

**JEE (ADVANCED) 2013 PAPER**  
**Paper 1 (Chemistry)**

**SECTION 1: (Only One Option Correct Type)**

This section contains **10 multiple choice questions**. Each question has 4 choices (A), (B), (C) and (D) out of which **ONLY ONE is correct**.

1. The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and glucose(s) at  $25^\circ\text{C}$  are  $-400 \text{ kJ mol}^{-1}$ ,  $-300 \text{ kJ mol}^{-1}$  and  $-1300 \text{ kJ mol}^{-1}$ , respectively. The standard enthalpy of combustion per gram of glucose at  $25^\circ\text{C}$  is  
(A)  $+2900 \text{ kJ}$  (B)  $-2900 \text{ kJ}$  (C)  $-16.11 \text{ kJ}$  (D)  $+16.11 \text{ kJ}$

**Solution**

(C) The reaction involved is  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

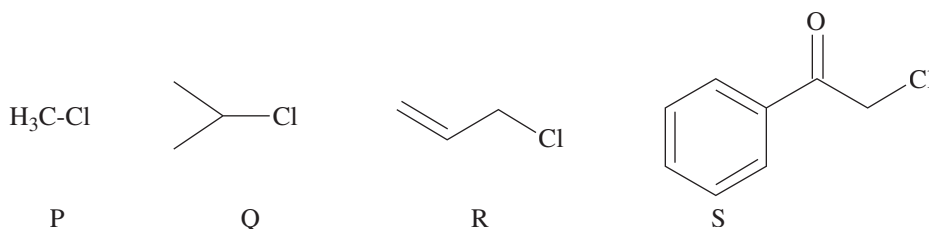
$$\Delta H = \sum \Delta H(\text{products}) - \sum \Delta H(\text{reactants})$$

$$= 6(-400) + 6(-300) - (-1300) = -2900 \text{ kJ mol}^{-1}$$

Now, 1 mol of glucose = 180 g of glucose, so enthalpy of combustion per gram of glucose at  $25^\circ\text{C}$  is

$$\Delta H = \frac{-2900}{180} = -16.11 \text{ kJ g}^{-1}$$

2. KI in acetone, undergoes  $\text{S}_{\text{N}}2$  reaction with each of P, Q, R and S. The rates of the reaction vary as



- (A)  $\text{P} > \text{Q} > \text{R} > \text{S}$  (B)  $\text{S} > \text{P} > \text{R} > \text{Q}$  (C)  $\text{P} > \text{R} > \text{Q} > \text{S}$  (D)  $\text{R} > \text{P} > \text{S} > \text{Q}$

**Solution**

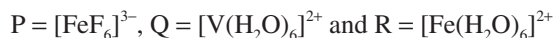
(B) The relative reactivities towards  $\text{S}_{\text{N}}2$  reaction  $\text{S} > \text{P} > \text{R} > \text{Q}$ .

3. The compound that does **NOT** liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is  
(A) Benzoic acid (B) Benzenesulphonic acid  
(C) Salicylic acid (D) Carboic acid (Phenol)

**Solution**

(D) Comparitively phenol is a weaker acidic than carbonic acid ( $\text{H}_2\text{CO}_3$ ), and hence does not liberate  $\text{CO}_2$  on treatment with aqueous  $\text{NaHCO}_3$  solution. The rest are more acidic than  $\text{H}_2\text{CO}_3$ , and so liberate  $\text{CO}_2$ .

4. Consider the following complex ions, P, Q and R.

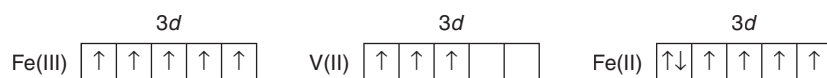


The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is

- (A)  $\text{R} < \text{Q} < \text{P}$  (B)  $\text{Q} < \text{R} < \text{P}$  (C)  $\text{R} < \text{P} < \text{Q}$  (D)  $\text{Q} < \text{P} < \text{R}$

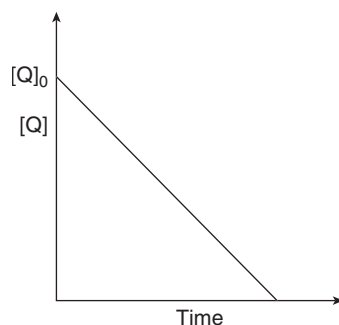
**Solution**

(B) The electronic configurations of the central metal ions are as follows:



The number of unpaired electrons is  $\text{P} = 5$ ,  $\text{Q} = 3$  and  $\text{R} = 4$ . From the relation  $\mu = \sqrt{n(n+2)}$ , where  $n$  is the number of unpaired electrons, we have the order of spin only magnetic moment as  $\text{Q} < \text{R} < \text{P}$ .

5. In the reaction,  $P + Q \rightarrow R + S$ , the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



- (A) 2                      (B) 3                      (C) 0                      (D) 1

**Solution**

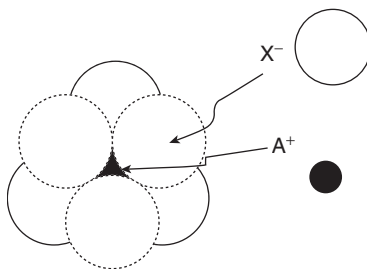
(D) This is a first order reaction because  $t_{75\%} = 2 \times t_{50\%}$ . The graph shows that the order with respect to Q is 0, so we can write the rate expression as  $\text{rate} = k[P]^1[Q]^0$ .

6. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of  
 (A) NO                      (B) NO<sub>2</sub>                      (C) N<sub>2</sub>O                      (D) N<sub>2</sub>O<sub>4</sub>

**Solution**

(B) The reaction involved is  $4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$ . The yellow-brown color appears due to the formation of NO<sub>2</sub>.

7. The arrangement of X<sup>-</sup> ions around A<sup>+</sup> ion in solid AX is given in the figure (not drawn to scale). If the radius of X<sup>-</sup> is 250 pm, the radius of A<sup>+</sup> is



- (A) 104 pm                      (B) 125 pm                      (C) 183 pm                      (D) 57 pm

**Solution**

(A) From the figure, it can be seen that the cation A<sup>+</sup> occupies octahedral void formed by the anion X<sup>-</sup>. The radius ratio for an octahedral void is  $r_{A^+}/r_{X^-} = 0.414$ . Now, given that the radius of anion X<sup>-</sup> is 250 pm. So the radius of A<sup>+</sup> is

$$r_{A^+} = 0.414 \times 250 = 103.50 \approx 104 \text{ pm}$$

8. Upon treatment with ammoniacal H<sub>2</sub>S, the metal ion that precipitates as a sulfide is  
 (A) Fe(III)                      (B) Al(III)                      (C) Mg(II)                      (D) Zn(II)

**Solution**

(D) On treatment with H<sub>2</sub>S, Zn(II) gets precipitated as ZnS. Mg(II) does not get precipitated, while Fe<sup>3+</sup> and Al<sup>3+</sup> get precipitated as hydroxides.

9. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is

- (A) The adsorption requires activation at 25°C.  
 (B) The adsorption is accompanied by a decrease in enthalpy.  
 (C) The adsorption increases with increase of temperature.  
 (D) The adsorption is irreversible.

**Solution**

(B) The adsorption of methylene blue on activated charcoal is physisorption, which causes decrease in enthalpy.

10. Sulfide ores are common for the metals

(A) Ag, Cu and Pb (B) Ag, Cu and Sn  
(C) Ag, Mg and Pb (D) Al, Cu and Pb

**Solution**

(A) The sulphide ores are  $\text{Ag}_2\text{S}$  (argentite),  $\text{CuFeS}_2$  (copper pyrites) and  $\text{PbS}$  (galena).

**SECTION 2: (One or More Options Correct Type)**

This section contains **5 multiple choice questions**. Each question has four choices (A), (B), (C) and (D) out of which **ONE OR MORE are correct**.

11. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)  
(A)  $\Delta G$  is positive. (B)  $\Delta S_{\text{system}}$  is positive (C)  $\Delta S_{\text{surroundings}} = 0$  (D)  $\Delta H = 0$

**Solution**

(B, C, D) For an ideal solution formed by benzene and naphthalene,  $\Delta H_{\text{mixing}} = 0$ ,  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} = 0$ .

12. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are)

(A)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (B)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$   
(C)  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  (D)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)\text{Cl}]$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

**Solution**

(B, D)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$  are octahedral and square planar complexes, which show geometrical isomerism.  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$  show ionization isomerism.

13. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1 M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The  $K_a$  of HA is  
(A)  $1 \times 10^{-4}$  (B)  $1 \times 10^{-5}$  (C)  $1 \times 10^{-6}$  (D)  $1 \times 10^{-3}$

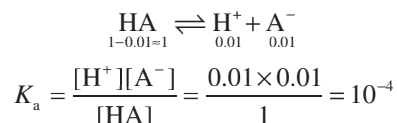
**Solution**

(A) The rate with respect to weak acid is  $\text{rate}_1 = k[\text{H}^+]_{\text{weak}}[\text{Ester}]$  and rate with respect to strong acid is

$$\text{rate}_2 = k[\text{H}^+]_{\text{strong}}[\text{Ester}]$$

$$\text{Now, given that } [\text{H}^+]_{\text{weak}} = \frac{[\text{H}^+]_{\text{strong}}}{100} = \frac{1}{100} = 0.01 \text{ M}$$

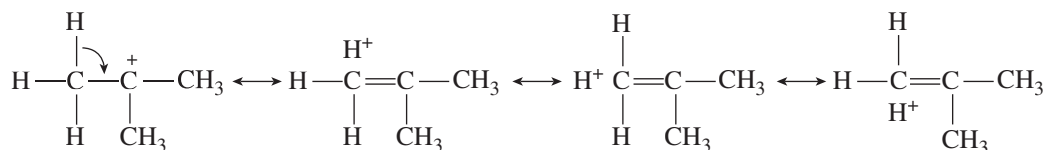
The reaction involved is



14. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to  
(A)  $\sigma \rightarrow \pi$  (empty) and  $\sigma \rightarrow \pi^*$  electron delocalizations  
(B)  $\sigma \rightarrow \sigma^*$  and  $\sigma \rightarrow \pi$  electron delocalizations  
(C)  $\sigma \rightarrow \pi$  (filled) and  $\sigma \rightarrow \pi$  electron delocalizations  
(D)  $\pi$  (filled)  $\rightarrow \sigma^*$  and  $\sigma \rightarrow \pi^*$  electron delocalizations

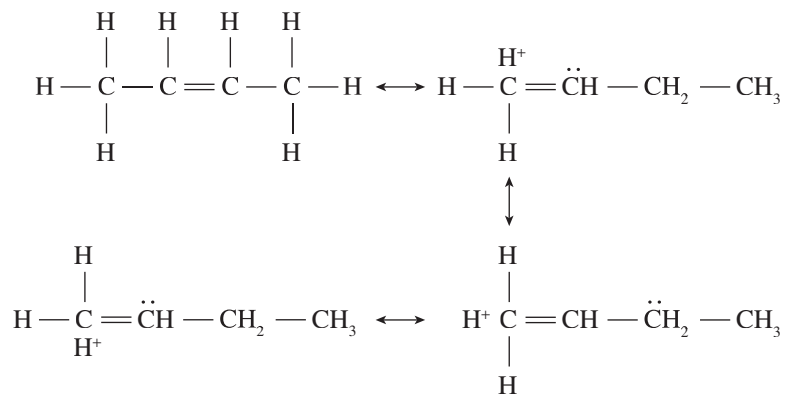
**Solution**

(A) The hyperconjugation for *tert*-butyl carbocation involves  $\sigma \rightarrow \pi$  (empty) electron delocalization. This is because carbon having + charge has one vacant *p*-orbital. It has nine  $\alpha$ -hydrogens and hence nine hyperconjugation structures.



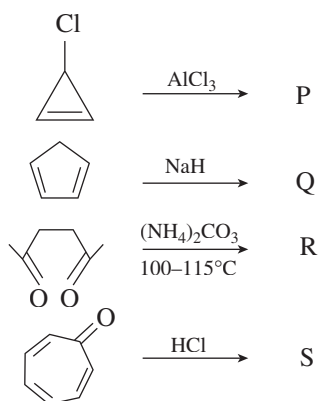
(Plus six more such structures from the other two methyl groups)

The hyperconjugation for 2-butene involves  $\sigma \rightarrow \pi^*$  electron delocalization. It has six  $\alpha$ -hydrogens and hence six hyperconjugation structures.



(Similarly three more structures from the other methyl group)

15. Among P, Q, R and S, the aromatic compound(s) is/are



(A) P

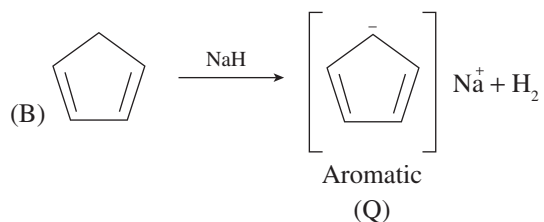
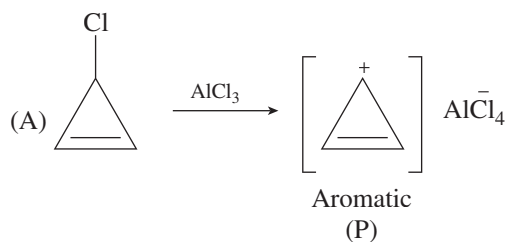
(B) Q

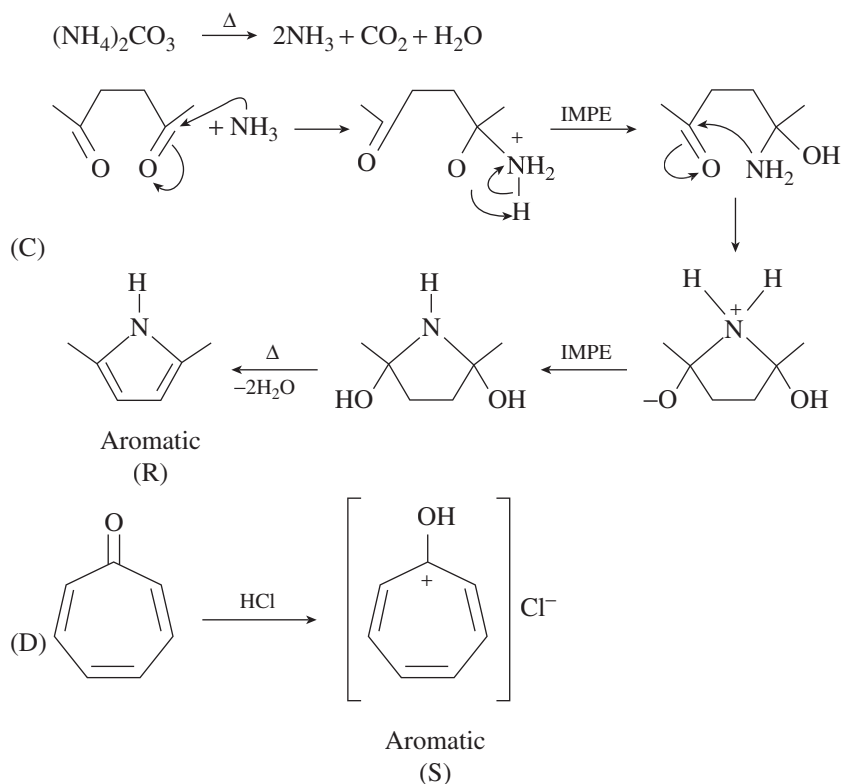
(C) R

(D) S

**Solution**

(A, B, C, D) The reactions involved are





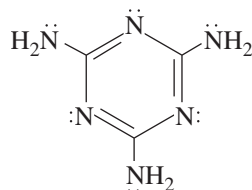
**SECTION 3: (Integer Value Correct Type)**

This section contains 5 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

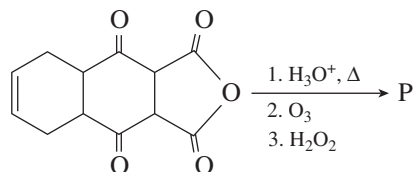
16. The total number of lone-pairs of electrons in melamine is \_\_\_\_\_.

**Solution**

(6) The structure is

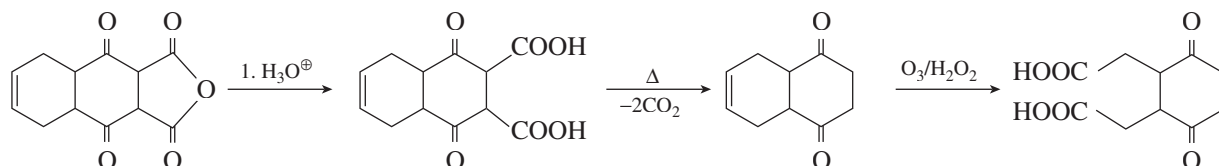


17. The total number of carboxylic acid groups is the product P is \_\_\_\_\_.



**Solution**

(2) The reaction involved is



18. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de Broglie wavelength of He gas at  $-73^\circ\text{C}$  is  $M$  times that of the de Broglie wavelength of Ne at  $727^\circ\text{C}$ .  $M$  is \_\_\_\_\_.

**Solution**

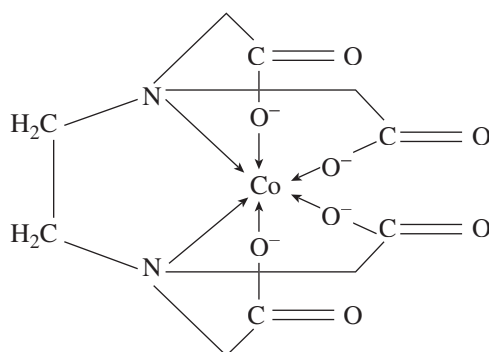
(5) We know that  $\lambda = \frac{h}{\sqrt{2mE}}$ , where  $E$  (kinetic energy)  $\propto T$ . Therefore,  $\lambda = \frac{h}{\sqrt{mT}}$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \frac{h/\sqrt{m_{\text{He}}T_{\text{He}}}}{h/\sqrt{m_{\text{Ne}}T_{\text{Ne}}}} = \sqrt{\frac{m_{\text{Ne}}T_{\text{Ne}}}{m_{\text{He}}T_{\text{He}}}} = \sqrt{\frac{20 \times 1000}{4 \times 200}} = 5$$

19.  $\text{EDTA}^{4-}$  is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in  $[\text{Co}(\text{EDTA})]^{1-}$  complex ion is \_\_\_\_\_.

**Solution**

(8) The structure is



20. A tetrapeptide has  $-\text{COOH}$  group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with  $-\text{NH}_2$  group attached to a chiral center is \_\_\_\_\_.

**Solution**

(4) The possible combinations with C-terminal as alanine and N-terminal with chiral carbon (i.e., excluding glycine) are:

- Val–Phe–Gly–Ala
- Val–Gly–Phe–Ala
- Phe–Val–Gly–Ala
- Phe–Gly–Val–Ala

## Paper 2 (Chemistry)

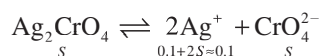
### SECTION 1: (One or More Options Correct Type)

This section contains **8 multiple choice questions**. Each question has four choices (A), (B), (C) and (D) out of which **ONE or MORE are correct**.

21. The  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298 K. The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a 0.1 M  $\text{AgNO}_3$  solution is  
 (A)  $1.1 \times 10^{-11}$  (B)  $1.1 \times 10^{-10}$  (C)  $1.1 \times 10^{-12}$  (D)  $1.1 \times 10^{-9}$

**Solution**

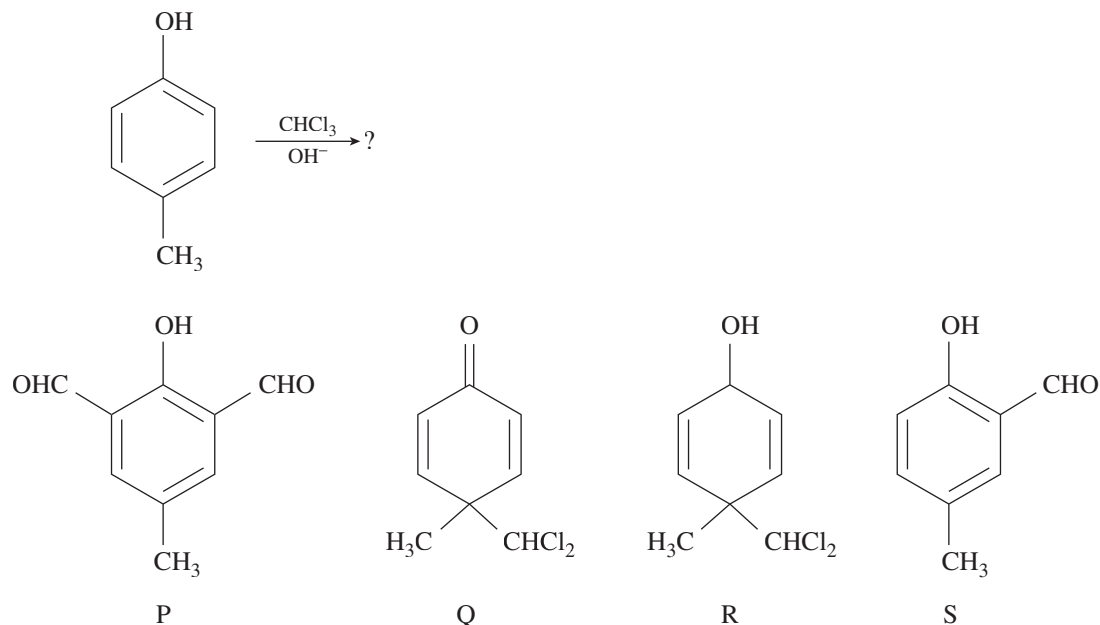
(B) The reaction involved is



The solubility product is  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \Rightarrow 1.1 \times 10^{-12} = (0.1)^2 \times S$

$$\text{Therefore, } S = [\text{CrO}_4^{2-}] = \frac{1.1 \times 10^{-12}}{(0.1)^2} = 1.1 \times 10^{-10} \text{ mol L}^{-1}$$

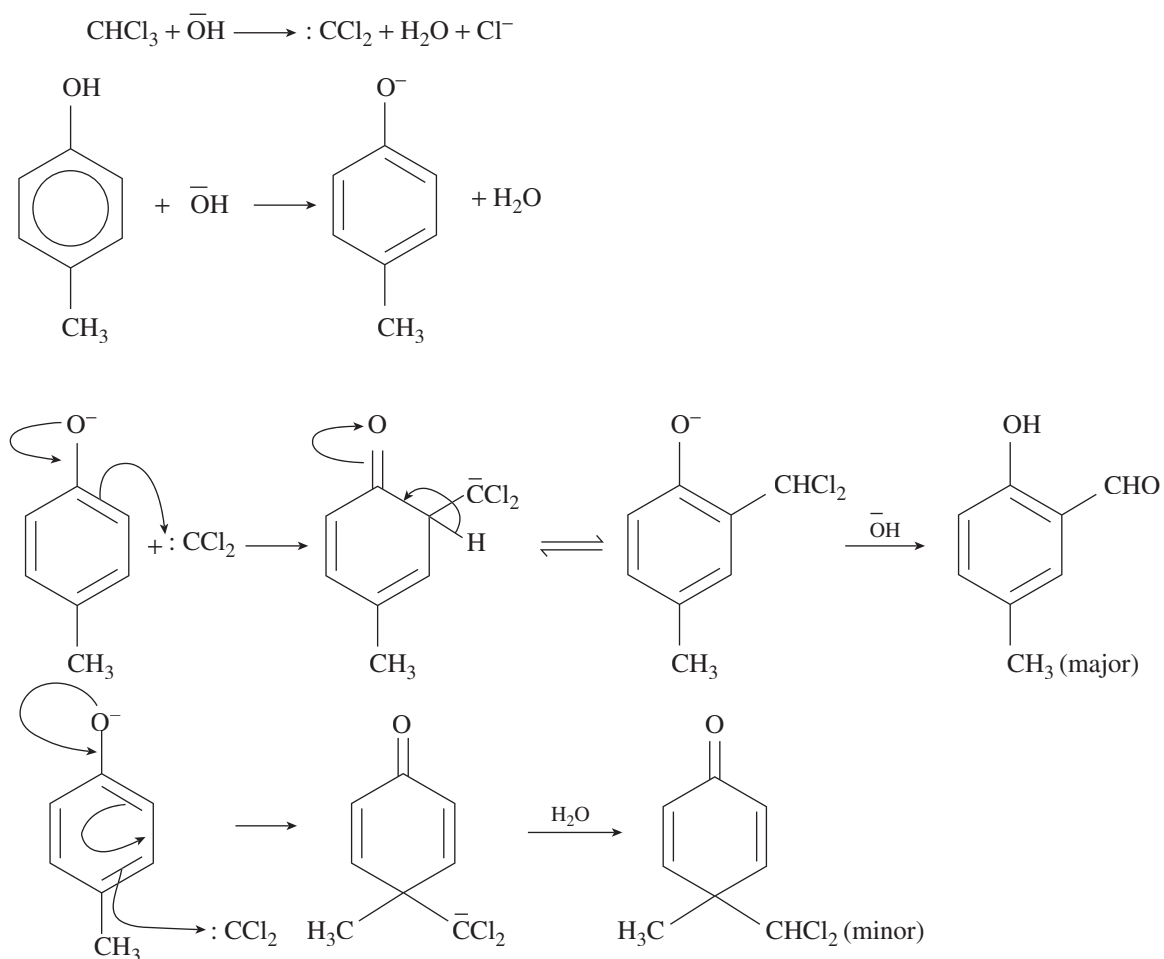
22. In the following reaction, the product(s) formed is(are)



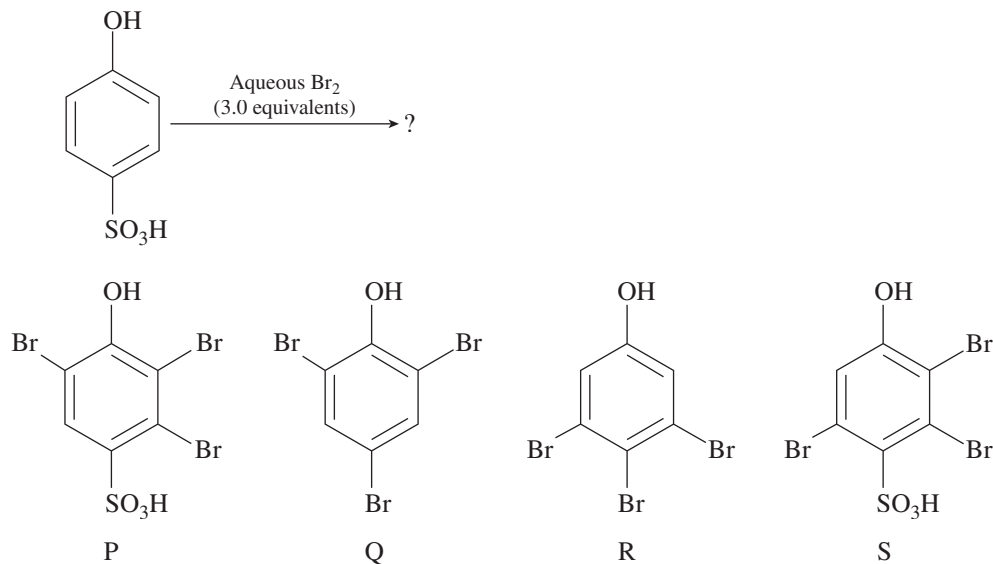
- (A) P (major)                      (B) Q (minor)                      (C) R (minor)                      (D) S (major)

**Solution**

(B, D) The mechanism involved is



23. The major product(s) of the following reaction is(are)



(A) P

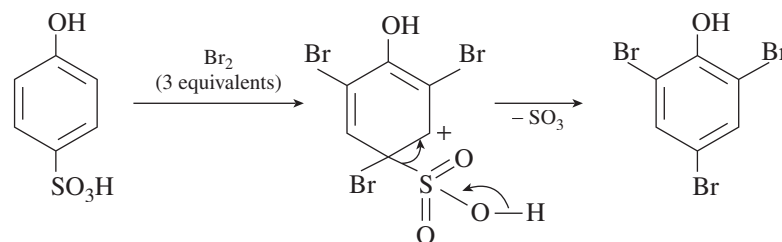
(B) Q

(C) R

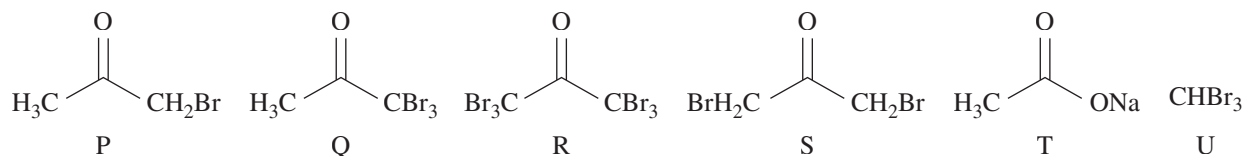
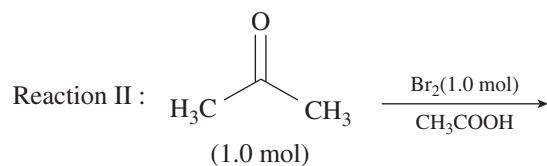
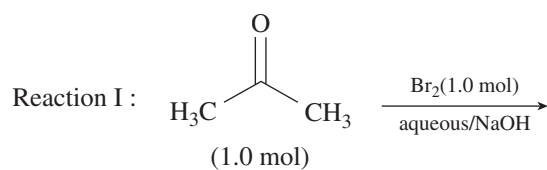
(D) S

**Solution**

(B) The reaction involved is



24. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)



(A) Reaction I: P and Reaction II: P

(B) Reaction I: U, acetone and Reaction II: Q, acetone

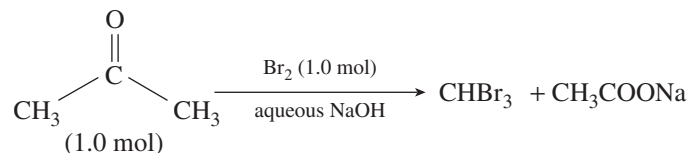
(C) Reaction I: T, U, acetone and Reaction II: P

(D) Reaction I: R, acetone and Reaction II: S, acetone

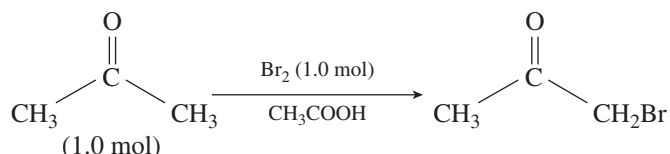


**Solution**

(C) In reaction I, in basic medium, with each  $\alpha$ -halogenation the rate of reaction increases and the complete haloform reaction takes place.



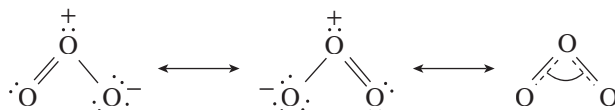
In reaction II, in acidic medium only 1 halogenated product is obtained with 1 mol of halogen.



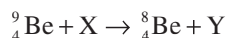
25. The correct statement(s) about  $\text{O}_3$  is(are)
- (A) O–O bond lengths are equal. (B) Thermal decomposition of  $\text{O}_3$  is endothermic.  
 (C)  $\text{O}_3$  is diamagnetic in nature. (D)  $\text{O}_3$  has a bent structure.

**Solution**

(A, C, D) As all electrons are paired, ozone is diamagnetic in nature. The structure is bent or V-shaped. The structure of ozone is resonance hybrid of the two structures with a delocalized  $p$ -orbital which covers all three atoms. Because of this, the two O–O bond lengths are equal.



26. In the nuclear transmutation

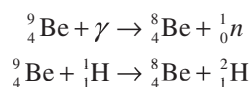


(X, Y) is(are)

- (A) ( $\gamma$ ,  $n$ ) (B) ( $p$ ,  $D$ ) (C) ( $n$ ,  $D$ ) (D) ( $\gamma$ ,  $p$ )

**Solution**

(A, B) The reactions involved are



27. The carbon-based reduction method is NOT used for the extraction of
- (A) Tin from  $\text{SnO}_2$  (B) Iron from  $\text{Fe}_2\text{O}_3$   
 (C) Aluminium from  $\text{Al}_2\text{O}_3$  (D) Magnesium from  $\text{MgCO}_3 \cdot \text{CaCO}_3$

**Solution**

(C, D)  $\text{SnO}_2$  and  $\text{Fe}_2\text{O}_3$  are reduced by carbon, while  $\text{Al}_2\text{O}_3$  and  $\text{MgCO}_3 \cdot \text{CaCO}_3$  are reduced by electrolytic reduction.

28. The thermal dissociation equilibrium of  $\text{CaCO}_3(\text{s})$  is studied under different conditions



For this equilibrium, the correct statement(s) is(are)

- (A)  $\Delta H$  is dependent on  $T$ .  
 (B)  $K$  is independent of the initial amount of  $\text{CaCO}_3$ .  
 (C)  $K$  is dependent on the pressure of  $\text{CO}_2$  at a given  $T$ .  
 (D)  $\Delta H$  is independent of catalyst, if any.

**Solution**

(A, C, D) For the reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ ,

$\Delta H$  is dependent on temperature according to Kirchhoff's equation  $\Delta H_2 - \Delta H_1 = C_p(T_2 - T_1)$ , but it is independent of addition of catalyst.

The equilibrium constant ( $K$ ) is independent of initial amount of  $\text{CaCO}_3$  but dependent on pressure of  $\text{CO}_2$  by the relation  $K = p_{\text{CO}_2}$ .

**SECTION 2: (Paragraph Type)**

This section contains 4 Paragraphs each describing theory, experiment, data etc. Eight questions relate to four paragraphs with two questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (A), (B), (C) and (D).

*Paragraph for Questions 29 and 30*

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with  $\text{H}_2\text{S}$  in a dilute mineral acid medium. However, it gave a precipitate (R) with  $\text{H}_2\text{S}$  in an ammoniacal medium. The precipitate R gave a colored solution (S), when treated with  $\text{H}_2\text{O}_2$  in an aqueous NaOH medium.

29. The precipitate P contains

- (A)  $\text{Pb}^{2+}$                       (B)  $\text{Hg}_2^{2+}$                       (C)  $\text{Ag}^+$                       (D)  $\text{Hg}^{2+}$

**Solution**

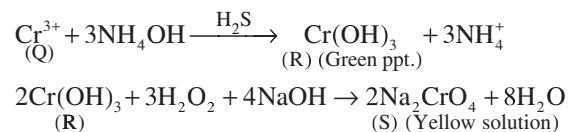
(A) Pb salts form white precipitate of  $\text{PbCl}_2$  with dil. HCl, which dissolves in hot water.

30. The colored solution S contains

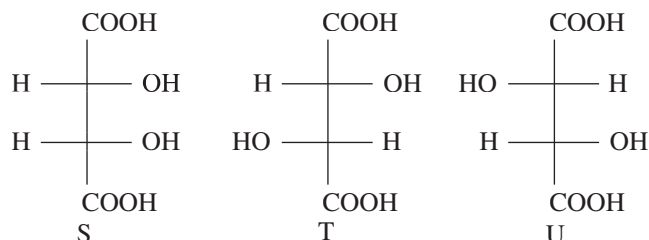
- (A)  $\text{Fe}_2(\text{SO}_4)_3$                       (B)  $\text{CuSO}_4$                       (C)  $\text{ZnSO}_4$                       (D)  $\text{Na}_2\text{CrO}_4$

**Solution**

(D) The reactions involved are.

*Paragraph for Questions 31 and 32*

P and Q are isomers of dicarboxylic acid  $\text{C}_4\text{H}_4\text{O}_4$ . Both decolorize  $\text{Br}_2/\text{H}_2\text{O}$ . On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline  $\text{KMnO}_4$ , P as well as Q could produce one or more than one from S, T and U.

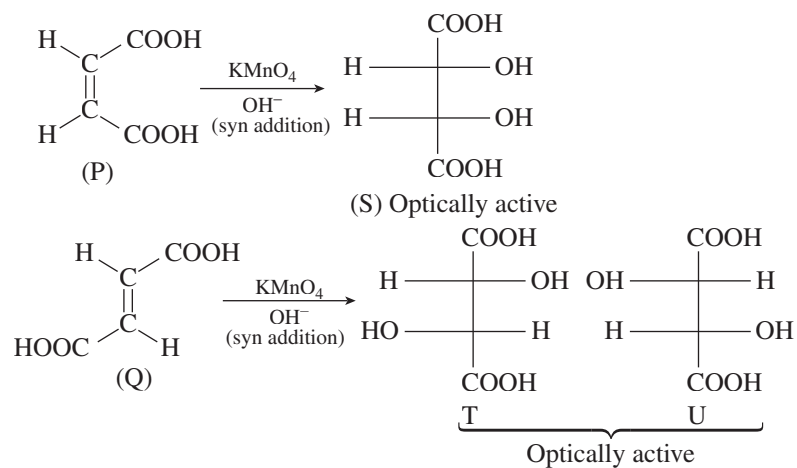


31. Compounds formed from P and Q are, respectively,

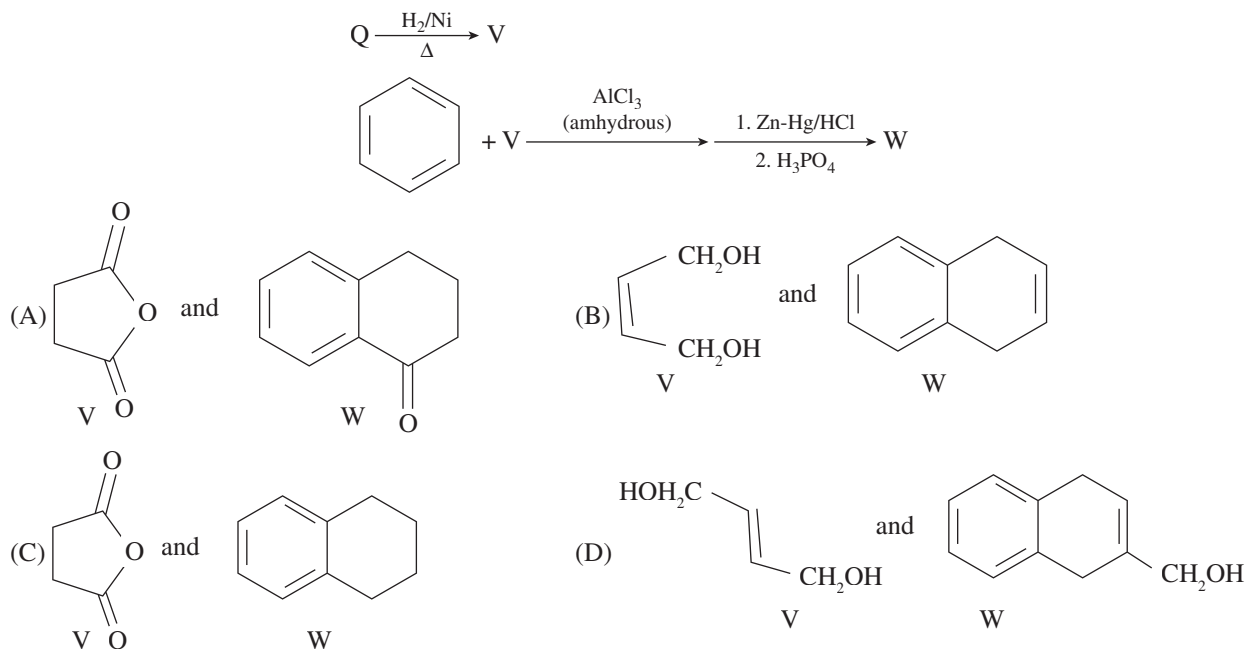
- (A) Optically active S and optically active pair (T, U).  
 (B) Optically inactive S and optically inactive pair (T, U).  
 (C) Optically active pair (T, U) and optically active S.  
 (D) Optically inactive pair (T, U) and optically inactive S.

**Solution**

(B) The reactions involved are

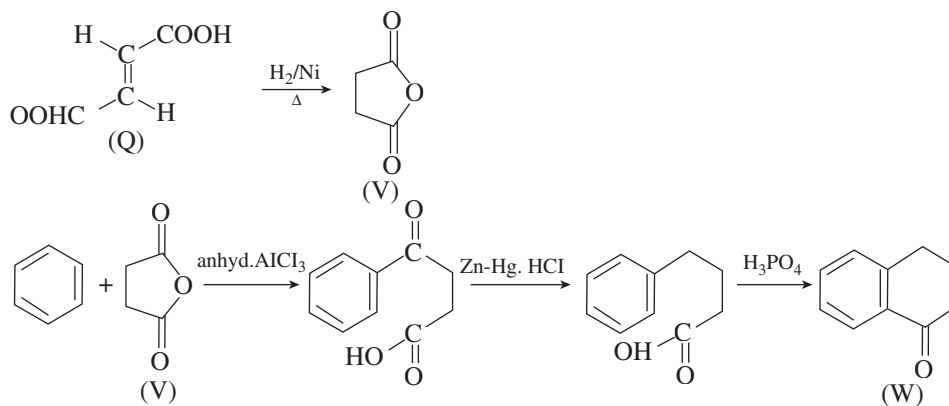


32. In the following reaction sequences V and W are, respectively,



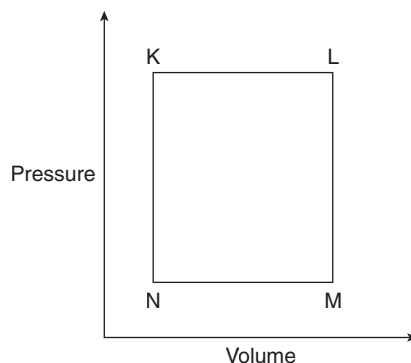
**Solution**

(A) The reactions involved are



Paragraph for Questions 33 and 34

A fixed mass  $m$  of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure



33. The succeeding operations that enable this transformation of states are  
 (A) Heating, cooling, heating, cooling (B) Cooling, heating, cooling, heating  
 (C) Heating, cooling, cooling, heating (D) Cooling, heating, heating, cooling

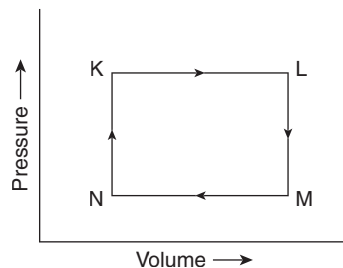
**Solution**

(C)

34. The pair of isochoric processes among the transformation of states is  
 (A) K to L and L to M (B) L to M and N to K  
 (C) L to M and M to N (D) M to N and N to K

**Solution**

(B)



As the term  $pV$  increases, the temperature increases; and when  $pV$  decreases with decrease in temperature.

The term  $pV$  increases  $K \rightarrow L$ , so this involves heating and is an isobaric process.

It increases from  $N \rightarrow K$ , so this involves heating and is an isochoric process.

It decreases from  $M \rightarrow N$ , so this involves cooling and is an isobaric process.

It decreases from  $L \rightarrow M$ , so this involves cooling and is an isochoric process.

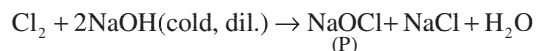
Paragraph for Questions 35 and 36

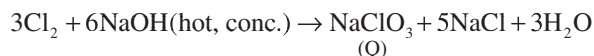
The reactions of  $\text{Cl}_2$  gas with cold-dilute and hot-concentrated  $\text{NaOH}$  in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The  $\text{Cl}_2$  gas reacts with  $\text{SO}_2$  gas, in presence of charcoal, to give a product R. R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus, T.

35. P and Q, respectively, are the sodium salts of  
 (A) Hypochlorous and chloric acids (B) Hypochlorous and chlorous acids  
 (C) Chloric and perchloric acids (D) Chloric and hypochlorous acids

**Solution**

(A) The reactions involved are





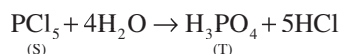
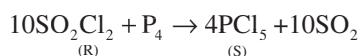
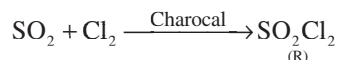
where NaOCl and NaClO<sub>3</sub> are salts of hypochlorous acid (HOCl) and chloric acid (HClO<sub>3</sub>), respectively.

36. R, S and T respectively, are



**Solution**

(A) The reactions involved are



**SECTION 3: (Matching List Type)**

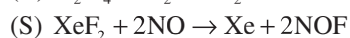
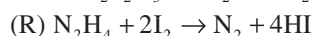
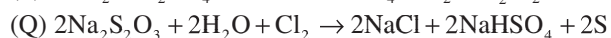
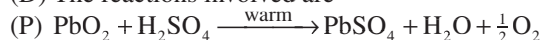
This section contains **4 multiple choice questions**. Each question has matching lists. The codes for the lists have choices (A), (B), (C) and (D) out of which **ONLY ONE is correct**.

37. The unbalanced chemical reactions given in List I show missing reagent or condition (?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists:



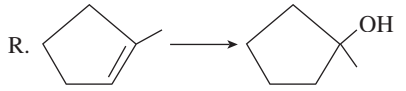
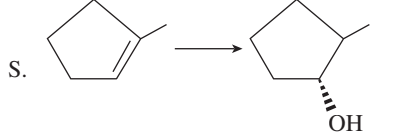
List I	List II
P. $\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{Other products}$	1. NO
Q. $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{Other products}$	2. I <sub>2</sub>
R. $\text{N}_2\text{H}_4 \xrightarrow{?} \text{N}_2 + \text{Other products}$	3. Warm
S. $\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{Other products}$	4. Cl <sub>2</sub>

**Solution**

(D) The reactions involved are

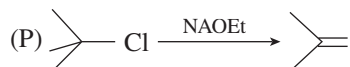
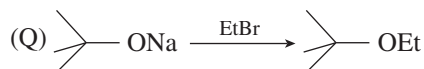
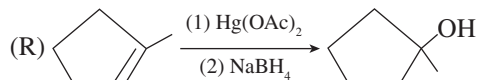


38. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists:

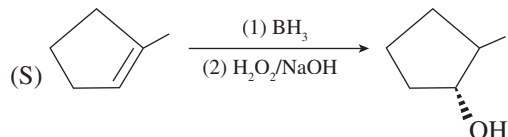
List I	List II
P. 	1. (i) Hg(OAc) <sub>2</sub> ; (ii) NaBH <sub>4</sub>
Q. 	2. NaOEt
R. 	3. Et-Br
S. 	4. (i) BH <sub>3</sub> ; (ii) H <sub>2</sub> O <sub>2</sub> /NaOH

**Solution**

(A) The reactions involved are

 $E_2$  reaction $S_N2$  reaction

Markovnikov addition



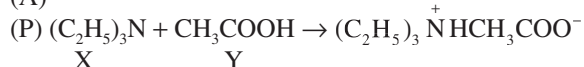
Anti-Markovnikov addition

39. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match list I with List II and select the correct answer using the code given below the lists:

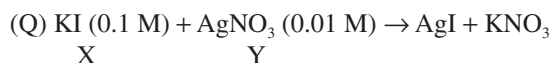
List I	List II
P. $(\text{C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$ X Y	1. Conductivity decreases and then increases
Q. $\text{KI} (0.1 \text{ M}) + \text{AgNO}_3 (0.01 \text{ M})$ X Y	2. Conductivity decreases and then does not change much
R. $\text{CH}_3\text{COOH} + \text{KOH}$ X Y	3. Conductivity increases and then does not change much
S. $\text{NaOH} + \text{HI}$ X Y	4. Conductivity does not change much and then increases

**Solution**

(A)



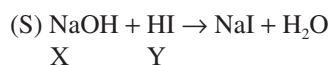
First, the conductivity increases due to neutralization of  $\text{CH}_3\text{COOH}$  and replacement of  $\text{H}^+$  by  $(\text{C}_2\text{H}_5)_3\text{NH}^+$ , after it becomes practically constant due to buffering, because of which  $[\text{H}^+]$  becomes constant and  $[(\text{C}_2\text{H}_5)_3\text{NH}^+]$  increases.



Initially, only  $\text{Ag}^+$  is replaced by  $\text{K}^+$ , so the number of ions in the solution remain constant till all of  $\text{AgNO}_3$  precipitated as  $\text{AgI}$ . After this precipitation, conductance increases due to increases in number of ions



Initially conductance decreases due to replacement of  $\text{OH}^-$  by  $\text{CH}_3\text{COO}^-$  and then slowly increases due to the increases in number of  $\text{H}^+$  ions.



Initially, conductance decreases due to replacement of  $\text{H}^+$  ions by  $\text{Na}^+$  and then increases due to the increase in  $\text{OH}^-$  ions.

40. The standard reduction potential data at  $25^\circ\text{C}$  is given below.

$$E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77 \text{ V};$$

$$E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$$

$$E^\circ(\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V};$$

$$E^\circ(\text{Cu}^+, \text{Cu}) = +0.52 \text{ V}$$

$$E^\circ[\text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}] = +1.23 \text{ V};$$

$$E^\circ[\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-] = +0.40 \text{ V}$$

$$E^\circ(\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V};$$

$$E^\circ(\text{Cr}^{2+}, \text{Cr}) = -0.91 \text{ V}$$

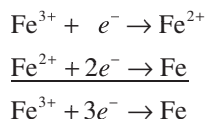
Match  $E^\circ$  of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

List I	List II
P. $E^\circ(\text{Fe}^{3+}, \text{Fe})$	1. $-0.18 \text{ V}$
Q. $E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$	2. $-0.4 \text{ V}$
R. $E^\circ(\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$	3. $-0.04 \text{ V}$
S. $E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$	4. $-0.83 \text{ V}$

### Solution

(D)

(P) The half reactions and net reactions are as follows:



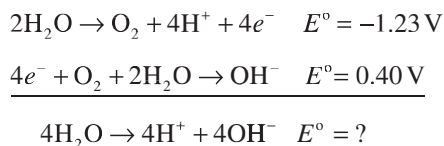
For the overall reaction,

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-3F \times E_{\text{Fe}^{3+}/\text{Fe}}^\circ = -1F \times 0.77 - 2F \times (-0.44)$$

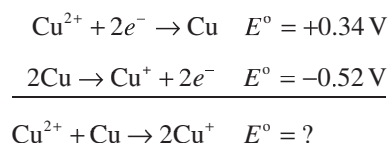
Solving, we get  $3E_{\text{Fe}^{3+}/\text{Fe}}^\circ = -0.11 \Rightarrow E_{\text{Fe}^{3+}/\text{Fe}}^\circ = -\frac{0.11}{3} = -0.036 \text{ V} \approx -0.04 \text{ V}$

(Q) The half reactions and net reactions are as follows:



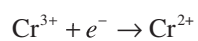
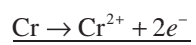
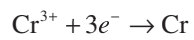
For the overall reaction,  $E^\circ = -1.23 + 0.40 = -0.83 \text{ V}$

(R) The half reactions and net reactions are as follows:



For the overall reaction,  $E^\circ = 0.34 - 0.52 = -0.18 \text{ V}$

(S) The half reactions and net reactions are as follows:



For the overall reaction,

$$\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$-1F \times E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\circ} = 3F \times 0.74 - 2F \times 0.91$$

Solving, we get  $E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\circ} = -0.4 \text{ V}$ .