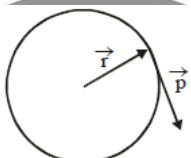


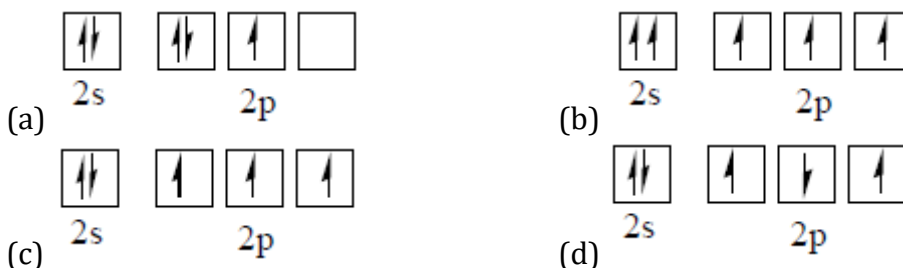


## IIT JAM 2009

- For an ideal gas, the plot that is NONLINEAR is  
(a) PV vs. T (b) PV vs. P, at constant T  
(c) P vs. V, at constant T (d)  $\ln P$  vs.  $\ln V$ , at constant T
- Consider two identical containers, one with 1 mole of  $H_2$  and the other with 1 mole of He. If the root-mean-square (RMS) velocities of the two gases are the same, then the ratio of the temperatures,  $T(H_2)/T(He)$  is  
(a)  $1/2$  (b) 2 (c)  $1/\sqrt{2}$  (d)  $\sqrt{2}$
- An electron moves around the nucleus in a circular orbit, according to the Bohr model. The radial vector  $\vec{r}$  and momentum vector  $\vec{p}$  are shown in the diagram below.  


The direction of the angular momentum vector is:  
(a) along  $\vec{r}$  (b) along  $\vec{p}$   
(c) opposite to  $\vec{p}$  (d) perpendicular to both  $\vec{r}$  and  $\vec{p}$
- X and Y transformed co-ordinates obtained from p and q as follows:  
$$\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} a_1 & a_3 \\ a_2 & a_4 \end{pmatrix} \begin{pmatrix} p \\ q \end{pmatrix}$$

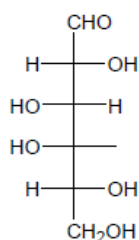
The correct set of linear equations that represent X and Y are  
(a)  $X = a_1p + a_2q$  (b)  $X = a_1p + a_3q$  (c)  $X = a_2p + a_4q$  (d)  $X = a_1p + a_4q$   
 $Y = a_3p + a_4q$   $Y = a_2p + a_4q$   $Y = a_1p + a_3q$   $Y = a_2p + a_3q$
- Which of the following is NOT a solution of the equation:  $\frac{d^2x}{dt^2} + \omega^2x = 0$   
(a)  $x = \cos \omega t$  (b)  $x = A \sin \omega t$  (c)  $x = at^2$  (d)  $x = A(e^{i\omega t} + e^{-i\omega t})$
- An electron is found in an orbital with one radial node and two angular nodes. Which orbital the electron is in?  
(a) 1s (b) 2p (c) 3d (d) 4d
- The acceptable valence shell electronic arrangement is :



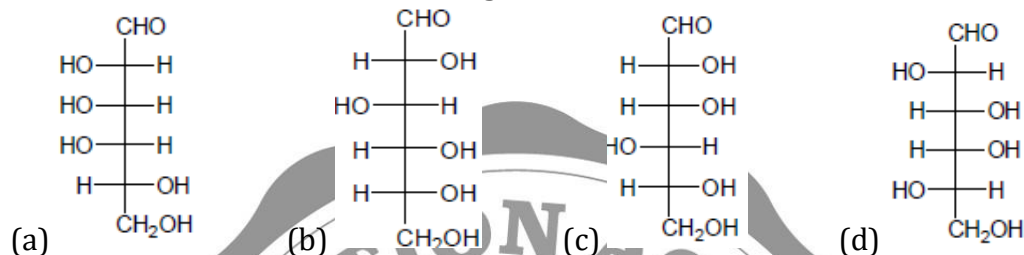
8. If  $K_{sp}$  is the solubility product of a sparingly soluble salt  $A_3X_2$ , then its solubility is  
(a)  $(K_{sp}/108)^{1/5}$  (b)  $(K_{sp})^{1/5}$  (c)  $(K_{sp}/72)^{1/5}$  (d)  $(K_{sp})^{1/2}$
9. For the formation of B from A, heat liberated is  $20 \text{ kJ mol}^{-1}$ , then the activation energy (in  $\text{kJ mol}^{-1}$ ) for the reaction  $A \rightarrow B$  is  
(a) 120 (b) 100 (c) 80 (d) 60
10. For the reaction  $A + B \rightarrow Z$ , the concentration of Z at time t is given by  $[Z] = [A]_{t=0} (1 - e^{-kt}) + [Z]_{t=0}$ , where k is the rate constant. The rate law is:  
(a)  $-\frac{d[Z]}{dt} = k[A]$  (b)  $\frac{d[Z]}{dt} = k[A]$   
(c)  $\frac{d[Z]}{dt} = k[Z]$  (d)  $\frac{d[Z]}{dt} = k[A][B]$
11. Identify the correct option:  
In the periodic table, on moving from left to right along a period,  
(a) The atomic size of the elements increases.  
(b) The first ionization potential of the element decreases.  
(c) The oxide of the element becomes less basic  
(d) The oxide of the element becomes more basic.
12. Among the following, the incorrect statement is:  
(a) Diamond and graphite are two allotropes of carbon  
(b) In diamond, each carbon is  $sp^3$  hybridized.  
(c) In graphite each carbon is  $sp^2$  hybridized  
(d) Graphite shows high electrical conductivity in one direction only
13. The pH of a  $1 \times 10^{-8} \text{ M HCl}$  solution is close to  
(a) 8.0 (b) 7.1 (c) 6.9 (d) 6.0
14. The indicator phenolphthalein changes colour at  $\text{pH} \sim 9$ . this indicator is NOT suitable for accurate determination of the end point in the titration of  
(a)  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$  (b)  $\text{HCl}$  with  $\text{NH}_4\text{OH}$   
(c)  $\text{HCl}$  with  $\text{NaOH}$  (d)  $\text{HCl}$  with  $\text{KOH}$



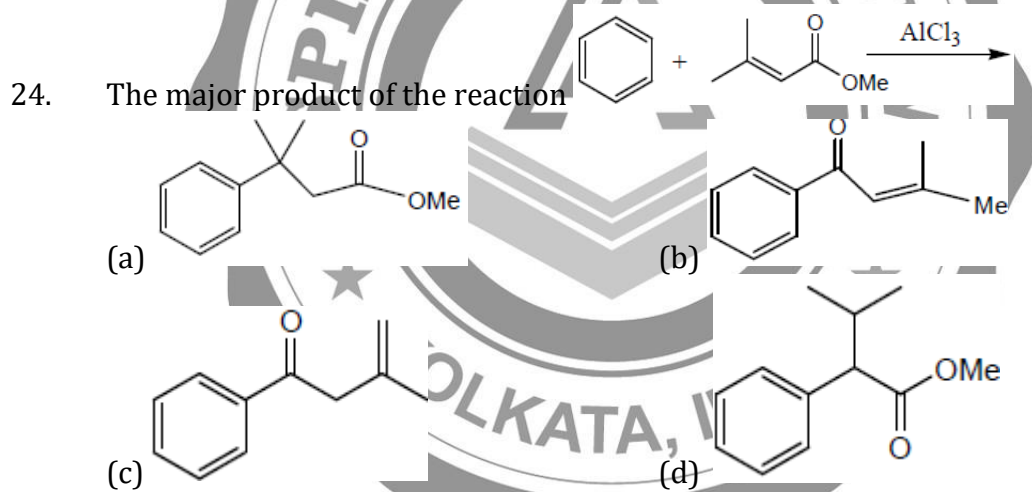
15. In the thermite process, iron oxide is reduced to molten iron by aluminum powder because  
(a) The melting point of iron is low  
(b) The reaction is highly endothermic  
(c) Large amount of heat is liberated in the formation of  $\text{Al}_2\text{O}_3$   
(d) Aluminium is an amphoteric element.
16. The number of  $\text{P} = \text{O}$  bonds present in the formation of  $\text{H}_4\text{P}_2\text{O}_7$  is:  
(a) Three (b) Two (c) One (d) None.
17. Egyptian blue  $\text{CaCuSi}_4\text{O}_{10}$  is an example of  
(a) Sheet silicate (b) Cyclic silicate (c) Pyrosilicate (d) Chain silicate
18. The formal charges on the nitrogen atom from left to right in the azide anion,  $[\text{N}=\text{N}=\text{N}]^-$  are  
(a) +1, -1, -1 (b) -1, +1, -1 (c) -1, -1, +1 (d) -2, +1, 0
19. The unit cell of diamond can be obtained from the unit cell of  
(a) ZnS (b) NaCl (c) CsCl (d) AgCl
20. Calgon used for water softening is  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$  and it is prepared by heating microcosmic salt. The microcosmic salt is:  
(a)  $\text{Na}_2\text{HPO}_3$  (b)  $\text{NaH}_2\text{PO}_4$  (c)  $\text{Na}_2\text{HPO}_4$  (d)  $\text{Na}(\text{NH}_4)\text{HPO}_4$
21. The major product obtained in the following reaction
- 
- (a) (b) (c) (d)



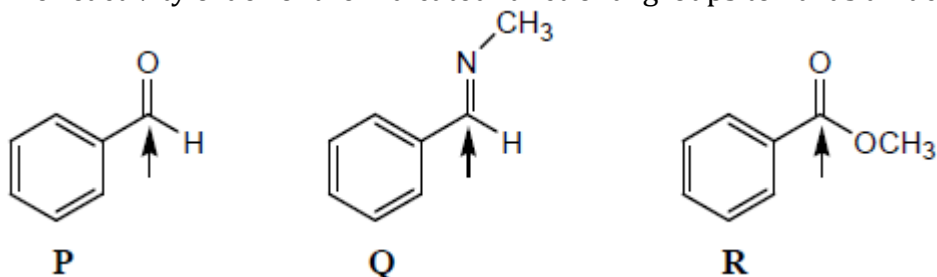
Which one of these structures is L-galactose?



23. The maximum number of stereoisomers possible for 4-phenylbut-3-en-2-ol is:  
(a) 1 (b) 2 (c) 3 (d) 4

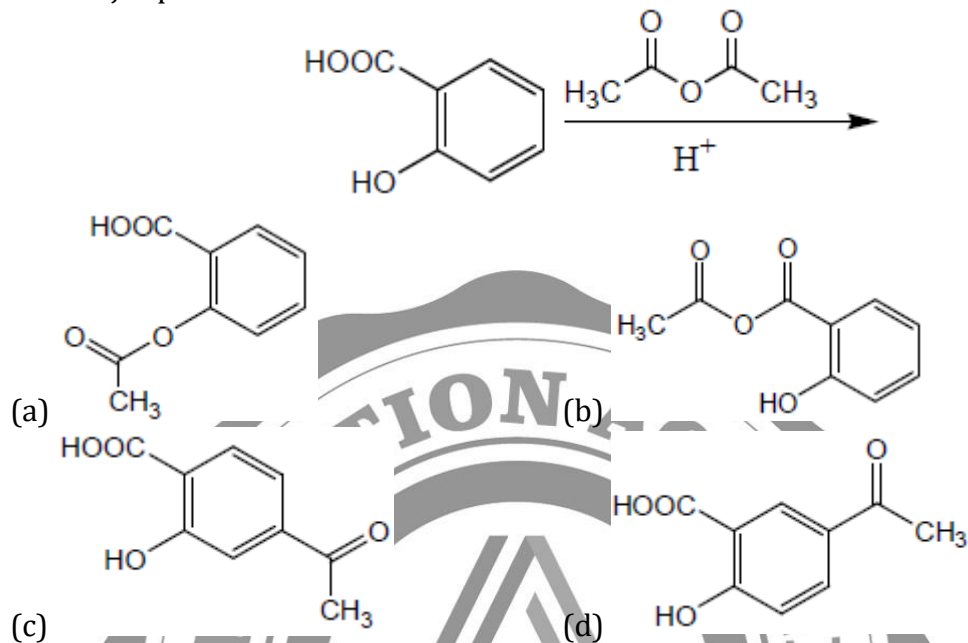


25. Which of the following is achiral?  
(a) Alanine (b) Glycine (c) Proline (d) Phenylalanine
26. The reactivity order of the indicated functional groups towards a nucleophile.

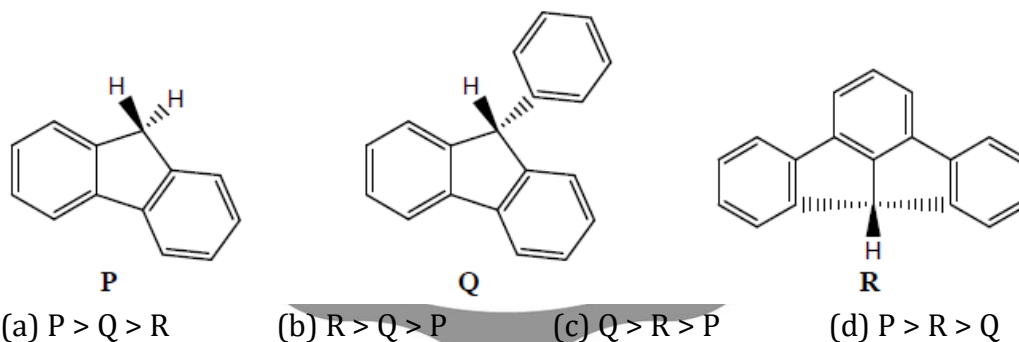


- (a)  $P > Q > R$       (b)  $Q > P > R$       (c)  $Q > R > P$       (d)  $R > P > Q$

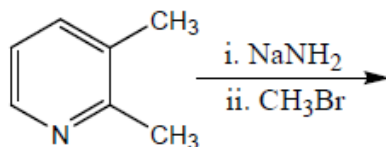
27. The major product formed in the reaction

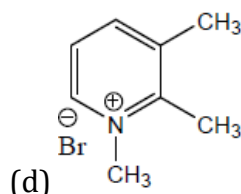
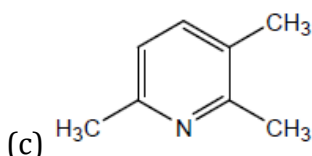
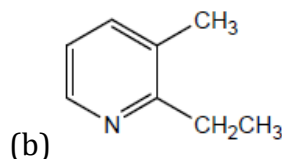
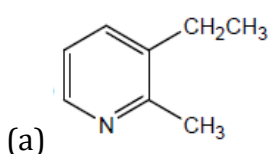


28. Arrange the following in the correct order of acidity of the hydrogen indicated in bold.

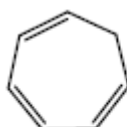


29. Among the following the major product obtained in the reaction below is:

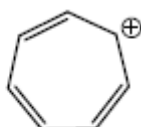




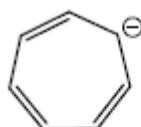
30. Which of the following are aromatic?



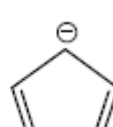
P



Q



R



S

(a) P and Q

(b) Q and R

(c) R and S

(d) Q and S

## Descriptive Questions

31. (a) A container is partitioned into two compartments, one of which contains 2 moles of He while the other contains 3 moles of Ar. The gases are ideal. The temperature is 300 K and the pressure is 1 bar.

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}, \quad \ln(2/5) = -0.92, \quad \ln(3/5) = -0.51.$$

(i) What is the total Gibbs free energy of the two gases?

(ii) If the partition between the two compartments is removed and the gases are allowed to mix, then what is the Gibbs free energy of the mixture?

(iii) What is the change in enthalpy in this process?

(b) Obtain (i) the molar heat of formation of  $\text{CH}_4(\text{g})$  and (ii) the average C - H bond energy, to the nearest kilo-joule [kJ], from the given data:

	$\Delta H$ [kJ mol <sup>-1</sup> ]
(1) $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	435
(2) $\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	444
(3) $\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	444
(4) $\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	339
(5) $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$	717
(6) $\text{C}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	436

32. (a) (i) Draw the P-T phase diagram of water.

(ii) Label the different regions in this diagram.



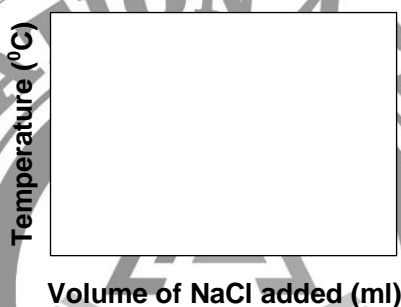
(iii) On the diagram, show the liquid-vapour equilibrium for a dilute solution of NaCl, with the help of a dashed curve.

(b) The temperature dependence of the Gibbs free energy  $G$  is: 
$$\left( \frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2}$$

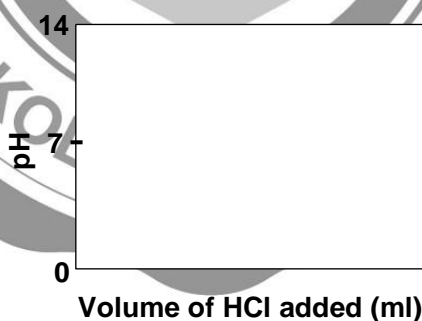
Obtain the expression for the temperature dependence of the equilibrium constant  $K$  given that  $\Delta H^\theta = A + BT$  (where  $A$  and  $B$  are constants).

33. (a) In the space provided, plot:

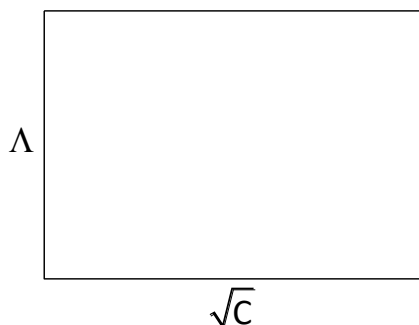
(i) Conductometric titration curve of 0.1 M  $\text{AgNO}_3$  with 1 M NaCl, extended beyond the end point ( $\lambda_{\text{Na}^+}^0 \approx \lambda_{\text{Ag}^+}^0$ ).



(ii) pH vs. Volume of HCl, for a potentiometric titration of 0.1 (N)  $\text{NH}_4\text{OH}$  with 0.1 N HCl.



(iii) Variation of the molar conductivity of NaCl with the square root of its concentration.

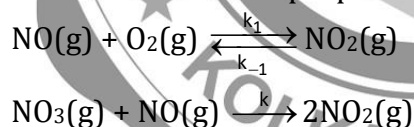


(b) The  $\text{Zn}^{2+} | \text{Zn}$  half cell ( $E^\theta = -0.762 \text{ V}$ ) is connected to a  $\text{Cu}^{2+} | \text{Cu}$  half cell ( $E^\theta = 0.340 \text{ V}$ ). What is the value of  $E_{\text{cell}}^\theta$  for spontaneous conversion of chemical energy of electrical energy? What is the value of  $\log_{10} K$ , where  $K$  is the equilibrium constant? Use  $(2.303 RT/F) = 0.06$ .

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	$2p_{\text{NO}}$	$p_{\text{O}_2}$	$4v$
Run 3	$p_{\text{NO}}$	$2p_{\text{O}_2}$	$2v$

- (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.

(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.  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

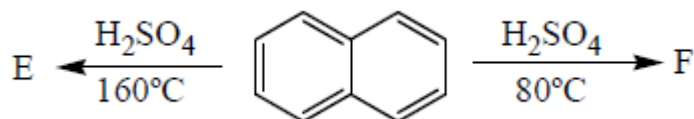
35. (a) In the Bohr model of a hydrogen-like atom with atomic number  $Z$ ,



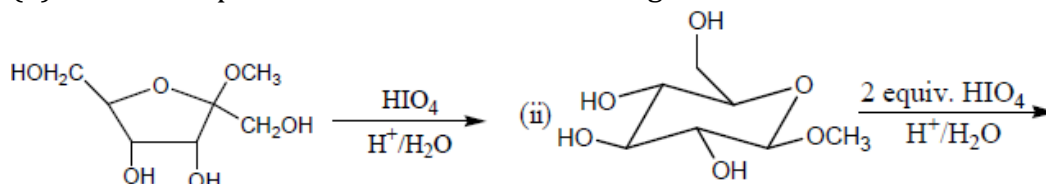


- The angular momentum of an electron (of mass  $m_e$  and charge  $e$ ) is a non-zero integral ( $n$ ) multiple of  $h/2\pi$ , where  $h$  is the Planck's constant. And
  - The electrostatic attraction exerted by the nucleus on the electron is balanced by the centrifugal force experienced by the electron.
    - (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  $Z$ .
  - (b) Complete the following nuclear reactions:
    - (i)  ${}^{14}_7\text{N} + {}^4_2\text{He} \rightarrow {}^1_1\text{H} + \dots\dots\dots$
    - (ii)  ${}^7_3\text{Li} + {}^1_1\text{H} \rightarrow \dots\dots\dots$
36. (a) Highly pure nickel metal can be prepared from its sulphide ore via  $\text{Ni}(\text{CO})_4$ . Write the chemical equations involved.  
(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.
37. The element  $E$  on burning in the presence of  $\text{O}_2$  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  $\text{HCl}$ . Identify  $F$ ,  $G$  and  $H$  and give balanced equations for their formation.
38. (a) Provide IUPAC names for the following complexes:  
(i)  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$       (ii)  $\text{K}_2[\text{PdCl}_4]$   
(b) The magnetic moment of  $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  is approximately  $6.0 \mu_B$ . Find the number of unpaired electrons, show crystal field splitting and calculate the CFSE.
39. A metal salt on heating with a mixture of  $\text{KCl}$  and conc.  $\text{H}_2\text{SO}_4$  yields a deep red vapour  $J$ . The vapour on passing through an aqueous solution of  $\text{KOH}$  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  $K \rightarrow M$ .

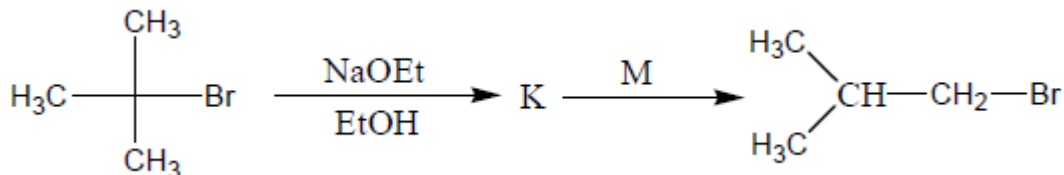
40. (a) Identify E and F in the following reactions and suggest a suitable reason for their formation.



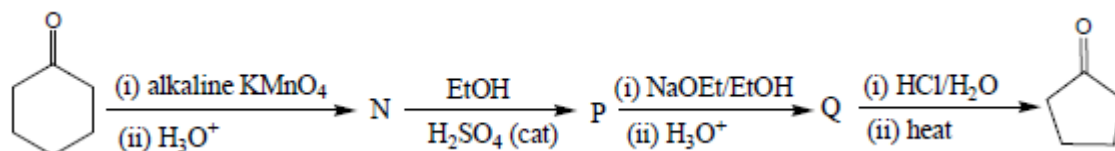
- (b) Predict the products in each of the following reactions.



41. (a) A compound G having molecular formula  $\text{C}_6\text{H}_{12}$  decolourless both permanganate and bromine water. G on ozonolysis followed by reductive work-up ( $\text{Zn}/\text{H}_3\text{O}^+$ ) produces equal amounts of H and J with identical molecular formula  $\text{C}_3\text{H}_6\text{O}$ . Both H and J form 2, 4-dinitrophenyl hydrazones, however, only J shows positive test with Tollen's reagent. Identify the compounds G, H and J.  
 (b) Identify K and M in the following reaction sequence.

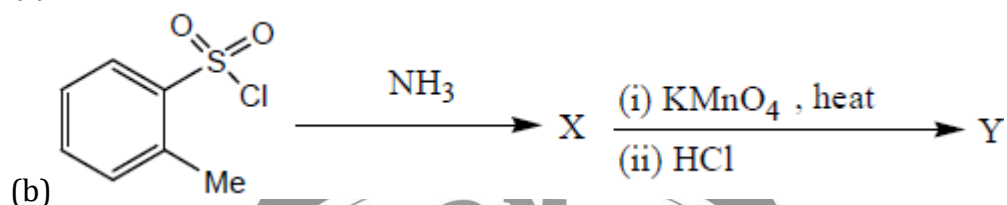
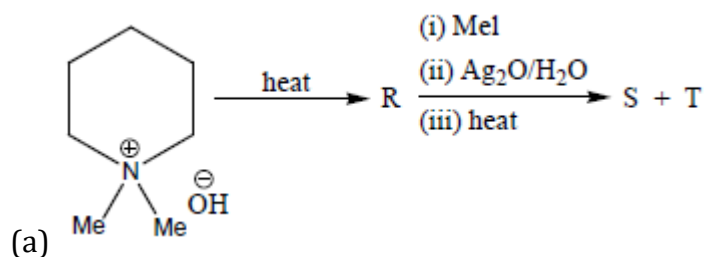


42. (a) Identify N, P and Q in the following synthetic transformation.

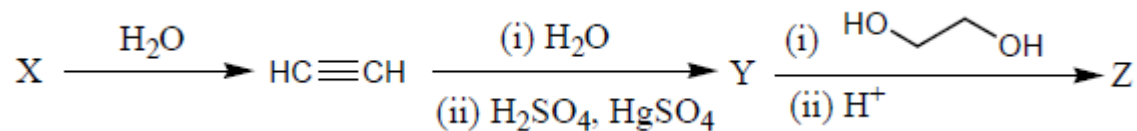


- (b) Draw the most as well as the least stable chair conformations of trans-1-tert-butyl-4-methylcyclohexane.

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



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



(b) Calculate the isoelectric point (p.I.) 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.