

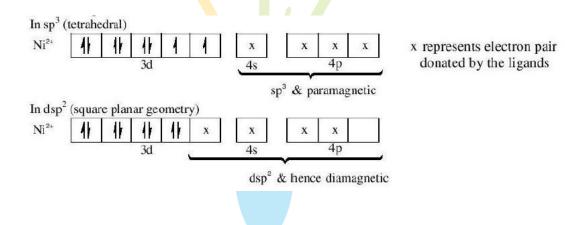
JEE ADVANCED-2012

CHEMISTRY

21. Sol. (A)

22. Sol. (C)

In both complexes Ni exists as Ni²⁺.



23. **Sol. (B)**

The reactions involved in cyanide extraction process are:

$$Ag_2S + 4NaCN = 2Na[Ag(CN)_2] + Na_2S$$
(argentite ore)

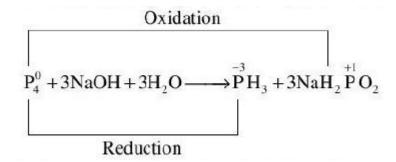
$$4Na_{2}S + 5[O_{2}] + 2H_{2}O = 2Na_{2}SO_{4} + 4NaOH + 2S$$

$$2Na[Ag(CN)_{2}] + Zn = Na_{2}[Zn(CN)_{4}] + 2Ag \downarrow$$



24. Sol. (C)

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

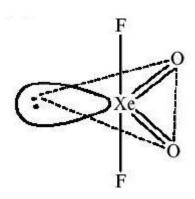


However, as the option involving +1 x oxidation state is completely missing, one might consider that NaH₂P₂O formed has undergone thermal decomposition as shown below:

$$2\text{NaH}_2\text{PO}_2 \xrightarrow{\Delta} \text{Na}_2\text{H} \overset{+5}{\text{PO}}_4 + \text{PH}_3$$

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. **Sol. (D)**



Hybridization = sp^3d

Shape = \sec - \sec



26. **Sol.** (A)

$$B \rightarrow Solute; A \rightarrow Solvent$$

$$W_B = 2.5 \,\mathrm{g}, W_A = 100 \,\mathrm{g}$$

$$\Delta T_b = 2^{\circ}$$

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

$$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{n_B}{n_A} :: n_B << n_A$$

$$\frac{p^{\circ} - p_{s}}{p^{\circ}} = \frac{n_{B}}{n_{A}}$$

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

and from boiling point elevation,

$$2 = 0.76 \times m$$

$$m = \frac{2}{0.76} \quad \dots (ii)$$

on equating (i) and (ii)

$$P_{soln} = 724 mm$$



27. **Sol. (B)**

 β -keto acids undergoes decarboxylation easily.

28. **Sol. (D)**

(i)
$$2C(s) + H_2(g) \rightarrow H - C \equiv C - H(g)$$
 $\Delta H = 225 \text{ kJ mol}^{-1}$

(ii)
$$2C(s) \rightarrow 2C(g)$$
 $\Delta H = 1410 \text{ kJ mol}^{-1}$

(iii)
$$H_2(g) \rightarrow 2H(g)$$
 $\Delta H = 330 \text{ kJ mol}^{-1}$

From equation (i):

$$\begin{split} 225 = & \left[2 \times \Delta H_{C(s) \to C(g)} + 1 \times BE_{H-H} \right] - \left[2 - BE_{C-H} + 1 \times BE_{C=C} \right] \\ 225 = & \left[1410 + 1 \times 330 \right] - \left[2 \times 350 + 1 \times BE_{C=C} \right] \\ 225 = & \left[1410 + 330 \right] - \left[700 + BE_{C=C} \right] \\ 225 = & 1740 - 700 - BE_{C=C} \\ 225 = & 1040 - BE_{C=C} \\ BE_{C=C} = & 1040 - 225 = 815 \text{kJ mol}^{-1} \end{split}$$

29. **Ans.** (A)



30. **Ans.** (**C**)

Sol. 29-30

$$(J) \xrightarrow{CH} \xrightarrow{H_2/Pd, C} \xrightarrow{CH_2} \xrightarrow{COOH} \xrightarrow{SOCI_2} \xrightarrow{COOH} \xrightarrow{SOCI_2} (K)$$

31. **Sol. (D)**

At anode: $M(s) + 2X^{-}(aq) \rightarrow MX_{2}(aq) + 2e^{-}$

At cathode: $M^{+2}(aq) + 2e^- \rightarrow M(s)$

n-factor of the cell reaction is 2.

$$\Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 0.059 = -113873/\text{mole} = -11.387 \,\text{KJ/mole} = -11.4 \,\text{KJ/mole}$$

32. Sol. (B)

$$M | M^{+}(\text{sat.}) | M^{2+}(0.001M)$$

emf of concentration cell,



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

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

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

$$MX_2 = M_{(S)}^{+2} + 2x^- (aq)$$

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

33. **Sol. (A)**

$$Ca(OCl)Cl \rightarrow Ca^{+2} + \overline{O}Cl + Cl^{-1}$$
(Bleaching Powder)

$$HOCl \rightarrow H^+ + OCl^-$$

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

Anhydride of oxoacid (HOCl) is Cl_2O .

34. **Sol.** (**C**)

$$\begin{array}{c} \text{CaOCl}_{2}\left(\text{aq}\right) + \underset{\text{\tiny 0.5(M)}}{25\text{mL}} \xrightarrow{30\text{mL}} I_{2} + \text{Ca}\left(\text{OH}\right)_{2} + \text{HCl} \end{array}$$

$$I_{2} + 2Na_{2}S_{2}O_{3} \rightarrow Na_{2}S_{4}O_{6} + 2NaI_{{\tiny 0.25(N)=0.25M}}^{48\,\text{mL}}$$

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



In reaction;

Number of millimoles of bleaching powder

$$\left(n_{\text{CaOCl}_2}\right) = n_{\text{I}_2 - \text{produced}} = \frac{1}{2} \times n_{\text{Na}_2\text{S}_2\text{O}_3} \text{ used} = 6$$

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

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

$$\begin{split} K_{3} \begin{bmatrix} ^{+3} \text{Fe}(\text{CN})_{6} \end{bmatrix} + \text{KI}(\text{excess}) &\rightarrow \text{K}_{4} \begin{bmatrix} ^{+2} \text{Fe}(\text{CN})_{6} \end{bmatrix} + \underset{\text{Brownish yellow solution}}{\text{KI}_{3}} \text{(redox reaction)} \\ I_{3}^{-} + 2\text{Na}_{2}\text{S}_{2}\text{O}_{3} &\rightarrow \text{Na}_{2}\text{S}_{4}\text{O}_{6} + +2\text{NaI} + \text{I}^{-} \\ \text{(Brownish yellow filterate)} \end{split}$$

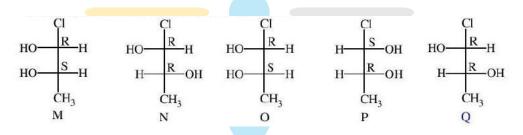
$$K_{4}\Big[\text{Fe}\big(\text{CN}\big)_{6}\Big] + Z\text{nSO}_{4} \rightarrow K_{2}Z\text{n}_{3}\Big[\text{Fe}\big(\text{CN}\big)_{6}\Big]_{3} \xrightarrow{\text{NaOH}} \text{Na}_{2}\Big[\underset{\text{Soluble}}{Z\text{n}}\big(\text{OH}\big)_{4}\Big]$$



37. Sol. (A, C, D)

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

Converting all the structure in the Fischer projection



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. **Sol. (B, D)**

- \Rightarrow 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.
- \Rightarrow In graphite, C-C bond acquires double bond character, hence higher bond order than in diamond.

40. **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.