(02) Chemistry

Structure of the Question Paper

Paper I - **Time : 02 hours**

This paper consists of **50** multiple choice questions with **5** options. **All** questions should be answered. Each question carries **01** mark. Total marks **50**.

Paper II - **Time : 03 hours.** (In addition, 10 minutes for reading.)

This paper consists of **three** parts as **A, B** and **C**. Some questions in these parts will be based on practicals prescribed in the syllabus.

Part A - **Four structured essay** type questions. **All** questions should be answered.

Question 1 : General Chemistry
Question 2 : Inorganic Chemistry
Question 3 : Physical Chemistry
Question 4 : Organic Chemistry

Each question carries 100 marks - altogether 400 marks.

Part B - **Three essay** type questions. **Two** questions should be answered.

Question 5 : Physical Chemistry
Question 6 : Physical Chemistry
Question 7 : Physical Chemistry and Inorganic Chemistry

Each question carries 150 marks - altogether 300 marks.

Part C - **Three essay** type questions. **Two** questions should be answered.

Question 8 : Organic Chemistry
Question 9 : Inorganic Chemistry
Question 10 : Industrial and Environmental Chemistry

Each question carries 150 marks - altogether 300 marks.

Total marks for paper II = 1000

Calculation of the final mark : Paper I = 50
Paper II = 1000 ÷ 20 = 50
Final mark = 100

(02) Chemistry
Paper I

Important :

* Answer **all** the questions.
* Select the **correct or the most appropriate** answer.

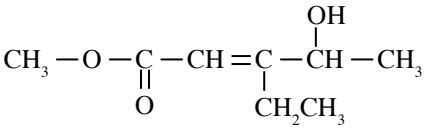
(A separate sheet will be provided to mark answers for multiple choice questions.)

Universal gas constant	R	=	$8.314\,J\,K^{-1}\,mol^{-1}$
Avogadro constant	N_A	=	$6.022 \times 10^{23}\,mol^{-1}$
Planck's constant	h	=	$6.626 \times 10^{-34}\,J\,s$
Velocity of light	c	=	$3 \times 10^{8}\,m\,s^{-1}$

1. Which of the following elements has the lowest third ionization energy?
(1) Mg (2) Ne (3) N (4) P (5) Cl

2. Which molecule from the molecules given below consists the highest number of pi (π) bonds?
(1) H_2SO_4 (2) H_2SO_3 (3) HNO_3 (4) H_3PO_4 (5) $HClO_4$

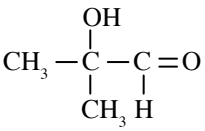
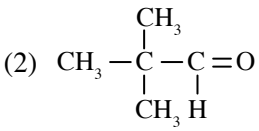
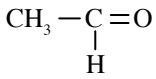
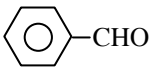
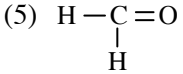
3. Which statement is true regarding $[Al(OH)_4]^-$ ion?
(1) Its central atom hybridization is sp^2.
(2) Its total number of lone pairs of electrons is 8.
(3) It contains d electrons.
(4) Its number of sigma (σ) bonds is 4.
(5) Its total number of electrons in the valence shell is 28.

4. The IUPAC name of the compound  is

(1) methyl-3-ethyl-4-hydroxypent-2-enoate
(2) methyl 3-ethyl-4-hydroxypent-2-enoate
(3) 3-ethyl-1-methoxy-1-oxopent-3-en-4-ol
(4) 3-ethyl-5-methoxy-5-oxopent-3-en-2-ol
(5) methyl 3-ethyl-2-hydroxypent-3-enoate

5. The production process which produces a gas as a by-product giving the highest contribution to global warming is,
(1) Soap production
(2) Nitric acid production
(3) Iron production
(4) Sulphuric acid production
(5) Bio - diesel production

6. Which one of the following compounds undergoes self condensation in basic condition?

(1) 
(2) 
(3) 
(4) 
(5) 

7. Consider the following reaction at 25 °C.

$$CO_2(g) + 2NH_3(g) \longrightarrow CO(NH_2)_2(s) + H_2O(l) \;;\; \Delta H^\circ = -134\,kJ\,mol^{-1}$$

Which of the following is correct regarding this reaction?
(1) ΔS° is always a negative value for the reaction.
(2) ΔH° increases with the temperature.
(3) The decrease in the entropy change can determine the spontaneity of the reaction.
(4) The reaction is spontaneous at all temperatures.
(5) At high temperatures the value of ΔG° becomes more negative.

8. At a given temperature, k is the rate constant of the first order elementary reaction $\mathbf{A}(g) \rightarrow \mathbf{B}(g) + \mathbf{C}(g)$. At the initial stage ($t$=0) pressure of the system is P_1 and after time t, pressure is P_2. What is the rate of the reaction at this instant?

(1) $k(P_2 - P_1)$ (2) $k(P_1 - P_2)$ (3) $k(2P_1 - P_2)$ (4) $k(P_1 - 2P_2)$ (5) $2k(P_1 - P_2)$

9. Which of the following solutions **cannot** be used to distinguish two aqueous solutions of $BaCl_2$ and $Ba(OH)_2$ from each other?

(1) $MgCl_2(aq)$ (2) $AgNO_3(aq)$ (3) $(NH_4)_2SO_4(aq)$ (4) $Na_2Cr_2O_7(aq)$ (5) $Na_2CO_3(aq)$

10. The mole fraction of NH_4NO_3 is $\frac{5}{6}$ in a solid mixture that consists only NH_4NO_3 and $CaCO_3$. The percentage mass of $CaCO_3$ in the mixture is, (N = 14, H = 1, O = 16, Ca = 40, C = 12)

(1) 20% (2) 40% (3) 60% (4) 67% (5) 80%

11. Which of the following statement is **incorrect** with regard to water pollution.

(1) NO_3^- and PO_4^{3-} ions contribute for the reduction of dissolved oxygen in water.
(2) Amount of dissolved oxygen in water is decreased when dissolved organic matter is present.
(3) Amount of dissolved oxygen in water is decreased when heavy metal ions are present.
(4) Oxygen circulation process in the blood is affected by taking water containing excessive amount of NO_3^- ions.
(5) Certain bacteria contributes for the addition of iron into water.

12. Which of the following statement is correct for the membrane cell used in the production of NaOH?

(1) Anode of the cell is graphite rod.
(2) NaOH is produced and Cl_2 gas is evolved in the cathode compartment.
(3) OH^- ions travel from cathodes to anode through membrane.
(4) NaOH is produced and H_2 gas is evolved in the cathode compartment.
(5) 60% NaOH solution is obtained as the final product.

13. Which of the following statement is **false** regarding $C_2H_5NH_2$? It

(1) is more basic than Aniline.
(2) reacts with $NaNO_2$/dil. HCl and evolves N_2 gas as a product.
(3) reacts with alkyl halide and give mixture of products.
(4) shows nucleophilic substitution reactions with aldehydes and ketones.
(5) forms salts with dilute mineral acids.

14. Consider the following reaction.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) + \text{Energy}$$

At 25 °C in a rigid closed container, certain amounts of $PCl_3(g)$ and $Cl_2(g)$ are mixed and allowed to reach above equilibrium. The following statements are mentioned as reasons to increase number of moles of $PCl_5(g)$ in equilibrium.

A - reduce the volume of the container at a constant temperature.
B - increase the temperature at a constant volume.
C - addition of a certain amount of Ar gas into the container at constant temperature and volume.

What is/are true among above statements?

(1) A only. (2) B only. (3) A and B only.
(4) A and C only. (5) B and C only.

15. The volume of 0.01 mol dm^{-3} $K_2Cr_2O_7$ (cm^3) required to react completely with 25.00 cm^3 of 0.02 mol dm^{-3} of FeI_2 aqueous solution in acidic medium is,

(1) 8.33 (2) 10.00 (3) 16.67 (4) 20.00 (5) 25.00

16. At room temperature solute **X** is dissolved in a system with two immiscible solvents **A** and **B**, which are in contact with each other. **X** present as single molecule (**X**) in solvent *A*. In solvent **B**, n number of molecules of **X** associated to form $\mathbf{X}_n$ molecules. Then $n\mathbf{X} \rightleftharpoons \mathbf{X}_n$ equilibrium exists, with equilibrium constant K_c. In addition, a few single molecules of **X** also present in solvent **B**. If C_1 is the concentration of **X** in solvent **A**, C_2 is the concentration of free - **X** in solvent **B** and C_3 is the concentration of $\mathbf{X}_n$ in solvent **B**, and partition coefficient of the system is K_D; which of the following gives the $\frac{K_D}{\sqrt[n]{K_C}}$ ratio?

(1) $\frac{C_1}{\sqrt[n]{C_3}}$ (2) $\frac{C_3}{\sqrt[n]{C_1}}$ (3) $\frac{C_1}{C_2}$ (4) $\frac{C_3}{C_2^n}$ (5) $\frac{C_1}{C_3^n}$

17. Consider the following bond energies at 25 °C,

Bond	Bond energy / kJ mol^{-1}
A - **A**	150
B - **B**	250
A - **B**	200

The enthalpy change $\Delta H°$ (kJ mol^{-1}) of the reaction, $\mathbf{A}_2(g) + 3\mathbf{B}_2(g) \longrightarrow 2\mathbf{AB}_3(g)$ is,

(1) −300 (2) 300 (3) −500 (4) 500 (5) 1200

18. Consider the following equilibrium in a closed rigid container of volume 1.0 dm^3 at 50 °C.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

At 50 °C ***a*** moles of $SO_2(g)$ and ***b*** moles of $O_2(g)$ are placed in the vessel. After reaching the equilibrium, it was found that ***x*** moles of $SO_3(g)$ were present in the container. Equilibrium constant K_C for the forward reaction is,

(1) $\frac{(a-2x)^2(b-x)}{x^2}$ (2) $\frac{x^2}{(a-x)^2(b-x)}$ (3) $\frac{x^2}{(a-x)^2(b-0.5x)}$

(4) $\frac{(a-x)^2(b-0.5x)}{x^2}$ (5) $\frac{x^2}{(a-2x)^2(b-x)}$

19. Which of the following organic compound shows geometrical isomerism?

(1) 3,3-dibromo-1-butene (2) 2-bromo-1-butene
(3) 1- bromo-2-methylpropene (4) 1-bromo-2-butene
(5) 1,1-dibromo-1-butene

20. Upon the addition of 42.5 g of a mixture of K and Na metal pieces, to 1.0 dm^3 of distilled water at 25 °C, mass of the gas evolved was 0.5 g. The pH value of the solution produced is,
(Na = 23, K = 39, H = 1, O = 16)

(1) 0.3 (2) 1.7 (3) 13.0 (4) 13.7 (5) 14.0

21. A required mass of solid NaI is dissolved in a certain quantity of water to prepare a 1.00 mol dm^{-3} solution of NaI at 25 °C. When two Pt electrodes were dipped in this solution and connected by a conducting wire, which of the following shows overall cell reaction and electro motive force (e.m.f.) of the cell at 25 °C?

$E°_{I_2/I^-} = 0.53$ V, $E°_{H_2O/H_2} = -0.83$ V

(1) $2I^-(aq) + 2H_2O(l) \longrightarrow I_2(s) + H_2(g) + 2OH^-(aq)$; −0.30 V

(2) $2I^-(aq) + 2H_2O(l) \longrightarrow I_2(s) + H_2(g) + 2OH^-(aq)$; +0.30 V

(3) $I_2(s) + H_2(g) + 2OH^-(aq) \longrightarrow 2I^-(aq) + 2H_2O(l)$; −1.36 V

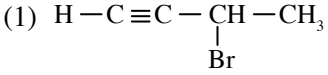
(4) $I_2(s) + H_2(g) + 2OH^-(aq) \longrightarrow 2I^-(aq) + 2H_2O(l)$; +1.36 V

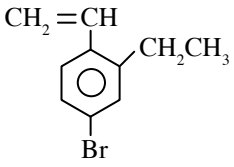
(5) $I_2(s) + H_2(g) + 2OH^-(aq) \longrightarrow 2I^-(aq) + 2H_2O(l)$; 0.00 V

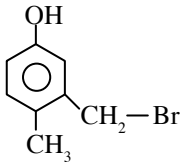
22. At 25°C, what is the pH of a buffer solution prepared by mixing 250.00 cm^3 of 2.20 mol dm^{-3} CH_3COOH and 250.00 cm^3 of 2.00 mol dm^{-3} NaOH?
(For CH_3COOH acid, at 25°C $K_a = 1.0 \times 10^{-5}$ mol dm^{-3})

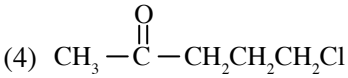
(1) 4 (2) 5 (3) 6 (4) 7 (5) 8

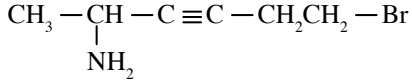
23. Of the compounds given below, which can be used to prepare Grignard reagent?

(1) 

(2) 

(3) 

(4) 

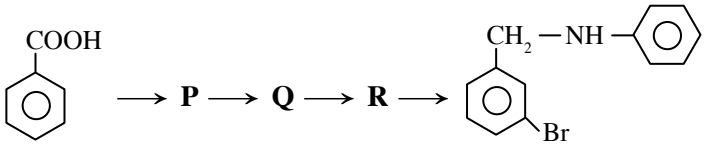
(5) 

24. Electroplating of a metal X with molar mass M was done by electrolyzing aqueous solution of XCl_2 for 10 hours with a constant current of I A. Which of the following gives the maximum mass of X that could be plated? (Faraday constant is F).

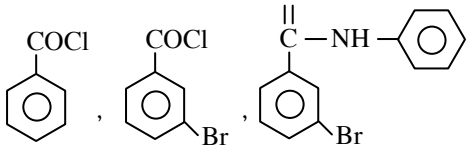
(1) $\frac{3600 \times 10 \times I \times M}{F}$ (2) $\frac{3600 \times 10 \times I \times M}{2F}$ (3) $\frac{10 \times 60 \times I \times M}{F}$

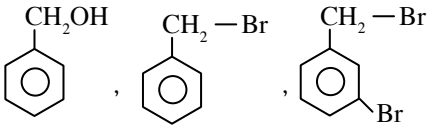
(4) $\frac{10 \times 60 \times I \times M}{2F}$ (5) $\frac{10 \times I \times M}{2F}$

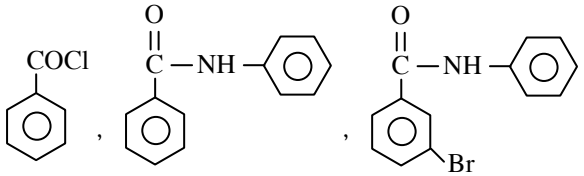
25. Consider the reaction sequence given below;

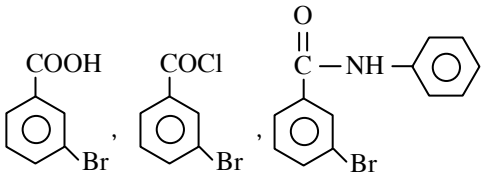


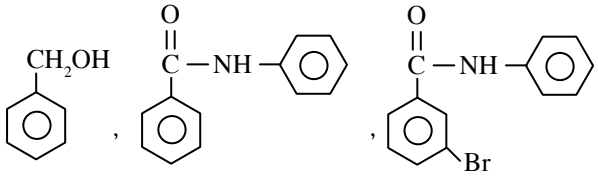
Which answer in the following shows the most appropriate structures for **P, Q, R** respectively?

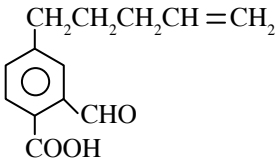
(1) 

(2) 

(3) 

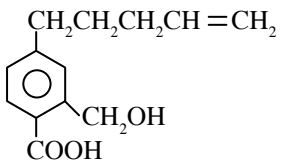
(4) 

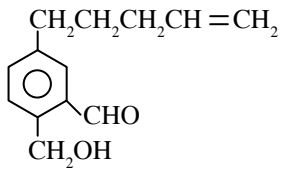
(5) 

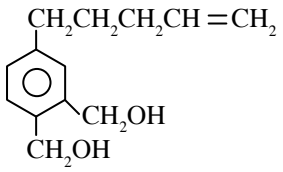
26. 

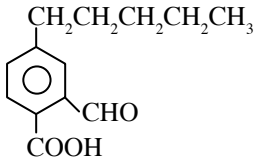
A

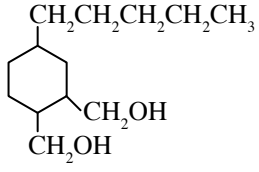
The product formed, when compound **A** was reacted with $LiAlH_4$ followed by the addition of water is,

(1) 

(2) 

(3) 

(4) 

(5) 

27. Given below are some experimental information of three isomers of **A**, **B**, **C** with molecular formula $C_5H_{10}O$.

A - shows geometrical isomerism and decolourizes Br_2 water.

B - shows enantiomerism and does not gives an orange colour precipitate with Brady's reagent.

C - gives silver mirror with Tollens' reagent.

Answer with correct structures of **A**, **B**, **C** are respectively,

(1) $CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_2OH$, $CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CHO$ and $CH_3CH_2CH_2CH_2CHO$

(2) $CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2CH_2OH$, $CH_2=CH-\overset{\overset{OH}{|}}{CH}-CH_2CH_3$ and $H-\overset{\overset{O}{||}}{C}-\overset{\overset{CH_3}{|}}{CH_2CH}CH_3$

(3) $CH_3CH_2-\overset{\overset{CH_2OH}{|}}{C}=CH_2$, $CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CHO$ and $CH_3CH_2-\overset{\overset{O}{||}}{C}-CH_2CH_3$

(4) $CH_3CH=CHCH_2CH_2OH$, $CH_2=CH-\overset{\overset{CH_3}{|}}{CH}-CH_2OH$ and $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO$

(5) $CH_3CH_2CH=CHCH_2OH$, $CH_2=CH-\overset{\overset{OH}{|}}{CH}-CH_2CH_3$ and $CH_3-\overset{\overset{CH_2OH}{|}}{CH}-CH=CH_2$

28. Which of the following is correct for the energy range of a photon of visible light in the wave length range λ_1 to λ_2, (nm) ($\lambda_1 < \lambda_2$)?
(h = planck constant, c = velocity of light)

(1) $hc\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)\times 10^9\,J$ (2) $hc\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)\times 10^9\,J$ (3) $hc\left(\frac{\lambda_2-\lambda_1}{\lambda_1\lambda_2}\right)\times 10^{-19}\,J$

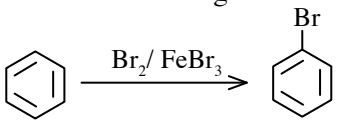
(4) $hc\left(\frac{\lambda_1-\lambda_2}{\lambda_1\lambda_2}\right)\times 10^{-19}\,J$ (5) $hc\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)\times 10^{-19}\,J$

29. In an experiment $V\,cm^3$ of $H_2(g)$ was collected at the pressure P and at temperature T by downward displacement of water. Saturated vapor pressure of water at this temperature is $P^\circ_{H_2O}$. The ratio of number of moles of $H_2(g)$ to $H_2O(g)$ and ratio of average speeds of $H_2(g)$ to $H_2O(g)$ are respectively.

(1) $\frac{P-P^\circ_{H_2O}}{P^\circ_{H_2O}}$ and 3 (2) $\frac{P-P^\circ_{H_2O}}{P^\circ_{H_2O}}$ and $\frac{1}{3}$ (3) $\frac{P^\circ_{H_2O}}{P}$ and 3

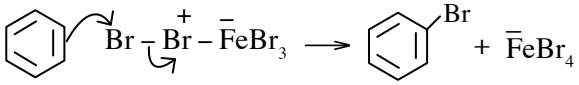
(4) $\frac{P}{P^\circ_{H_2O}}$ and 3 (5) $\frac{P}{P^\circ_{H_2O}}$ and $\frac{1}{3}$

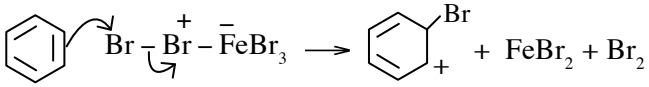
30. Consider the following reaction.

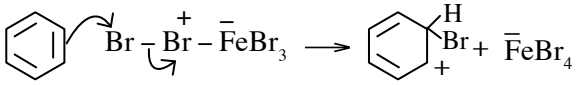


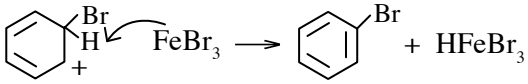
Which answer shows a correct step in mechanism of the above reaction.

(1) $Br_2 + FeBr_3 \longrightarrow Br - Br - \bar{F}eBr_2 + Br^+$

(2) 

(3) 

(4) 

(5) 

- 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
  - (1) if only (*a*) and (*b*) are correct.
  - (2) if only (*b*) and (*c*) are correct.
  - (3) if only (*c*) and (*d*) are correct.
  - (4) if only (*d*) and (*a*) are correct.
  - (5) if **any other** number or combination of responses is correct.

Summary of above Instructions

(1)	(2)	(3)	(4)	(5)
Only (*a*) and (*b*) are correct.	Only (*b*) and (*c*) are correct.	Only (*c*) and (*d*) are correct.	Only (*d*) and (*a*) are correct.	**Any other** number or combination of responses is correct

31. Ions consisting ^{16}O and ^{15}N are given below. Among these ion(s) contain(s) higher number of neutrons than electrons?

(*a*) NO_2^+ (*b*) N_3^- (*c*) NO_3^- (*d*) O_2^{2-}

32. Which of the following statement/s is/are true regarding O_3 and O_2,

(*a*) Bond length of O_3 is less than the bond length of O_2.

(*b*) Dipole moment of both species is zero.

(*c*) O_3 gas is a green house gas eventhough O_2 is not.

(*d*) Ozone layer consist of O_2 and O_3.

33. In an experiment to determine the molar enthalpy change of dissolution ($\Delta H_{dissolution}$) of urea in water, 6 g of urea (H_2NCONH_2) was dissolved in 100 g of water in a calorimeter at 25°C. The final temperature of the solution was found to be 22 °C. Assume that no volume change occurs during dissolution of urea in water and density of solution is same as that of water ($1.0\,g\,cm^{-3}$), no heat loss occurred and specific heat capacity of the solution is $4.0\,J\,g^{-1}\,K^{-1}$. Which of the following statement/s is/are better describe the above experiment?

(H = 1, C = 12, N = 14, O = 16)

(*a*) During the dissolution of 6 g of urea 1.2 kJ of heat is released to the surroundings.

(*b*) During the dissolution of 6 g of urea 1.2 kJ of heat is absorbed by the system.

(*c*) During the dissolution of 1 mole of urea 12 kJ of heat is absorbed by the system.

(*d*) During the dissolution of 1 mole of urea 12 kJ of heat is released to the surrounding.

34. In any unimolecular reaction which is not at equilibrium,

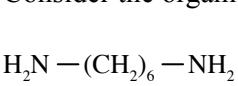
(*a*) Only one reactant is present in the rate determining step.

(*b*) In the slowest step both molecularity and order is one.

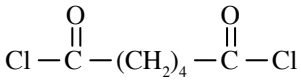
(*c*) Molecularity is one and it is zeroth order.

(*d*) Both molecularity and order are zero.

35. Consider the organic compounds given below.

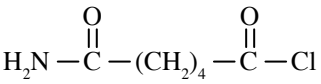


A

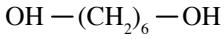


B

C



D



E

Which statement/statements below is/are true about the above organic compounds.

(*a*) A and B can be used to prepare a type of polyester.

(*b*) A and B can be used to prepare a type of nylon.

(*c*) C can be used to prepare a type of addition polymer.

(*d*) D can be used to prepare a type of nylon.

36. 1.0 mol of HI(g), 0.2 mol of $H_2(g)$ and 0.5 mol of $I_2(g)$ were placed in a rigid closed container with volume 1.0 dm^3, and allowed to reach equilibrium at 750 K.

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$; $K_C = 2.5 \times 10^{-2}$. Q_C is reaction quotient.

Which of the following statement(s) is/are correct regarding this system?

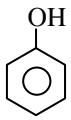
(*a*) Initially $Q_C > K_C$; reaction proceeds to produce more HI(g).

(*b*) Initially $Q_C > K_C$; reaction proceeds to produce more $I_2(g)$ and $H_2(g)$.

(*c*) Initially $Q_C > K_C$; more $H_2(g)$ and $I_2(g)$ consumed.

(*d*) Initially $Q_C < K_C$; more $H_2(g)$ and $I_2(g)$ consumed.

37.



A

CH_3CH_2OH

B

What is/are the most correct statement/s about two compounds A and B given above.

(*a*) Rate of nucleophilic substitution reactions of A is higher that of B.

(*b*) A undergoes electrophilic substitution reactions whereas B does not do so.

(*c*) In A, C — O bond has partial double bond nature and in B, C — O bond is a single bond.

(*d*) Carbon which is combined to oxygen in A is more electron deficient than carbon atom corresponds to B.

38. Cooling of the following equilibrium system changes its colour from green to blue.

$Cu^{2+}(aq) + 4Br^{-}(aq) \rightleftharpoons [CuBr_4]^{2-}(aq)$

blue green

Which of the following statement/s is/are correct regarding the above system when cooled?

(*a*) The value of K_C decreases.

(*b*) Initial Q_C is greater than K_C.

(*c*) Forward reaction is exothermic

(*d*) The value of K_C increases.

39. In endothermic reaction $\mathbf{A}_2(g) + \boldsymbol{B}_2(g) \longrightarrow 2\mathbf{AB}(g)$ which occurs in a closed container at 298 K, rate equation is, rate = $\boldsymbol{k}[\mathbf{A}_2(g)][\mathbf{B}_2(g)]$. Which of the following statement(s) is/are better describe this reaction?

(*a*) When $A_2(g)$ is added at constant temperature and volume, rate increases.

(*b*) When volume of container is increased at constant temperature, rate decreases.

(*c*) When a catalyst is added at constant temperature and pressure, activation energy of the reaction decreases.

(*d*) When $A_2(g)$ is added keeping temperature and volume constant, rate decreases.

40. Heating of small amount of $KMnO_4(s)$ by using platinum wire,

(*a*) Turns the Bunsen flame in to dark green.

(*b*) Increases the brightness of the Bunsen flame.

(*c*) The solid residue formed consists of K_2MnO_4 and MnO_2.

(*d*) Disproportionation reaction occurs.

- In question numbers **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 statements	Second statements
(1)	True	True, and correctly explains 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.	Black colour precipitate is formed when H_2S gas is bubbled through aqueous solution of $AgNO_3$.	Ag^+ is precipitated as Ag_2S in group I in the group analysis of cations.
42.	Temperature of the lower part of the blast furnace is around 1300 °C.	All the reactions occur in the blast furnace are exothermic.
43.	Nucleophilic substitution reaction rate of carboxylic acid is greater than acid chlorides.	Electron deficiency at carbonyl carbon of carboxylic acid is greater than carbon of acid chlorides.
44.	At room temperature when a Zn rod is immersed in a $ZnSO_4(aq)$ solution, the potential difference between the Zn rod and the solution is the electrode potential.	At room temperature when two different electrodes are connected through a salt bridge, the potential difference between the two electrodes is the electromotive force of the cell.
45.	Covalent character of NaI is greater than that of NaF.	Polarizability of halide ions increases with increasing radii.
46.	$NaClO_3$ can be obtained by the reaction between NaOH and Cl_2.	NaOH can act as an oxidizing agent.
47.	All the addition polymers are saturated.	Addition polymers can be formed by only unsaturated monomers.
48.	Aqueous solutions of Cu^{2+}, Zn^{2+} and Fe^{2+} produce clear transparent solutions with excess aqueous NH_3.	All 3*d* cations containing vacant valence orbitals form complex ions by gaining lone pairs of electrons from NH_3.
49.	For an equilibrium system with an endothermic forward reaction, increasing of temperature causes the position of equilibrium to shift towards left.	Increasing temperature of endothermic equilibrium reaction causes to increase the value of equilibrium constant.
50.	$CH_4(g)$ does not behave as an ideal gas at high pressures.	Gaseous molecules get closer at high pressures and the volume of the gas is a considerable percentage of the volume of the vessel.

* * *

(02) Chemistry

Paper II

Important :

* Answer **all** the questions in Part **A**.
* Answer **four** questions selecting **two** questions from Part **B** and **two** questions from Part **C**.

Part A - Structured Essay

1.(*a*) Consider the first seven elements in the third period of the periodic table.

(i) Identify and write the symbols of the elements showing the following properties.

I. highest second ionization energy .....

II. highest melting point .....

III. amphoteric property .....

(ii) Write the chemical formula of the compound formed by the reactions of elements having the highest and the lowest electro-negativities from the above elements.

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(iii) Explain briefly why the above compound in (ii) has a very high melting point.

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(25 marks)

(*b*) NO and NO_2 are odd electron compounds of nitrogen containing an unpaired electron on each N.

(i) Draw the most acceptable Lewis structures for NO and NO_2.

(ii) Write the chemical formula and IUPAC name of the compound formed when NO and NO_2 react with each other.

.....

(iii) Draw the most acceptable Lewis structure for the compound state in (ii) above.

(iv) Draw the resonance structures associated with the compound in (iii) above.

(v) From the resonance structures drawn above (iv) which structure/structures largely contribute to the true structure?

(vi) Which is the weakest bond in a molecule of the compound in (ii) above? State the reason for your choice.

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(vii) If the compound in (ii) above is heated to a higher temperature, what would you expect to happen?

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(viii) Label the two N atoms as N_1 and N_2 in the structure in part (iv) above and complete the table below.

	N_1	N_2
hybridization		
electron pair geometry		
shape around the atom		
Oxidation number		

(50 marks)

(*c*) Arrange the following (i) - (v) in the ascending order of the property as given in parentheses.

(i) K_2CO_3, $MgCO_3$, $CaCO_3$, $BaCO_3$ (decomposition temperature)

..... < ..... < ..... < .....

(ii) H_2CO, CO, CO_2, $COCl_2$ (electronegativity of carbon)

..... < ..... < ..... < .....

(iii) NO_2^-, NO_3^-, NO^+, NOF (N — O bond length)

..... < ..... < ..... < .....

(iv) energy released in the process $M(g) + e \rightarrow M^-(g)$ Where M is C, F, Mg and Cl.

..... < ..... < ..... < .....

(v) C_3H_7OH, CH_3CH_2COOH, C_2H_5CHO, $C_2H_5OCH_3$ (saturated vapour pressure at STP)

..... < ..... < ..... < .....

(25 marks)

2 (*a*) An alloy containing Al and Mg metals only and is weighing 3.0 g reacted with 0.10 mol dm^{-3}, aqueous solution of NaOH. The volume of gas evolved at STP was 1680 cm^3.
(Al = 27, Mg = 24 ; 1 mole of gas at STP occupies a volume of 22400 cm^3)

(i) Write relevant balanced chemical equations for above process.

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(ii) Calculate the mass percentage of Al in the alloy.

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(iii) Another portion of the alloy weighing 3.0 g of the above alloy is completely reacted with dilute HCl solution. Write the relevant balanced chemical equations for the reactions with HCl.

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(iv) Calculate the volume of gas evolved at STP in part (iii) above.

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(v) State **two** industrial uses of the gas/gases evolved in part (i) and (iii) above?

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(50 marks)

(*b*) $TiFeO_3$ is a stable compound. Given that the oxidation states of the two metal ions are different,

(i) Stare the oxidation states of the two metal ions.

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(ii) Write the electronic configuration of the constituent metal ions of the above compound.

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(iii) Predict the colour of the solution giving reasons, when $TiFeO_3$ is dissolved in HCl acid.

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(iv) State the observation when dilute NaOH solution is added to the solution in (iii) above?

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(25 marks)

(*c*) Five test tubes labelled as **A**, **B**, **C**, **D** and **E** contain white solids. These are $ZnCO_3$, $Ca(NO_3)_2$, NH_4NO_2, Li_2CO_3 and $NaNO_3$ (not in the same order). The observations of experiments done to identify each compound is given below.

Compound	Vigorous heating	Residue
A	no solid residue	–
B	yellow solid residue + colourless gas	became white on cooling.
C	white solid residue + brown gas	dissolve in dilute HCl and subjected to the flame test. Brick red colour observed.
D	white solid residue + colourless gas	dissolve in water giving a clear solution which turns pink with phenolphthalein.
E	white solid residue + colourless gas	gives brown colour gas with dilute HCl.

(i) Identify the compounds **A**, **B**, **C**, **D** and **E**.

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(ii) Write balanced chemical equations for the thermal decomposition of each compound above.

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(25 marks)

3 (*a*) $I^-(aq)$ ion is oxidized to hypoiodite, $[IO^-(aq)]$, when reacted with hypochlorite, $[ClO^-]$ in basic medium as follows.

$$I^-(aq) + ClO^-(aq) \xrightarrow{OH^-(aq)} IO^-(aq) + Cl^-(aq)$$

Initial rate method was used to study the kinetics of the above reaction at 25 °C. The time taken to occur a known concentration change in $IO^-(aq)$, $\Delta[IO^-(aq)]$ was measured. The results obtained in such an experiment are shown in the following table.

Experiment	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial $[ClO^-(aq)]$/ mol dm^{-3}	$\Delta[IO^-(aq)]$/ mol dm^{-3}	Time/(s)	Initial rate / mol dm^{-3} s^{-1}
1	0.010	0.020	0.015	100	.....
2	0.030	0.020	0.090	200	.....
3	0.010	0.080	0.180	300	.....

(i) Calculate the initial rates in each experiment and fill the relevant column.

(ii) By taking **a** and **b** as orders of the reaction with respect to $I^-(aq)$ and $OCl^-(aq)$ respectively and **k** as the rate constant of the reaction at 25 °C, Calculate values of **a**, **b** and **k**.

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(iii) Write the rate law of the reaction.

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(iv) A separate set of rate measurement experiments was carried out by keeping the concentration of $[I^-(aq)]$ constant with different concentrations of $[ClO^-(aq)]$. Compare the variation of rate with $[ClO^-(aq)]$ in a graph, if such experiments carried out with and without a catalyst.

(60 marks)

(*b*) (i) Write a mathematical expression for Raoult's Law, and define the terms appearing in it.

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(ii) At 50 °C, 43 g of liquid hexane(C_6H_{14}) is mixed with 39 g of liquid benzene (C_6H_6). At 50 °C saturated vapor pressures of pure hexane and benzene are 75 kPa and 50 kPa respectively. Calculate the total vapor pressure of the mixture at 50 °C. (C = 12, H = 1)

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(iii) State the assumptions made in the above calculation.

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(40 marks)

4. (*a*) **A**, **B**, **C** and **D** are four compounds which are isomers of molecular formula C_4H_9Br. Only **A** shows optical isomerism. The carbon skeletons of **B** and **D** are same and it differs from the skeleton of **A**. Dehydrobromination followed by addition of HBr to **D** produces **B**.

(i) Draw the structures of **A**, **B**, **C** and **D** in the boxes given below.

A	**B**
C	**D**

with aqueous NaOH to give compounds with molecular formula $C_4H_{10}O$.

I. Draw the structures of the products **X** and **Y** formed by **B** and **C** with aqueous NaOH.

B $\xrightarrow{\text{aqueous NaOH}}$ **X** :

C $\xrightarrow{\text{aqueous NaOH}}$ **Y** :

II. What are the type(s) of reactions that occur in **B** and **C** from types given below? (Electrophilic addition $\boldsymbol{A_E}$, Electrophilic substitution $\boldsymbol{S_E}$, Neucleophilic substitution $\boldsymbol{S_N}$, Neucleophilic addition $\boldsymbol{A_N}$, Elimination reaction ***E***)

B ☐ **C** ☐

(iii) State a simple experiment to distinguish **X** and **Y** from each other with the relevant observations.

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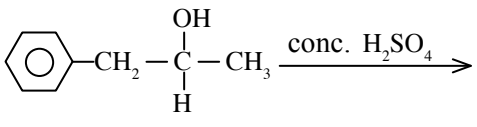
(40 marks)

(*b*) Draw the structures of the main product formed in reactions given below in the boxes given below.

(i) $CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle CH_2CH_3}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow{\text{alcoholic KOH}}$ ☐

(ii)  ☐

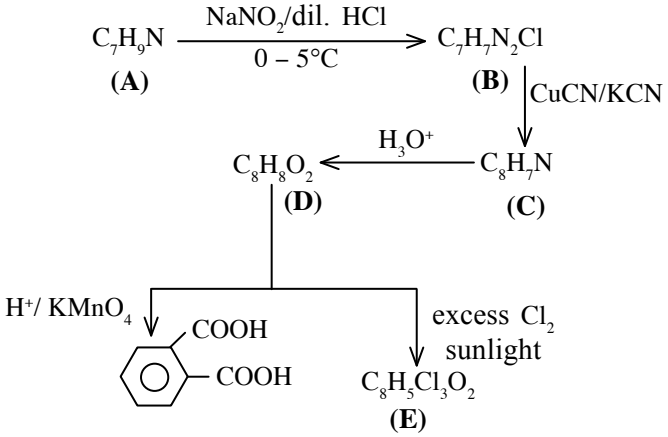
(iii) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) excess } \langle\!\bigcirc\!\rangle\text{-MgBr, (dry ether)}}$ ☐

(iv) $CH_3CH_2-C\equiv C-H \xrightarrow[60\,^\circ C]{HgSO_4/\text{dil. } H_2SO_4}$ [ ]

(v) $CH_3-C\equiv C-H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2}$ [ ]

(25 marks)

(*c*) Primary aromatic amine of **A** was subjected to the following reaction sequence.



(i) Draw the structures of **A**, **B**, **C**, **D** and **E** in the boxes given below.

A

B

C

D

E

(ii) Draw the structure of the product formed when compound **A** reacts with $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$.

(iii) Draw the structure of the product formed when compound **B** reacts with phenol in the presence of NaOH at 0 - 5 °C.

(35 marks)

* *

Part B - Essay

5 (*a*) At 600 K, a rigid closed 5.00 dm^3 vessel contains 56 g of $N_2(g)$ and 64 g of $O_2(g)$. At 600 K , $RT = 5.0\times10^3\ J\ mol^{-1}$ (N = 14, O = 16)

(i) What is the total pressure of the gas mixture in the vessel?

(ii) Temperature of the above gas mixture is decreased to 300 K. Calculate the partial pressures of $N_2(g)$ and $O_2(g)$ under the new condition. At 300 K, $RT = 2.5 \times 10^3\ J\ mol^{-1}$.

(iii) In a separate experiment, 0.16 mol of $NO_2(g)$ was introduced into a 5.00 dm^3 rigid container at 600 K, allowed to reach the following equilibrium and the pressure in the container was found to be 2.0×10^5 Pa.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

Calculate K_P and K_C for the above equilibrium at 600 K.

(iv) At 600 K, 0.20 mol of $NO_2(g)$, 0.10 mol of NO(g) and 0.05 mol of $O_2(g)$ are placed in 1.00 dm^3 rigid closed container and allowed to reach the equilibrium. With the help of your answer for K_C in part (iii) above, compare (increase or decrease) the equilibrium concentrations of $NO_2(g)$, NO(g) and $O_2(g)$ with their initial concentrations, by considering reaction quotient (Q_c) at the initial point.

(v) In an another experiment, 0.20 mol of $O_2(g)$ were added to 5.00 dm^3 rigid vessel containing 0.20 mol of NO(g) at 600 K. The added $O_2(g)$ reacts with the NO(g) in the container.

I. Write balanced chemical equation for the reaction occurring in the container.

II. Calculate the total pressure in the container assuming that the reaction take place completely. **(75 marks)**

(*b*) Liquid heptane $C_7H_{16}(l)$ undergoes complete combustion as follows.

ΔH°_C = Standard Enthalpy of Combustion

$$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(l) \qquad \Delta H^\circ_C = -4850\ kJ\ mol^{-1}$$

(i) Using the information given below, calculate Standard Enthalpy of Formation ΔH°_f of $C_7H_{16}(l)$ in $kJ\ mol^{-1}$

	ΔH°_f / $kJ\ mol^{-1}$
$CO_2(g)$	−393.5
$H_2O(l)$	−285.8

(ii) In a practical examination, a student was instructed to determine the standard neutralization enthalpy ($kJ\ mol^{-1}$) ΔH°_{neu} for the reaction, $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$.

1.00 mol dm^{-3} HCl and 1.00 mol dm^{-3} NaOH solutions, measuring cylinders, polystyrene cup and a thermometer were provided.

I. Explain how you would design the above experiment and the necessary assumptions to be made in the process.

II. What are the measurements those have to be made for the estimation of the heat, **q** released in the experiment?

III. In a certain experiment, 200.00 cm^3 of 1.00 mol dm^{-3} HCl and 200.00 cm^3 of 1.00 mol dm^{-3} NaOH solutions at 25 °C were mixed in a polystyrene cup and the maximum temperature was found as 31.5 °C. Calculate the ΔH°_{neu} ($kJ\ mol^{-1}$) for the reaction. You are given that density of water is 1.00 g cm^{-3} and specific heat capacity of water is 4.2 J $g^{-1}\ K^{-1}$.

IV. The student repeated the experiment with the same volumes in (III) by using of 2.00 mol dm^{-3} HCl and 2.00 mol dm^{-3} NaOH solutions. Here,

(A) Is the value of **q** increased, decresed or stable? Give reasons for your answer.

(B) Is the value of ΔH°_{neu} increased, decresed or stable? Give reasons for your answer.

V. If there was a significant amount of heat lost during the experiment, how would this affect the value of ΔH°_{neu}?

(75 marks)

6 (*a*) At 25 °C propanoic acid $C_2H_5COOH(aq)$ ionizes in aqueous solution as given below.

$C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)$

at 25 °C $K_a = 1.00 \times 10^{-5}\,mol\,dm^{-3}$

(i) Write the expression for the acid dissociation constant K_a.

(ii) Calculate the pH of $0.100\,mol\,dm^{-3}$ $C_2H_5COOH(aq)$ solution at 25 °C.

(iii) At 25 °C, 25.00 cm^3 the solution in (ii) was titrated with $0.100\,mol\,dm^{-3}$ NaOH solution.

I. State whether the mixture at the equivalence point is acidic or basic by using an appropriate reaction.

II. Calculate the value of pH.
(at 25 °C, $K_w = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$)

(60 marks)

(*b*) At 25 °C, following equilibrium exists in an aqueous saturated solution of Ag_2CrO_4.

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$ $\quad K_{sp} = 3.2 \times 10^{-11}\,mol^3\,dm^{-9}$ at 25 °C

(i) Write the expression for solubility product constant of the above system.

(ii) Determine the concentration of $[Ag^+(aq)]$ in a saturated solution of Ag_2CrO_4 at 25 °C.

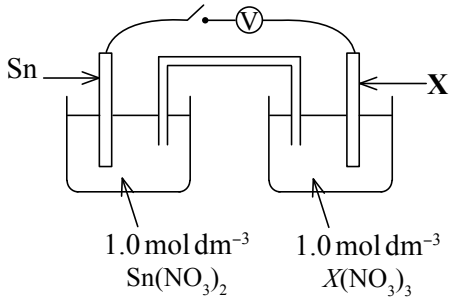
(iii) Calculate the maximum mass of $Ag_2CrO_4(s)$ in grams that can be dissolved in 100.00 cm^3 of water at 25 °C. ($Ag_2CrO_4 = 332\,g\,mol^{-1}$)

(60 marks)

(*c*) State the conditions to be satisfied for the application of distribution law in the determination of partition coefficient, K_D of a system formed by dissolving a solute in two immiscible solvents.

(30 marks)

7 (*a*)



An electrochemical cell was constructed by using Sn and unknown metal **X** electrodes as shown in the above diagram at 25 °C. When the switch is kept 'ON' for some time, the mass of the Sn electrode was increased.

(i) Giving reasons identify the anode and cathode.

(ii) Write down the half - reactions of above cell by identifying the oxidation state of **X**.

(iii) Indicate the direction of electron flow.

(iv) At 25 °C $E°_{Sn^{2+}/Sn} = -0.14$ V. It was found that electro motive force of cell $E°_{cell}$ as +0.60 V. What is the value of $E°_{X^{3+}/X}$ electrode. Is the answer consistent with the half reactions identified in (ii) above?

(v) Write the overall cell reaction when the cell is operation.

(vi) How many moles of electrons are transferred when 1.0 mol of $Sn^{2+}(aq)$ is consumed in the cell.

(vii) At 25 °C, an electric current of 1.0 A is passed through the cell for one hour. Calculate the mass of Sn (in grams) that is deposited on the Sn electrode.
(Sn = 119, Faraday constant (F) = 96500 C)

(75 marks)

(*b*) (i) **A** and **B** are two octahedral coordination compounds with molecular formula $CoN_5H_{12}Br_2O_2$. H atoms exists as NH_3 only. In both compounds cobalt is in the same oxidation state. Only compound **B** gives a pale yellow precipitate with $AgNO_3$(aq) that is insoluble in dilute NH_3 but soluble in conc.NH_3.

I. Of above compounds what is the oxidation state of Co?
II. Write the complete electronic configuration of Co ion given in above.
III. Identify common ligands coordinated in compounds **A** and **B**.
IV. Give the structural formule of compounds **A** and **B** giving reasons.
V. Give a chemical test to identify the anion in compound **A**.

(25 marks)

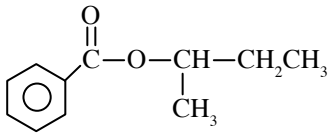
(*c*) This question is based on an experiment carried out to determine dissolved oxygen content in a water sample. An amber colour bottle was completely filled with the water sample that has to be tested and alkaline KI and $MnSO_4$ solutions are added immediately using a dropper in small amounts. The bottle was closed and mixed and then a small amount of conc. H_2SO_4 solution was added. When reactions are completed, 50.0 cm^3 from solution was taken into a titration flask, and titrated with 0.002 mol dm^{-3} $Na_2S_2O_3$ solution.

(i) Explain why an amber colour bottle should be used in this experiment.
(ii) Explain why KI solution used in here should be alkaline.
(iii) Why H_2SO_4 acid used should be concentrated?
(iv) What is the indicator used in the titration? The indicator is usually not added at the beginning but closer to the end point. Explain the resons.
(v) Identify the chemical species that reacts with dissolved oxygen in the water sample and write the balanced ionic equation.
(vi) Write balanced ionic equations for all other reactions taking place.
(vii) If the burette reading is 20.00 cm^3, calculate the dissolved oxygen content in mol dm^{-3} and in ppm. Assume that the density of the solution is 1.0 g cm^{-3}. (O = 16)

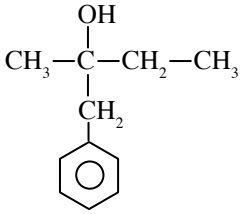
(50 marks)

Part C - Essay

8 (*a*) Consider the organic compounds **A** and **B** given below.



A

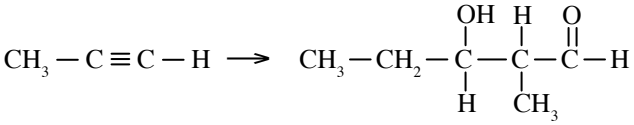


B

Write down the appropriate path for the conversion of **A** to **B**. Your conversion should **not** be more than eight steps and no other organic compound can be used as reagents.

(50 marks)

(*b*) Work out the following conversion using not more than **six** steps.



(30 marks)

(*c*) Consider the compounds **E**, **F**, **G** and **H** given below.

E $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ **F** $CH_3-\overset{\overset{O}{\|}}{C}-Cl$

G CH_3CH_2Cl **H** $CH_3CH_2NH_2$

(i) Indicate whether the reactant pair of **E** and **G** or **F** and **H** can be used to prepare the compound, $CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2CH_3$.

(ii) Give reasons for selecting particular pair of reactant and also not to select the other reactant pair.

(iii) Draw the structures of the products formed by the reaction between **G** and **H** above.

(40 marks)

(*d*) (i) Draw the structure of the intermediate positive-ion formed in the reaction between $CH_2=CH_2$ and Br_2/CCl_4.

(ii) When the above reaction is carried out in the aqueous medium, $Br-CH_2-CH_2-OH$ is formed as a product. Suggest a mechanism considering that H_2O molecule can act as a nucleophile.

(30 marks)

9 (*a*) **A** is a coloured solid. Addition of dil. H_2SO_4 to it gives a colorless gas **B** and solution **C**. Precipitate **D** is formed by the addition of dil. $NH_3(aq)$ to solution **C**. Further addition of $NH_3(aq)$ dissolves the precipitate and gives a dark blue solution **E**. Addition of dil.HCl to the solution **C**, followed by bubbling $H_2S(g)$ doesn't form a precipitate. When gas **B** is bubbled through acidic $K_2Cr_2O_7$, a green turbid solution is formed.

(i) Write chemical formulae of **A**, **B**, **C**, **D** and **E**.

(ii) Write the balanced chemical equation for the reaction between **A** + H_2SO_4.

(iii) Write the balanced chemical equation for the reaction between **B** + $K_2Cr_2O_7$ using half ionic equations.

(30 marks)

(*b*) **R** is a well water soluble crystalline white compound with high boiling point (1304 °C) and high melting point (661 °C). Tests were carried out using an aqueous solution of **R** and the observations obtained are given in the following table.

Experiment	Observation
1. Addition of acidic KIO_3 solution	Brown color solution
2. Addition of aqueous $Cu(NO_3)_2$ solution	Reddish brown turbid solution labeled as **S**.
3. Addition of $Na_2S_2O_3$ solution to solution **S**	Disappearance of reddish brown colour and appearance of a white precipitate
4. Flame test with solid **R**	Yellow colour flame

(i) Identify **R**.

(ii) Write balanced chemical equations for the above tests 1, 2 and 3.

(iii) Briefly explain why should **R** has high boiling and melting point.

(30 marks)

(*c*) 10.0 g of alloy containing only Fe, Cr and Ni when heated with dil. HNO_3 dissolved to give Fe^{3+}, Cr^{3+} and Ni^{2+} respectively. The resulting solution was diluted to a total volume of 250.00 cm^3 by adding distilled water. 25.00 cm^3 of the diluted solution was treated with excess NaOH and H_2O_2. The obtained precipitate **P** was filtered and yellow colour filtrate **Q** was acidified with dil. H_2SO_4 acid, and titrated with 1.0 mol dm^{-3} Fe^{2+} solution. The volume of Fe^{2+} required to reach the end point was 30.00 cm^3.

(i) Name the species responsible for yellow colour in the above filtrate **Q**.

(ii) Write balanced ionic equation for the reaction of metal ion in filtrate **Q**.

(iii) Give the colour of the solution formed by acidifying the filtrate **Q** and chemical species responsible for this colour.

(iv) Write balanced ionic equations for the reactions between chemical species given in (iii) above with Fe^{2+} in acidic medium.

(v) Calculate the mass percentage of the metal in the alloy given in part (ii).

(vi) Precipitate **P** was dissolved completely in H_2SO_4 and excess KI was added. The volume of 0.20 mol dm^{-3} $Na_2S_2O_3$ required to titrate I_2 evolved was 20.00 cm^3. Write balanced chemical equations for all reactions that occur in this process.

(vii) Calculate mass percentages of the remaining two metals in the alloy separately.

(viii) How you would confirm the presence of Ni metal in alloy by using a solution / precipitate in above experiment.

(90 marks)

10(*a*) Production of ammonia by using Haber process is one of the major chemical industry.

(i) State the main raw materials of the Haber process.

(ii) Write the balanced chemical equation along with the appropriate conditions for the reaction occuring.

(iii) Though the optimum conditions have been used, raw materials are not converted completely to NH_3 within the reaction container. Give reasons.

(iv) How does the unreacted raw materials used effectively in ammonia production.

(v) Production of NH_3 decreases with increasing temperature. Explain this by using enthalpy change, entropy change, Gibbs energy change related to the reaction.

(vi) Name **one** renewable resource that can be used for the energy generation in this process. State an environmental advantage of it.

(vii) Give **one use** of NH_3 except for the use in the production of fertilizers.

(50 marks)

(*b*) Effluent gases released by various industries causes acid rain.

(i) Name **two** gases that contribute to acid rain.

(ii) Explain how the gases stated in (i) contribute to acid rain by using balanced chemical equations.

(iii) Identify **two** industries that contribute to acid rain.

(iv) Briefly explain the gases stated in (i) are evolved to the atmosphere by these industries.

(v) Give **two** effects to the soil due to acid rain.

(50 marks)

(*c*) Natural rubber is used to produce number of commercially valuable products.

(i) Draw the repeating unit of natural rubber molecule.

(ii) Elasticity of natural rubber should be controlled in some production processes.

I. Name the above mentioned process.

II. Name the main reagent (chemical) other than rubber that is being used in this process.

III. State the structural change that occurs in rubber molecule during this process.

IV. Name **two** mechanical properties other than controlling elasticity of the product obtained from the above process.

(iii) Explain why the process described in (ii) I is not appropriate for poly propylene.

(iv) Name **two** pollutants present in effluent water from a natural rubber latex storing center.

(50 marks)

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