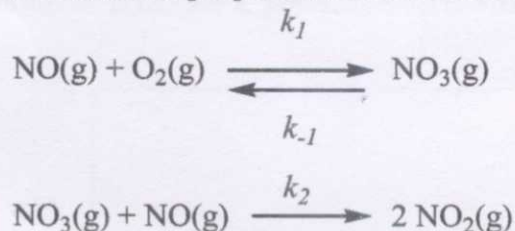


Q.34 (a) The following initial rate data were obtained for the reaction  
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

	Partial pressure of		Initial rate
	NO	O <sub>2</sub>	
Run 1	$p_{\text{NO}}$	$p_{\text{O}_2}$	$v$
Run 2	$2 p_{\text{NO}}$	$p_{\text{O}_2}$	$4v$
Run 3	$p_{\text{NO}}$	$2 p_{\text{O}_2}$	$2v$

- (i) What is the rate law for this reaction?  
 (ii) One of the mechanisms proposed for this reaction is



Obtain the rate law predicted for this mechanism, assuming a steady state concentration of  $\text{NO}_3$ .

- (iii) Predict the rate law for this mechanism, if the first equilibrium step is established quickly and the second step is slow. (9)  
 (b) (i) Write the expression for the vibrational contribution to the total energy of  $\text{CH}_4(\text{g})$  at 500 K. All the vibrational modes are active at this temperature.  
 (ii) Calculate the total internal energy of 1 mole of the gas at this temperature.  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . (6)

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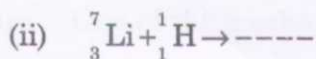
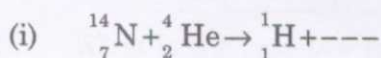
Q.35 (a) In the Bohr model of a hydrogen-like atom with atomic number  $Z$ ,

- the angular momentum of an electron (of mass  $m_e$  and charge  $e$ ) is a non-zero integral ( $n$ ) multiple of  $h/2\pi$ , where  $h$  is the Planck's constant, and
- the electrostatic attraction exerted by the nucleus on the electron is balanced by the centrifugal force experienced by the electron.

(i) Write mathematical expressions for the above statements.

(ii) Hence obtain the expression for the radius  $r$  of the Bohr orbit of the electron in terms of  $e$ ,  $n$ , and  $Z$ . (9)

(b) Complete the following nuclear reactions : (6)

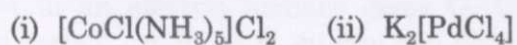


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- Q.36 (a) Highly pure nickel metal can be prepared from its sulphide ore *via*  $\text{Ni(CO)}_4$ . Write the chemical equations involved. (9)
- (b) Addition of excess of aqueous  $\text{NH}_3$  followed by ethanolic solution of dimethylglyoxime to a dilute aqueous solution of nickel sulphate changes the solution colour from green to blue to red. Write the structures of the metal complexes corresponding to green, blue and red colours. (6)

- Q.37 The element **E** on burning in the presence of  $O_2$  gives **F**. Compound **F** on heating with carbon in an electric furnace gives **G**. On passing nitrogen over a heated mixture of **F** and carbon produces **H**. Steam can decompose **H** to produce boric acid and a colourless gas that gives white fumes with  $HCl$ . Identify **F**, **G** and **H** and give balanced equations for their formation. (15)

Q.38 (a) Provide IUPAC names for the following complexes :



(6)

(b) The magnetic moment of  $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  is approximately  $6.0\mu_{\text{B}}$ . Find the number of unpaired electrons, show crystal field splitting and calculate the CFSE.

(9)

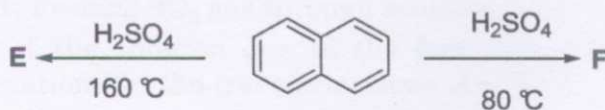
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Q.39

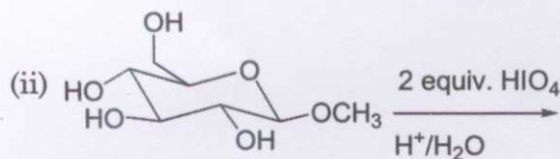
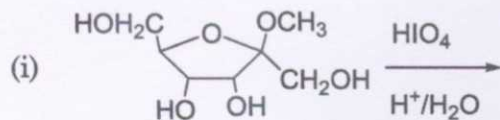
A metal salt on heating with a mixture of KCl and conc.  $\text{H}_2\text{SO}_4$  yields a deep red vapour **J**. The vapour on passing through an aqueous solution of KOH gives a yellow solution of compound **K**. Passing  $\text{SO}_2$  gas through acidified solution (with  $\text{H}_2\text{SO}_4$ ) of **K** leads to green colouration of the solution due to the formation of **M**. Identify **J**, **K** and **M** giving balanced equations for the transformations, **J**  $\rightarrow$  **K** and **K**  $\rightarrow$  **M**. (15)



- Q.40 (a) Identify E and F in the following reactions and suggest a suitable reason for their formation (9)

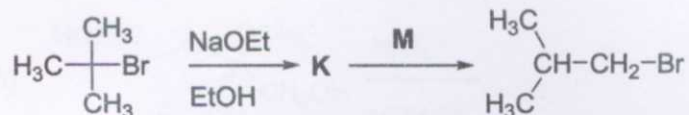


- (b) Predict the products in each of the following reactions. (6)



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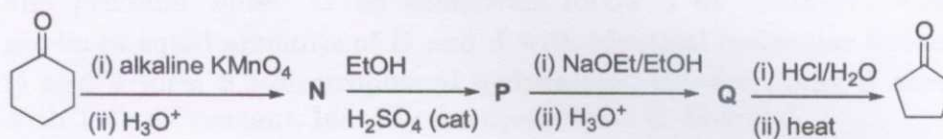
- Q.41 (a) A compound **G** having molecular formula  $C_6H_{12}$  decolourises both permanganate and bromine water. **G** on ozonolysis followed by reductive work-up ( $Zn/H_3O^+$ ) produces equal amounts of **H** and **J** with identical molecular formula  $C_3H_6O$ . Both **H** and **J** form 2,4-dinitrophenyl hydrazones, however, only **J** shows positive test with Tollens' reagent. Identify the compounds **G**, **H** and **J**. (9)
- (b) Identify **K** and **M** in the following reaction sequence. (6)





Q.42 (a) Identify **N**, **P** and **Q** in the following synthetic transformation.

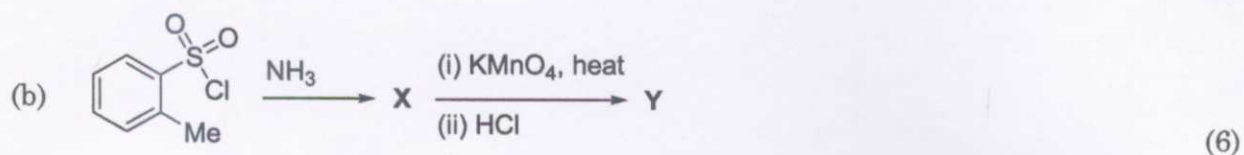
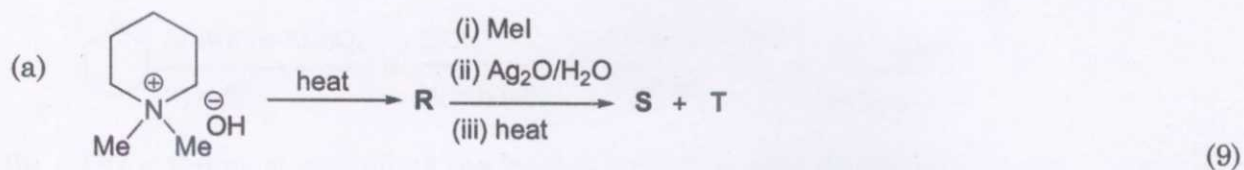
(9)



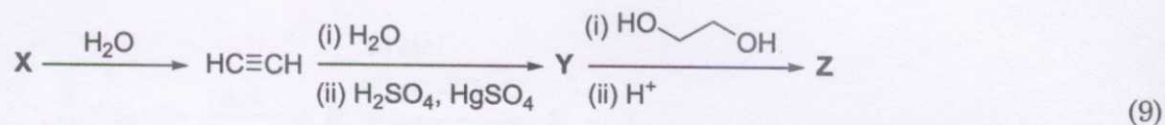
(b) Draw the most as well as the least stable chair conformations of *trans*-1-*tert*-butyl-4-methylcyclohexane.

(6)

Q.43 Identify R, S, T, X and Y in the following reaction sequences.



Q.44 (a) Complete the following reaction sequence with the structures of X, Y and Z.



(b) Calculate the isoelectric point ( $pI$ ) of lysine. Given the  $pK_a$  of  $\alpha\text{-NH}_3$  is 8.95,  $pK_a$  of side chain  $\text{NH}_3$  is 10.53 and  $pK_a$  of  $\alpha\text{-COOH}$  is 2.18. (6)