IIT - JEE ADVANCED - 2012

PAPER-2 [Code – 8]

PART - II: CHEMISTRY

SECTION I : Single Correct Answer Type

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

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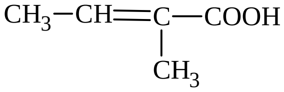
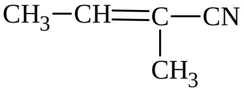
21. The major product **H** of the given reaction sequence is

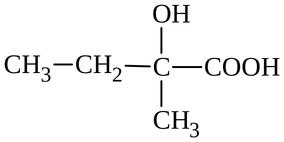
$CH_3-CH_2-CO-CH_3 \xrightarrow{\overset{\ominus}{C}N} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$

(A) 

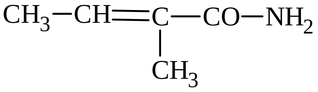
$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-COOH$

(B) 

$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CN$

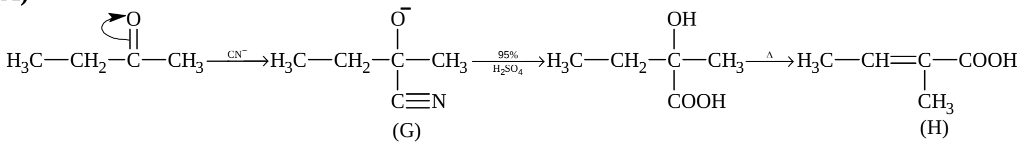
(C) 

$CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH$

(D) 

$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CO-NH_2$

Sol. **(A)**



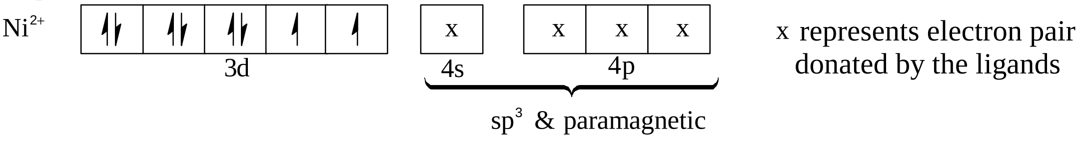
22. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

(A) tetrahedral and tetrahedral
(B) square planar and square planar
(C) tetrahedral and square planar
(D) square planar and tetrahedral

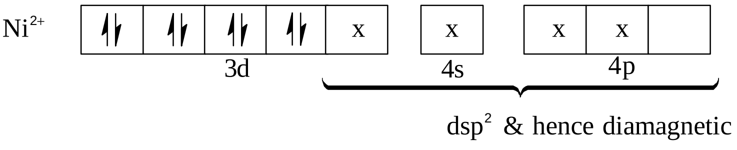
Sol. **(C)**

In both complexes Ni exists as Ni^{2+}.

In sp^3 (tetrahedral)



In dsp^2 (square planar geometry)



23. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are

(A) O_2 and CO respectively
(B) O_2 and Zn dust respectively
(C) HNO_3 and Zn dust respectively
(D) HNO_3 and CO respectively

Sol. **(B)**

The reactions involved in cyanide extraction process are:

$$\underset{(\text{argentite ore})}{Ag_2S} + 4NaCN \rightleftharpoons 2Na\left[Ag(CN)_2\right] + Na_2S$$

$$4Na_2S + \underset{(\text{oxidising agent})}{5[O_2]} + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$2Na\left[Ag(CN)_2\right] + \underset{(\text{reducing agent})}{Zn} \longrightarrow Na_2\left[Zn(CN)_4\right] + 2Ag\downarrow$$

24. The reaction of white phosphorous with aqueous NaOH gives phosphine along with another phosphorous containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively

(A) redox reaction; −3 and −5 (B) redox reaction; +3 and +5

(C) disproportionation reaction; −3 and +5 (D) disproportionation reaction; −3 and +3

Sol. **(C)**

The balanced disproportionation reaction involving white phosphorus with aq. NaOH is

Oxidation

$$P_4^0 + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{P}O_2$$

Reduction

* However, as the option involving +1 oxidation state is completely missing, one might consider that NaH_2PO_2 formed has undergone thermal decomposition as shown below:

$$2NaH_2PO_2 \xrightarrow{\Delta} Na_2H\overset{+5}{P}O_4 + PH_3$$

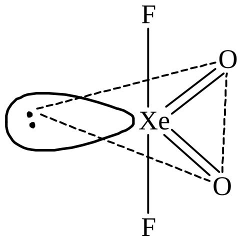
Although heating is nowhere mentioned in the question, the "other product" as per available options seems to be Na_2HPO_4 (oxidation state = +5).

*25. The shape of XeO_2F_2 molecule is

(A) trigonal bipyramidal (B) square planar

(C) tetrahedral (D) see–saw

Sol. **(D)**



Hybridization = sp^3d

Shape = see – saw

26. For a dilute solution containing 2.5 g of a non–volatile non–electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76\ K\ kg\ mol^{-1}$)

(A) 724 (B) 740

(C) 736 (D) 718

Sol. **(A)**

B → Solute; A → Solvent

$W_B = 2.5$ g, $W_A = 100$ g

$\Delta T_b = 2^o$

$$\frac{p^o - p_s}{p^o} = X_B = \frac{n_B}{n_B + n_A}$$

$$\frac{p^o - p_s}{p^o} = \frac{n_B}{n_A} \quad \because n_B << n_A$$

$$\frac{p^o - p_s}{p^o} = \frac{n_B}{n_A}$$

$$\frac{760 - P_{soln}}{760} = \frac{2.5/M}{\frac{100}{18}\times\frac{1000}{1000}} = \frac{m\times 18}{1000} \qquad \ldots(i)$$

and from boiling point elevation,

$2 = 0.76 \times m$

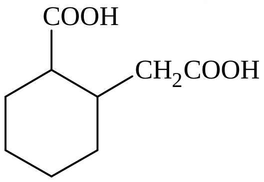
$$m = \frac{2}{0.76} \qquad \ldots(ii)$$

on equating (i) and (ii)

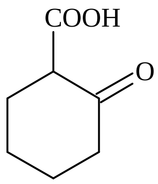
P_{soln} = 724 mm

27. The compound that undergoes decarboxylation most readily under mild condition is

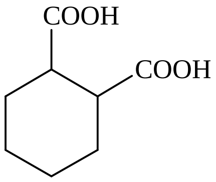
(A)



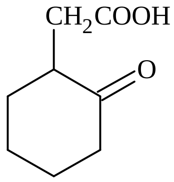
(B)



(C)

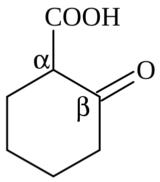


(D)



Sol. **(B)**

β - keto acids undergoes decarboxylation easily.



(β – keto acid)

*28. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond in C_2H_2. That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1})

$2C(s) \longrightarrow 2C(g) \qquad \Delta H = 1410\ kJmol^{-1}$

$2C(s) \longrightarrow 2C(g) \qquad \Delta H = 1410\,kJmol^{-1}$

$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 330\,kJmol^{-1}$

(A) 1165 (B) 837

(C) 865 (D) 815

Sol. **(D)**

(i) $2C(s) + H_2(g) \longrightarrow H-C\equiv C-H(g) \qquad \Delta H = 225\ kJmol^{-1}$

(ii) $2C(s) \longrightarrow 2C(g) \qquad \Delta H = 1410\ kJmol^{-1}$

(iii) $H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 330\ kJmol^{-1}$

From equation (i):

$$225 = \left[2\times\Delta H_{C(s)\longrightarrow C(g)} + 1\times BE_{H-H}\right] - \left[2\times BE_{C-H} + 1\times BE_{C\equiv C}\right]$$

$$225 = [1410 + 1\times 330] - [2\times 350 + 1\times BE_{C\equiv C}]$$

$$225 = [1410 + 330] - [700 + BE_{C\equiv C}]$$

$$225 = 1740 - 700 - BE_{C\equiv C}$$

$225 = 1040 - BE_{C\equiv C}$

$BE_{C\equiv C} = 1040 - 225 = 815\ \text{kJ mol}^{-1}$

SECTION II : Paragraph Type

This section contains 6 **multiple choice questions** relating to three paragraphs with **two questions on each paragraph**. Each question has four choices (A), (B), (C) and (D) out of which **ONLY ONE is correct**.

Paragraph for Questions 29 and 30

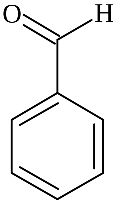
In the following reaction sequence, the compound **J** is an intermediate.

$$\mathbf{I} \xrightarrow[CH_3COONa]{(CH_3CO)_2O} \mathbf{J} \xrightarrow[\substack{\text{(ii) } SOCl_2 \\ \text{(iii) anhyd. } AlCl_3}]{\text{(i) } H_2,\ Pd/C} \mathbf{K}$$

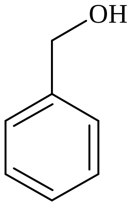
J($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and a positive Baeyer's test.

29. The compound **I** is

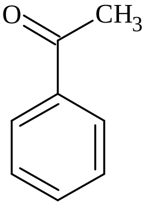
(A)



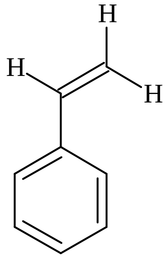
(B)



(C)



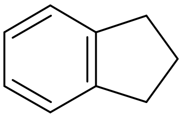
(D)



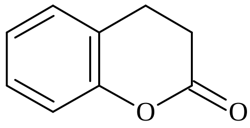
Ans. **(A)**

30. The compound **K** is

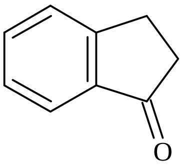
(A)



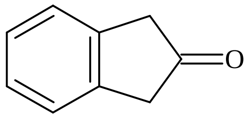
(B)



(C)

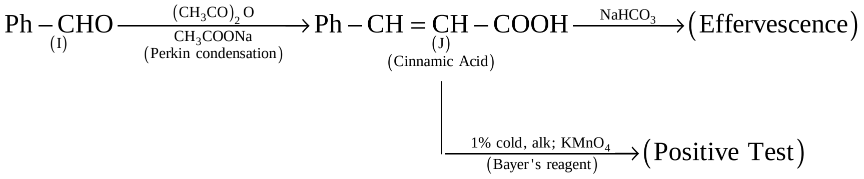


(D)



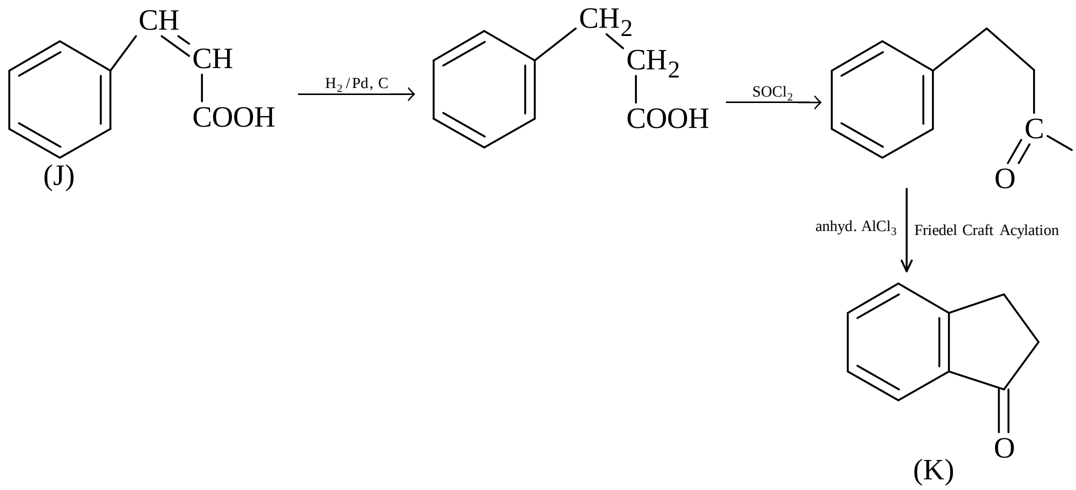
Ans. **(C)**

Sol. **29–30**



$$\underset{(I)}{Ph-CHO} \xrightarrow[\substack{CH_3COONa \\ \text{(Perkin condensation)}}]{(CH_3CO)_2O} \underset{\substack{(J) \\ \text{(Cinnamic Acid)}}}{Ph-CH=CH-COOH} \xrightarrow{NaHCO_3} (\text{Effervescence})$$

$$\xrightarrow[\text{(Bayer's reagent)}]{1\%\ \text{cold, alk; } KMnO_4} (\text{Positive Test})$$



Paragraph for Questions 31 and 32

The electrochemical cell shown below is a concentration cell.
$M \mid M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $\mid\mid M^{2+}$ (0.001 mol dm^{-3}) $\mid M$
The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

31. The value of ΔG (kJ mol^{-1}) for the given cell is (take 1F = 96500 C mol^{-1})
(A) –5.7 (B) 5.7
(C) 11.4 (D) –11.4

Sol. **(D)**
At anode: $M(s) + 2X^-(aq) \to MX_2(aq) + 2e^-$
At cathode: $M^{+2}(aq) + 2e^- \to M(s)$
n–factor of the cell reaction is 2.
$\Delta G = -nFE_{cell} = -2 \times 96500 \times 0.059 = -113873 / \text{mole} = -11.387 \text{ KJ / mole} \approx -11.4 \text{ KJ / mole}$

32. The solubility product (K_{sp}; mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is (take 2.303 × R × 298/F = 0.059 V)
(A) 1×10^{-15} (B) 4×10^{-15}
(C) 1×10^{-12} (D) 4×10^{-12}

Sol. **(B)**
$M \mid \underset{(K_{sp}=?)}{M^+(\text{sat.})} \mid\mid M^{2+}(0.001\text{ M})$
emf of concentration cell,

$$E_{cell} = \frac{-0.059}{n}\log\frac{\left[M^{+2}\right]_a}{\left[M^{+2}\right]_c}$$

$$0.059 = \frac{0.059}{2}\log\frac{[0.001]}{\left[M^{+2}\right]_a}$$

$[M^{+2}]_a = 10^{-5}$ = S (solubility of salt in saturated solution)

$$\underset{(S)}{MX_2} \rightleftharpoons \underset{(S)}{M^{+2}} + \underset{(2S)}{2x^-}(aq)$$

$K_{sp} = 4S^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

Paragraph for Questions 33 and 34

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.

*33. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

(A) Cl_2O (B) Cl_2O_7

(C) ClO_2 (D) Cl_2O_6

Sol. **(A)**

$$\underset{(\text{Bleaching Powder})}{Ca(OCl)Cl} \rightarrow Ca^{+2} + \overset{-}{O}Cl + Cl^{-}$$

$$\underset{(\text{oxo acid})}{HOCl} \rightarrow H^{+} + OCl^{-}$$

$$2HOCl \xrightarrow{\Delta} H_2O + Cl_2O$$

Anhydride of oxoacid (HOCl) is Cl_2O.

*34. 25 mL of household solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(A) 0.48 M (B) 0.96 M

(C) 0.24 M (D) 0.024 M

Sol. **(C)**

$$\underset{\substack{25\text{ mL}\\(M)\text{molar}}}{CaOCl_2(aq)} + \underset{\substack{30\text{ mL}\\0.5(M)}}{2KI} \rightarrow I_2 + Ca(OH)_2 + KCl$$

$$I_2 + \underset{\substack{48\text{ mL}\\0.25\,(N)=0.25\text{ M}}}{2Na_2S_2O_3} \rightarrow Na_2S_4O_6 + 2NaI$$

So, number of millimoles of I_2 produced $= 48\times\frac{0.25}{2} = 24\times0.25 = 6$

In reaction;

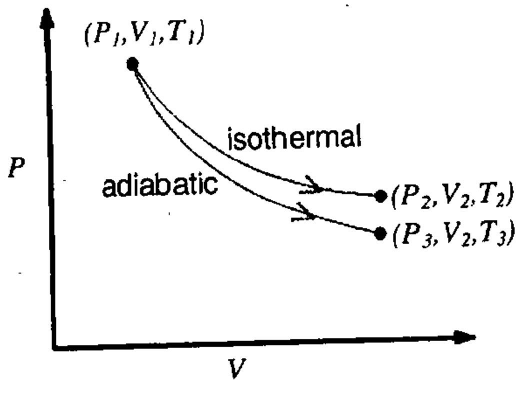
Number of millimoles of bleaching powder $\left(n_{CaOCl_2}\right) = n_{I_2-\text{produced}} = \frac{1}{2}\times n_{Na_2S_2O_3}$ used = 6

So, (M) = $\frac{n_{CaOCl_2}(\text{millimoles})}{V(\text{in mL})} = \frac{6\text{ millimoles}}{25\text{ mL}} = 0.24$

SECTION III : Multiple Correct Answer(s) Type

The section contains **6 multiple choice questions.** Each question has four choices (A), (B), (C) and (D) out of which **ONE or MORE are correct.**

*35. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct?



(A) $T_1 = T_2$ (B) $T_3 > T_1$

(C) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ (D) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Sol. **(A, C, D)**

$T_1 = T_2$ because process is isothermal.

Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.

In adiabatic process expansion occurs by using internal energy hence it decreases while in isothermal process temperature remains constant that's why no change in internal energy.

36. For the given aqueous reactions, which of the statement(s) is (are) true?

$$\begin{tikzcd} \text{excess KI} + K_3\left[Fe(CN)_6\right] \arrow[r, "\text{dilute } H_2SO_4"] & \text{brownish-yellow solution} \arrow[d, "ZnSO_4"] \\ & \text{white precipitate} + \underbrace{\text{brwonish-yellow filtrate}} \arrow[d, "Na_2S_2O_3"] \\ & \text{colourless solution} \end{tikzcd}$$

(A) The first reaction is a redox reaction.
(B) White precipitate is $Zn_3[Fe(CN)_6]_2$.
(C) Addition of filtrate to starch solution gives blue colour.
(D) White precipitate is soluble in NaOH solution.

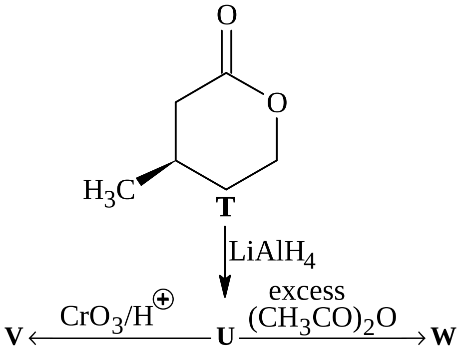
Sol. **(A, C, D)**

$$K_3\left[\overset{+3}{Fe}(CN)_6\right] + KI(\text{excess}) \rightarrow K_4\left[\overset{+2}{Fe}(CN)_6\right] + \underset{\text{Brownish yellow solution}}{KI_3} \quad (\text{redox reaction})$$

$$\underset{(\text{Brownish yellow filterate})}{I_3^-} + 2Na_2S_2O_3 \rightarrow \underset{\text{Clear solution}}{Na_2S_4O_6 + +2NaI + I^-}$$

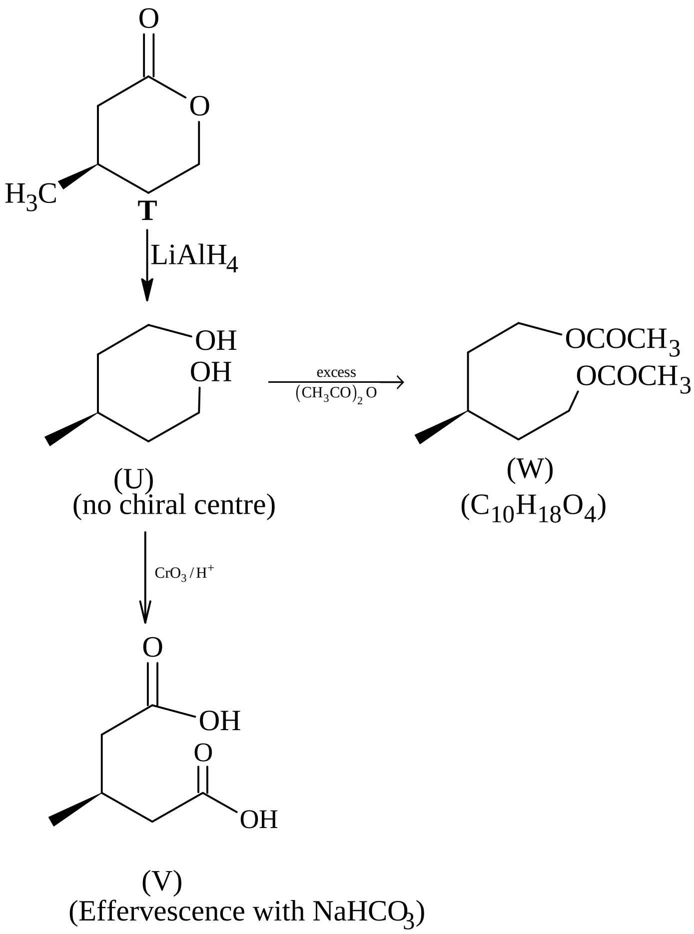
$$K_4\left[Fe(CN)_6\right] + ZnSO_4 \rightarrow \underset{(\text{White ppt.})}{K_2Zn_3\left[Fe(CN)_6\right]_3} \xrightarrow{NaOH} \underset{\text{Soluble}}{Na_2\left[Zn(OH)_4\right]}$$

37. With reference to the scheme given, which of the given statement(s) about **T, U, V** and **W** is (are) correct?

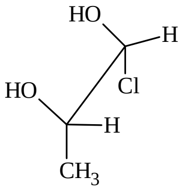


(A) **T** is soluble in hot aqueous NaOH
(B) **U** is optically active
(C) Molecular formula of **W** is $C_{10}H_{18}O_4$
(D) **V** gives effervescence on treatment with aqueous $NaHCO_3$

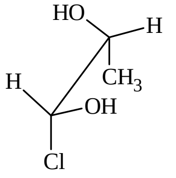
Sol. **(A, C, D)**



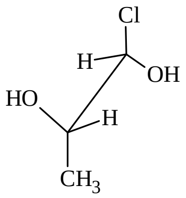
38. Which of the given statement(s) about **N, O, P** and **Q** with respect to **M** is (are) correct?



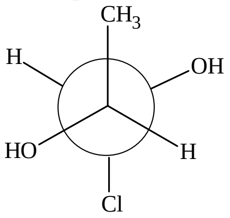
M



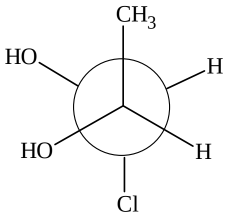
N



O



P

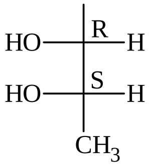


Q

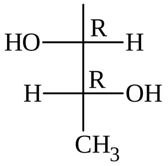
(A) **M** and **N** are non–mirror image stereoisomers
(B) **M** and **O** are identical
(C) **M** and **P** are enantiomers
(D) **M** and **Q** are identical

Sol. **(A, B, C)**

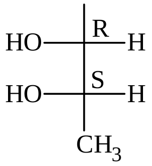
Converting all the structure in the Fischer projection



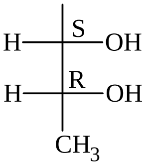
M



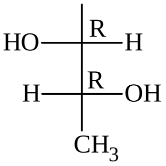
N



O



P



Q

M and N are diastereoisomers
M and O are identical
M and P are enantiomers
M and Q are diastereoisomers
Hence, the correct options are A, B, C.

39. With respect to graphite and diamond, which of the statement(s) given below is (are) correct?

(A) Graphite is harder than diamond.
(B) Graphite has higher electrical conductivity than diamond.
(C) Graphite has higher thermal conductivity than diamond.
(D) Graphite has higher C–C bond order than diamond.

Sol. **(B, D)**

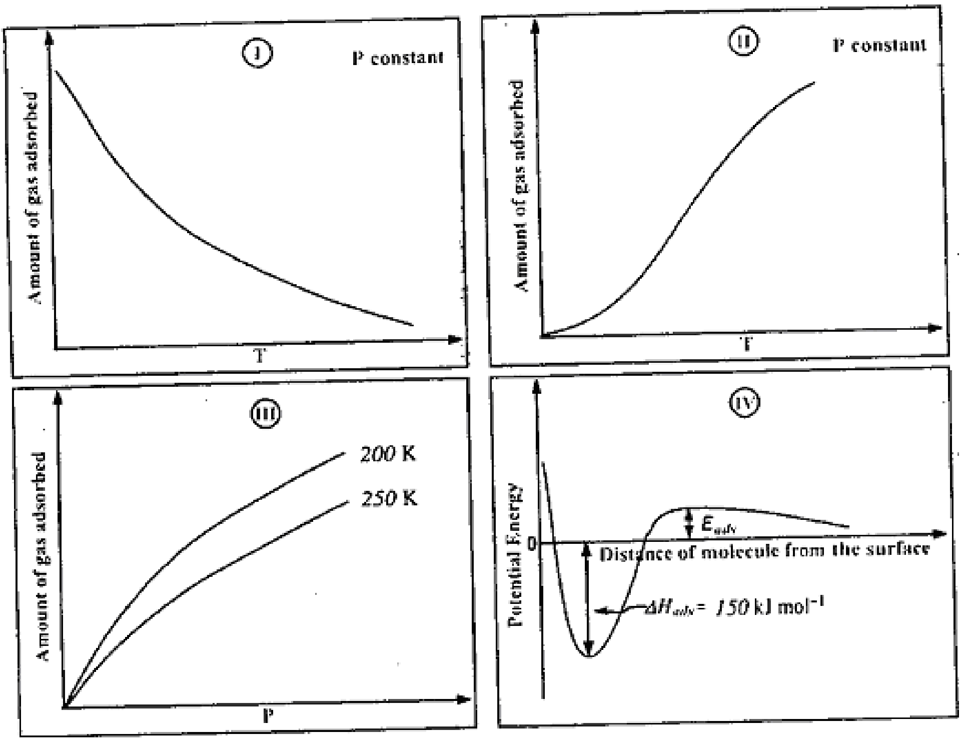
⇒ Diamond is harder than graphite.

⇒ Graphite is good conductor of electricity as each carbon is attached to three C-atoms leaving one valency free, which is responsible for electrical conduction, while in diamond, all the four valencies of carbon are satisfied, hence insulator.

⇒ Diamond is better thermal conductor than graphite. Whereas electrical conduction is due to availability of free electrons; thermal conduction is due to transfer of thermal vibrations from atom to atom. A compact and precisely aligned crystal like diamond thus facilitates fast movement of heat.

⇒ In graphite, C – C bond acquires double bond character, hence higher bond order than in diamond.

40. The given graphs / data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct?



(A) **I** is physisorption and **II** is chemisorption
(B) **I** is physisorption and **III** is chemisorption
(C) **IV** is chemisorption and **II** is chemisorption
(D) **IV** is chemisorption and **III** is chemisorption

Sol. **(A, C)**

Graph (I) and (III) represent physiosorption because, in physiosorption, the amount of adsorption decreases with the increase of temperature and increases with the increase of pressure.

Graph (II) represent chemisorption, because in chemisorption amount of adsorption increase with the increase of temperature. Graph (IV) is showing the formation of a chemical bond, hence chemisorption.