.

- 9) a) Following tests were carried out to identify the cations and anions present in a mixture of compounds M.

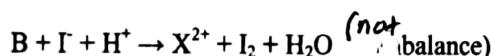
	Test	Observation
1	M was dissolved in aqueous HCl	A pink solution "y" was obtained with colorless gas "X"
2	The gas X was bubbled through a litmus solution.	The color of the solution was decolorized.
3	M was dissolved in water and filtered. H_2O_2 was added to the filtrate and then excess of CaCl_2 was added.	White precipitate Z was obtained.
4	Z was dissolved in dilute HCl.	Part of the precipitate was dissolved while liberating a gas which can turn lime water milky.
5	Water was added in to solution Y.	white precipitate P was obtained.
6	H_2S was bubbled through the solution Y	A clear solution Q and a black precipitate were obtained.
7	The solution obtained from the 6 th test was boiled to remove all H_2S and then NH_4Cl and NH_4OH were added.	White precipitate S was formed.
8	Excess of conc. HCl was added to solution Y.	Blue colored solution R was formed.

Answer the following Questions based on the above test and observations

- i) Identify three cations and two anions present in the mixture M (S^{2-} is not present).
- ii) Write down the balanced chemical equation for the evolution of gas / gases in the test (1)
- iii) Identify the precipitates Z and S.
- iv) Write down the balanced chemical equation for the formation of precipitate P.
- v) Identify R and write down the IUPAC Name of R.
- b) Pale pink solution of XSO_4 forms a yellowish – white precipitate “A” with bases. “A” readily reacts with oxygen forming a brown-black precipitate “B” in basic medium. This property of “A” is used in the determination of dissolved oxygen concentration in water. XSO_4 is oxidized and gives a purple colored solution when reacted with strong oxidizing agents.
- i) Identify metal X
- ii) Write down the balanced chemical equations for the formation of A and B
- iii) The following procedure was used to determine the dissolved oxygen Concentration in a water sample.

Procedure I

200 cm³ brown colored reagent bottle was filled with a water sample. Then little excess amount of XSO_4 and NaOH solutions were added to the bottle. Then Little excess of KI also added and shaken well and then allowed to complete the reaction. Then the mixture was acidified with dilute H_2SO_4 . 15 cm³ of $Na_2S_2O_3$ was required to completely react with I_2 formed in this reaction.



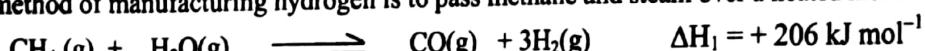
Procedure II

Excess of KI was added to 15 cm³ of 0.005 mol dm⁻³ KIO_3 solution in acidic medium. Then the resultant solution was titrated with the $Na_2S_2O_3$ solution used in above procedure (procedure I). 45 cm³ of $Na_2S_2O_3$ was required to complete the reaction.

- i) Write down the balanced chemical equations for the reactions taking place in this procedure other than you wrote in procedure I.
- ii) What is the indicator that can be used in the titrations in procedure I and II
- iii) What are the color changes occur at the end point of the titration.
- iv) Calculate the concentration of $Na_2S_2O_3$ solution.
- v) Calculate the dissolved O₂ concentration in the water Sample in ppm.

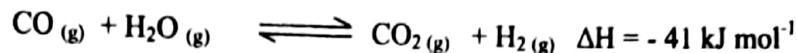
- 10) a) i) By means of a balanced chemical equation illustrate the term “the average C – H bond energy in CH₄”
- ii) Define the term standard enthalpy of reaction.

- b) Hydrogen is used in large quantities in industry to convert nitrogen in to ammonia, for use in fertilizers. One method of manufacturing hydrogen is to pass methane and steam over a heated nickel catalyst.



Bond	Bond energy /kJ mol ⁻¹
C – H	412
O – H	463
H – H	436
C – O	360
C = O	743

- Calculate the total bond energy in the carbon monoxide molecule.
- Suggest why the bond energy you have calculated in (i) above is larger than C – O or C = O bond energies given in the table.
- Carbon monoxide further reacted with more steam over a copper / zinc catalyst.

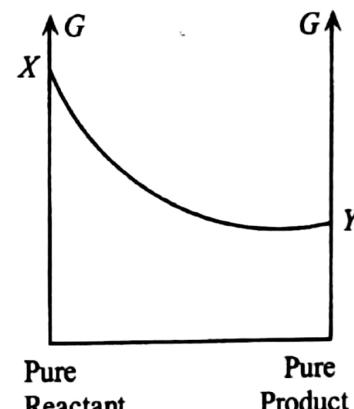


Suggest and explain a method where the carbon dioxide could be removed from the product gas stream.

- c) i) 1 mol of CH₄(g) is reacted with excess of O₂(g) forming CO₂(g) and water vapor. The enthalpy change for this reaction is -802.4 kJ mol⁻¹. The vaporization enthalpy of water is 44 kJ mol⁻¹. Find out the combustion enthalpy of methane (CH₄(g)) under these conditions.
- ii) A sample of water was heated from 25°C to 95°C using the heat evolve when 256 g of CH₄(g) was completely burn. If the specific heat capacity of water is 4200 J K⁻¹ kg⁻¹ and density is 1000 kg m⁻³ and the heat efficiency of burner is 60% calculate the volume of water sample heated. (C - 12, H - 1)
- iii) Due to incomplete combustion of methane, while another burner is used, some amount of CO(g) also formed. Under this condition 1 mol of methane released -859.7 kJ mol⁻¹ calculate the amount of CO_(g) in moles formed when 1 mol of CH₄ is burned.

Compound	Formation Enthalpy / kJ mol ⁻¹
CO (g)	-110
CO ₂ (g)	-393
CH ₄ (g)	-75
H ₂ O(l)	-285

- iv) The Gibb's energy change for the complete combustion of methane is depicted by the following graph.



It is given that

Substance	$\Delta G^\circ/\text{kJ mol}^{-1}$	$\Delta S_f^\circ/\text{J mol}^{-1} \text{K}^{-1}$
CO ₂ (g)	-394	213
H ₂ O(g)	-237	70
O ₂ (g)	0	205
CH ₄ (g)	-51	186

- Calculate the Gibb's energy change (ΔG°) for complete combustion of one mole of CH₄.
- Find out entropy change (ΔS°) for complete combustion of CH₄(g)
- Calculate combustion enthalpy of methane.
- What are the values of x and y in the above graph.

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