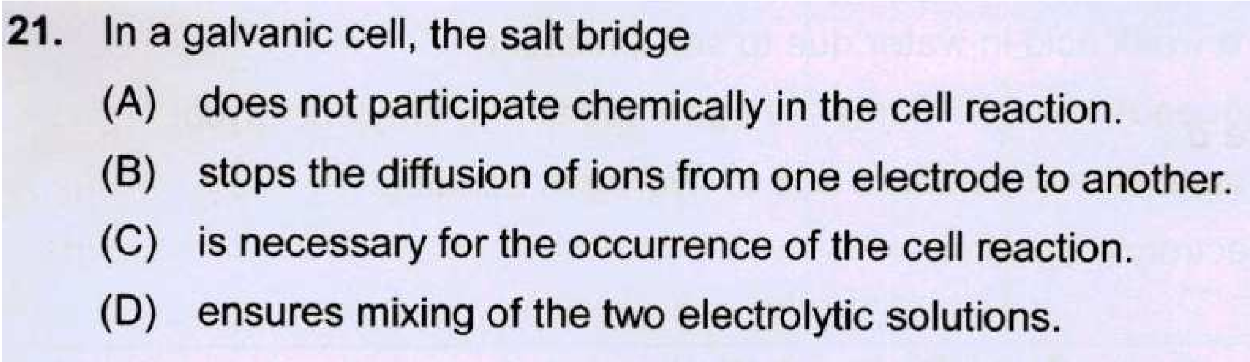
JEE Advanced -2014 Paper-1 Chemistry Solution (Code-2)



21. In a galvanic cell, the salt bridge

(A) does not participate chemically in the cell reaction.

(B) stops the diffusion of ions from one electrode to another.

(C) is necessary for the occurrence of the cell reaction.

(D) ensures mixing of the two electrolytic solutions.

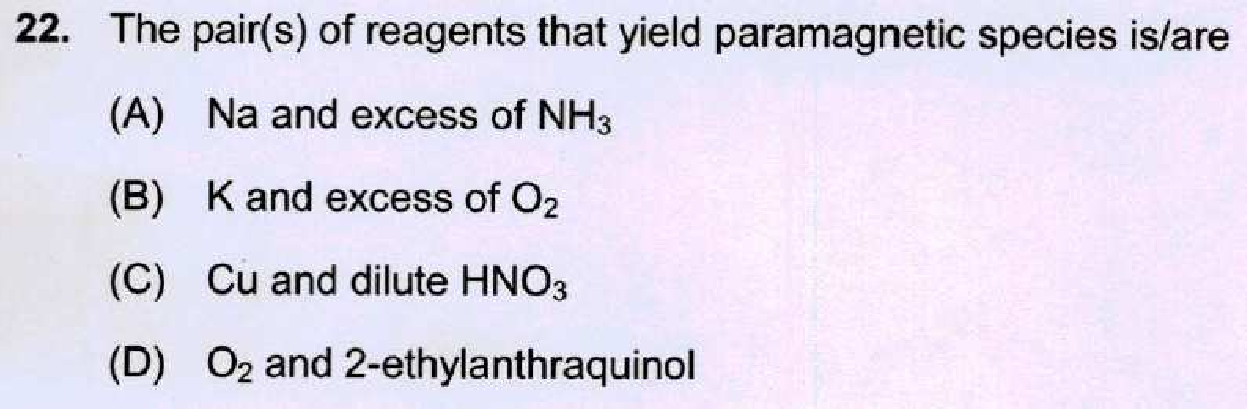
Answers (A), (B)

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralize these negative ions, sufficient number of positive ions is provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.



22. The pair(s) of reagents that yield paramagnetic species is/are

(A) Na and excess of NH_3

(B) K and excess of O_2

(C) Cu and dilute HNO_3

(D) O_2 and 2-ethylanthraquinol

Solution:

The required reactions are as follows:

(a) Reaction of Na with excess NH_3:

$$Na(s) + (x+y)NH_3(l) \rightarrow Na(NH_3)_x^+(aq) + e^-(NH_3)_y(aq)$$

Each sodium atom on dissolving loses an electron and becomes a cation. Thus it isparamagnetic in nature.

(b) Reaction of K with excess of O_2:

$$K(s) + O_2(g) \longrightarrow KO_2$$

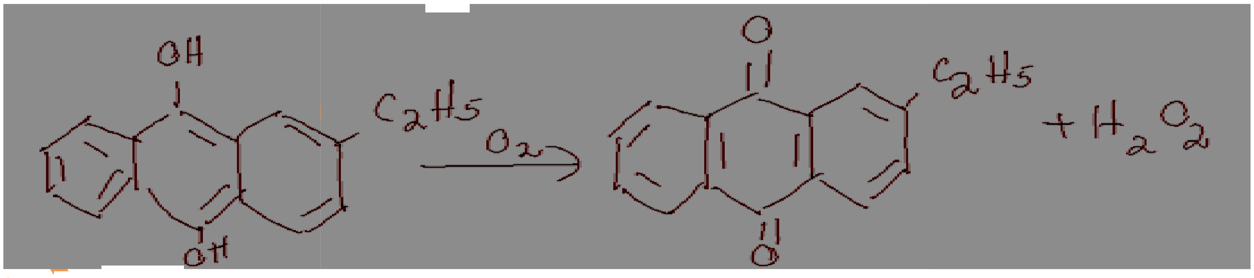
Potassium superoxide is paramagnetic in character.

(c) Reaction of Cu with HNO_3:

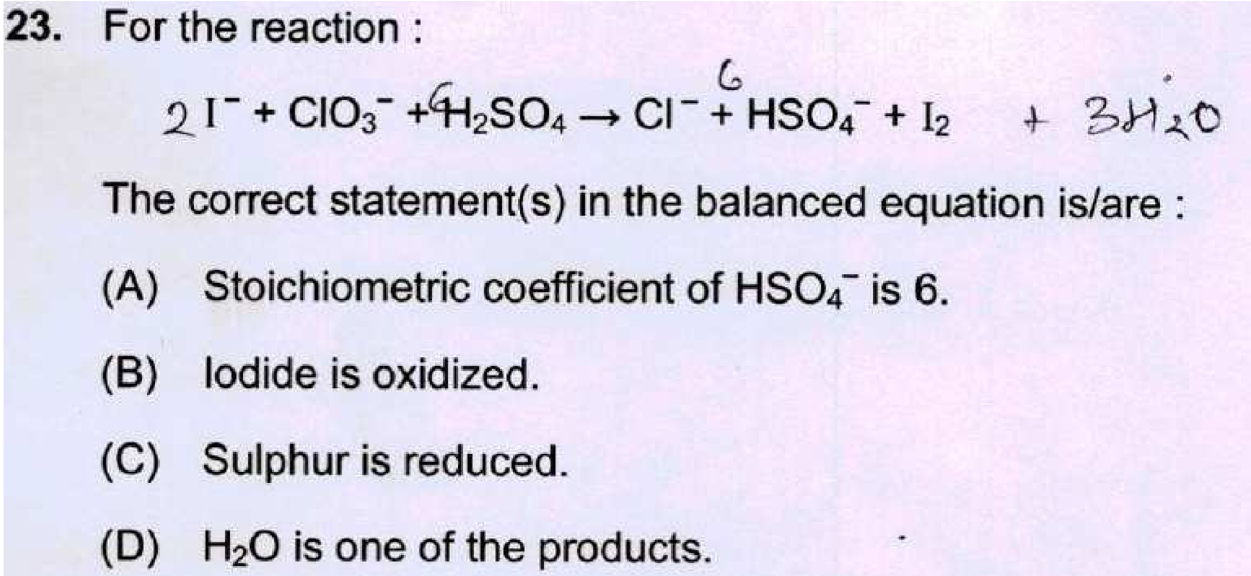
$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

NO is paramagnetic.

(d) Reaction of O_2 with 2 – ethylanthorquinol



Hydrogen peroxide is diamagnetic.



23. For the reaction :

$$2\,I^- + ClO_3^- + 6H_2SO_4 \rightarrow Cl^- \overset{6}{+} HSO_4^- + I_2 \quad + 3H_2O$$

The correct statement(s) in the balanced equation is/are :

(A) Stoichiometric coefficient of HSO_4^- is 6.

(B) Iodide is oxidized.

(C) Sulphur is reduced.

(D) H_2O is one of the products.

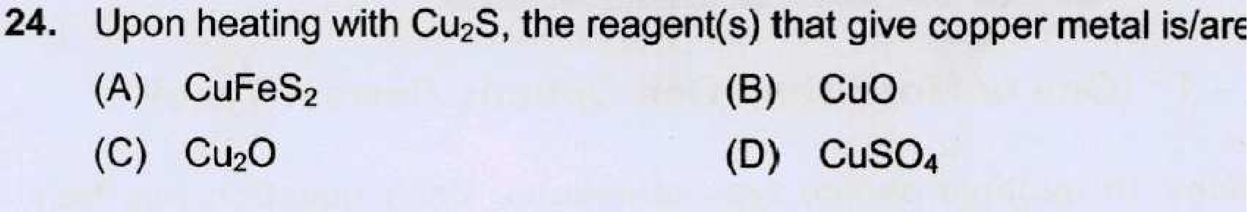
Solution: (A), (B), (D)

The reaction would be given by:

$$2I^- + ClO_3^- + 6H_2S\text{[illegible]}_4 \rightarrow \text{[illegible]}^- + 6\text{[illegible]}O_4^- + I_2 + 3H_2O$$

Thus,

- Iodine loses electrons so it gets oxidized.
- Chlorine gets reduced as oxygen molecule is lost.
- Sulphur is oxidized as it loses hydrogen.
- Water is produced.



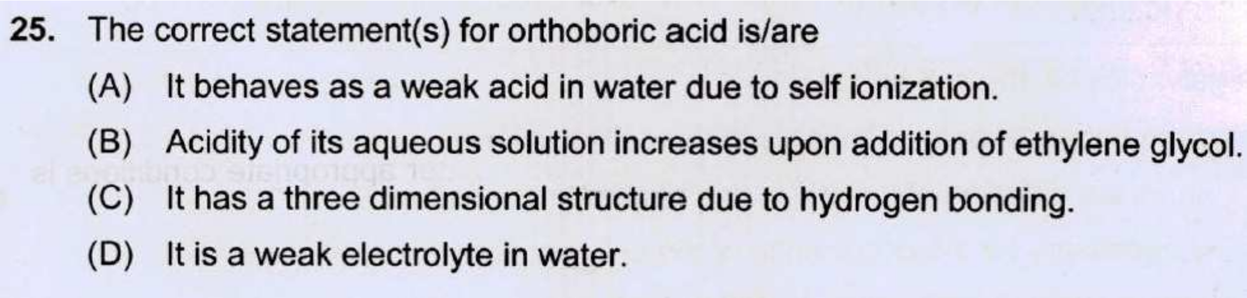
24. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are

(A)	$CuFeS_2$	(B)	CuO
(C)	Cu_2O	(D)	$CuSO_4$

Solution: (B), (C), (D)

The reactions go as follows:

(a) $Cu_2S + 2\,Cu_2O \rightarrow 6\,Cu + SO_2$
(b) $CuSO_4 + Cu_2S \rightarrow 3\,Cu + 2SO_2$
(c) $2CuO + Cu_2S \rightarrow 4\,Cu + SO_2$



25. The correct statement(s) for orthoboric acid is/are

(A) It behaves as a weak acid in water due to self ionization.

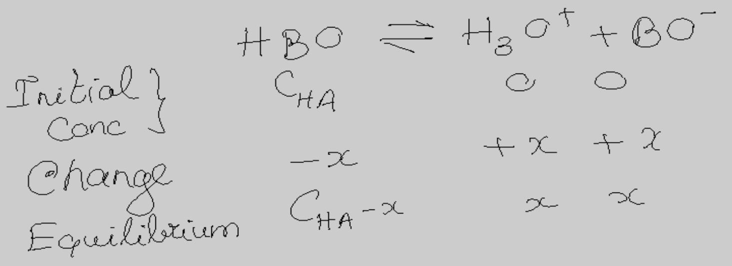
(B) Acidity of its aqueous solution increases upon addition of ethylene glycol.

(C) It has a three dimensional structure due to hydrogen bonding.

(D) It is a weak electrolyte in water.

Solution: (A), (B), (C), (D)

The reaction goes as follows: $B(OH)_3(aq) + 2H_2O \rightarrow B(OH)_4^- + H\ O$



	HBO $\rightleftharpoons$	H_3O^+ +	BO^-
Initial Conc	C_{HA}	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$C_{HA}-x$	x	x

Thus, we have:

$$K_a = \frac{[H_3O^+][BO^-]}{[HBO]} = \frac{x^2}{C_{HA} - x}$$

This results into:

$$x^2 + K_a x - K_a C_{HA} = 0$$

Here:

$$x = [H_3O^+] = [BO^-] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_{HA}}}{2}$$

And thus,

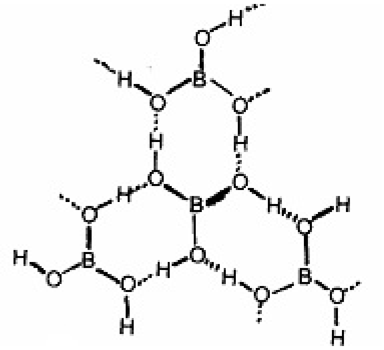
$$pH = -\log x = -\log\left(\frac{-K_a + \sqrt{K_a^2 + 4K_a C_{HA}}}{2}\right)$$

And the conditions of ionization would be given by:

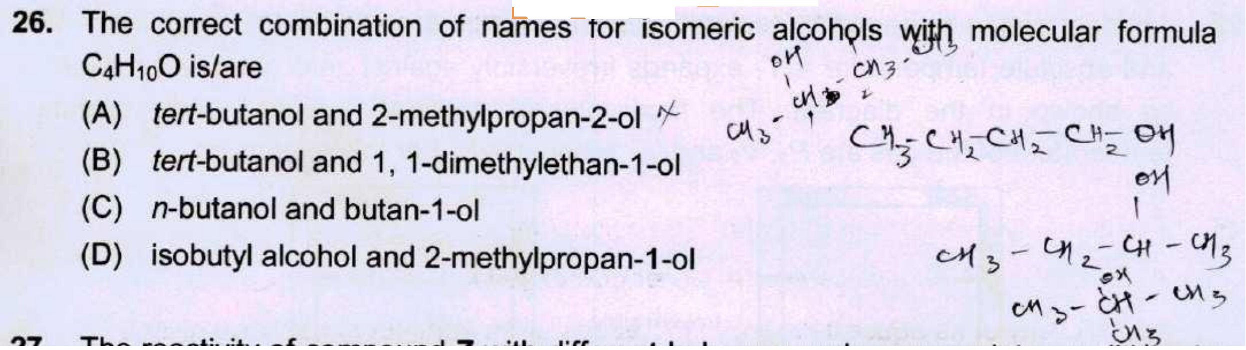
$$\frac{[A^-]}{C_{HA}} = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

This results into a small value of the degree of ionization and hence it has a weak reactivity in water. Also, its acidity would increase with an addition of ethylene glycol.

The structure of orthoboric acid is:



This forms this structure because of the presence of hydrogen bond.



26. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are

(A) *tert*-butanol and 2-methylpropan-2-ol ×

(B) *tert*-butanol and 1, 1-dimethylethan-1-ol

(C) *n*-butanol and butan-1-ol

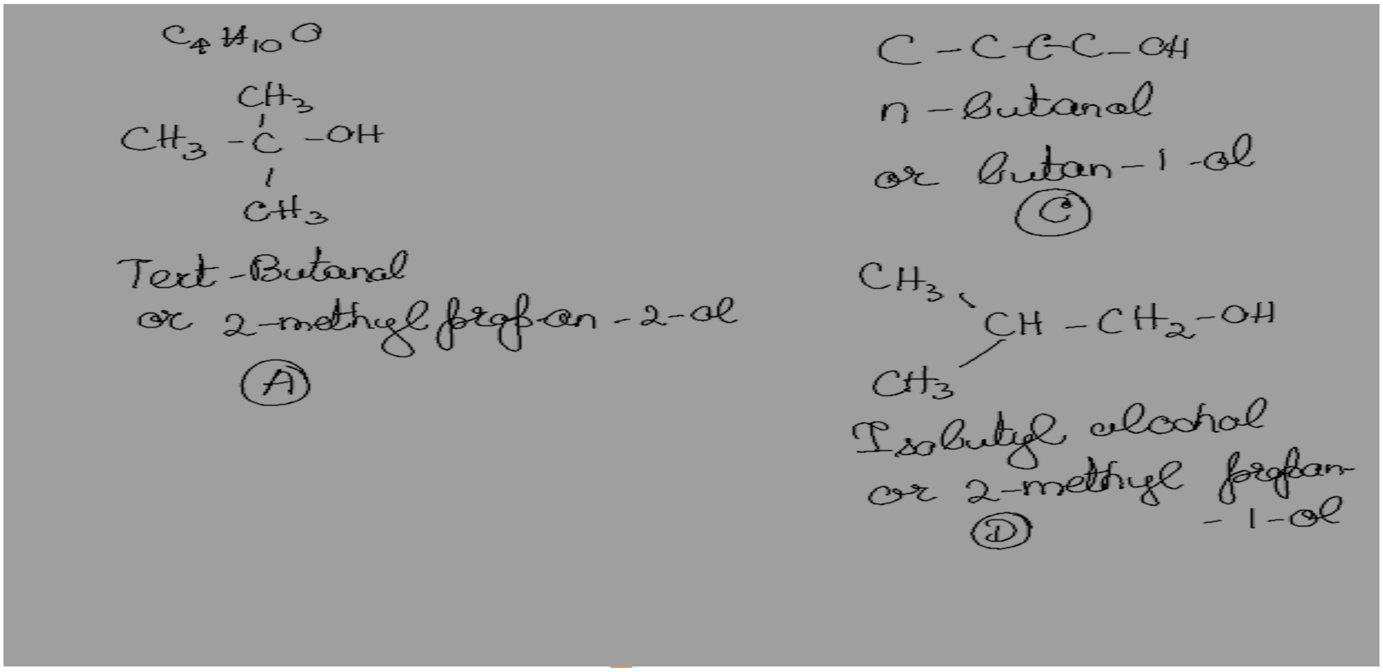
(D) isobutyl alcohol and 2-methylpropan-1-ol

$CH_3-CH_2-CH_2-CH_2-OH$

$CH_3-CH_2-\overset{OH}{CH}-CH_3$

$CH_3-\underset{CH_3}{\overset{OH}{CH}}-CH_3$

Solution:



$C_4H_{10}O$

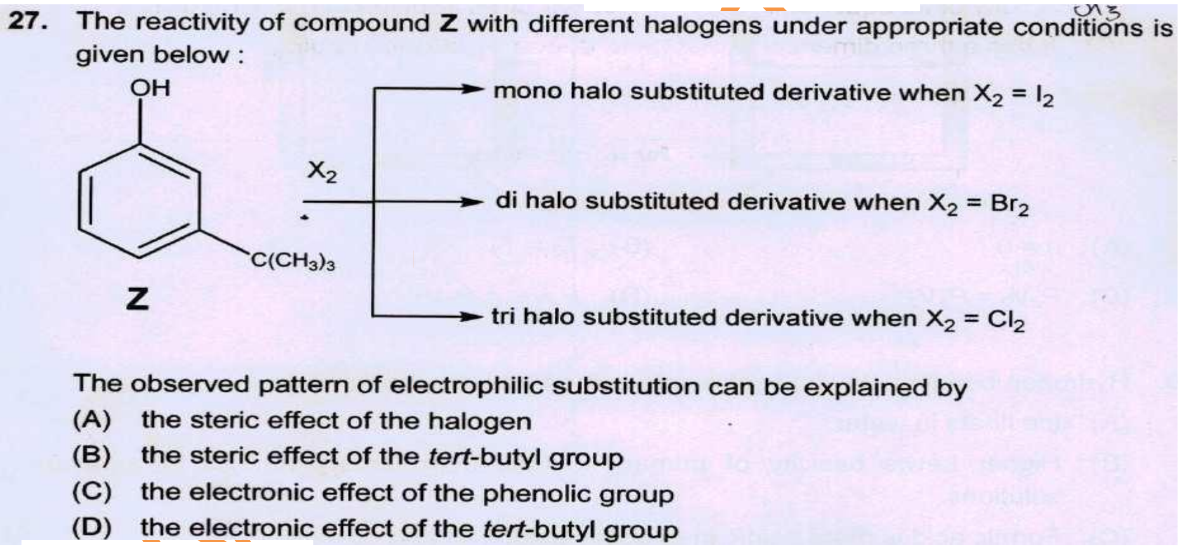
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

Tert-Butanol
or 2-methyl propan-2-ol
Ⓐ

C-C-C-C-OH
n-Butanol
or Butan-1-ol
Ⓒ

$(CH_3)_2CH-CH_2-OH$

Isobutyl alcohol
or 2-methyl propan-1-ol
Ⓓ



27. The reactivity of compound **Z** with different halogens under appropriate conditions is given below :

Z

mono halo substituted derivative when $X_2 = I_2$

di halo substituted derivative when $X_2 = Br_2$

tri halo substituted derivative when $X_2 = Cl_2$

The observed pattern of electrophilic substitution can be explained by

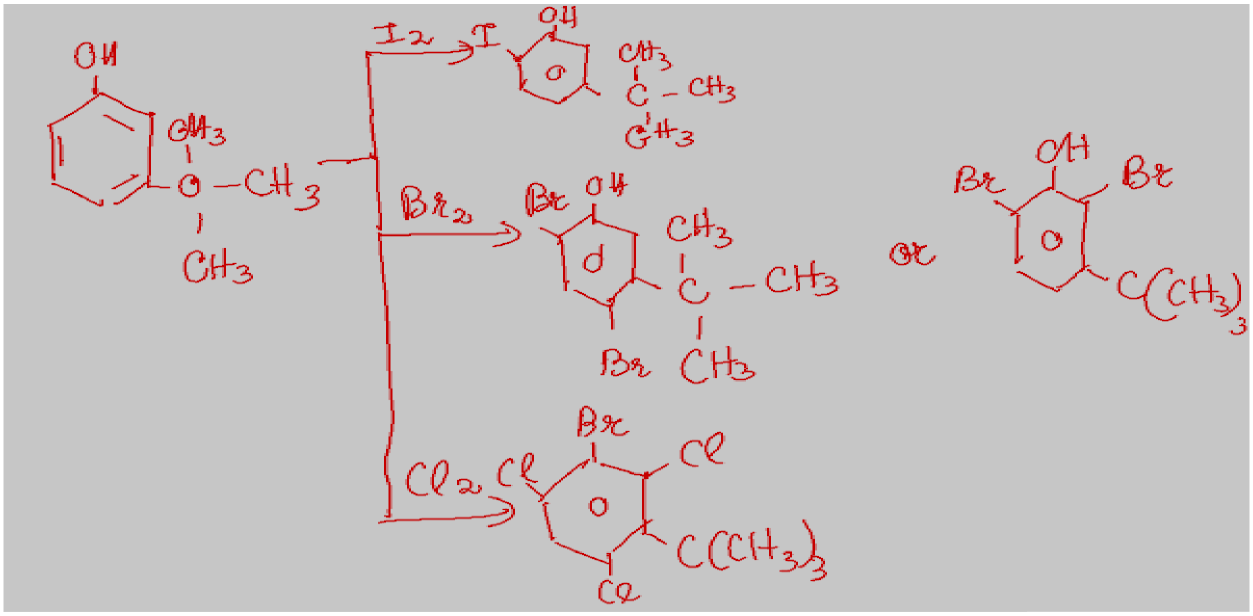
(A) the steric effect of the halogen

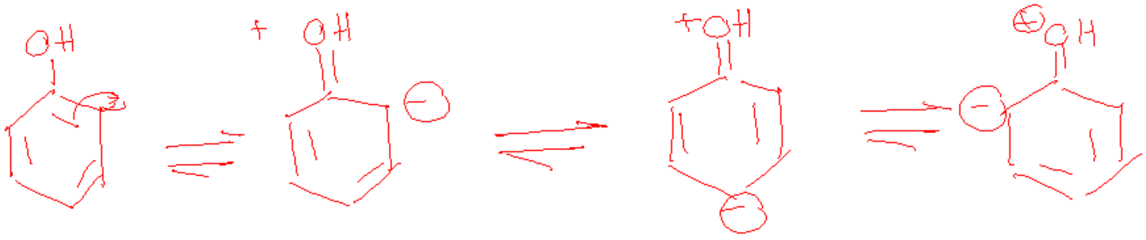
(B) the steric effect of the *tert*-butyl group

(C) the electronic effect of the phenolic group

(D) the electronic effect of the *tert*-butyl group

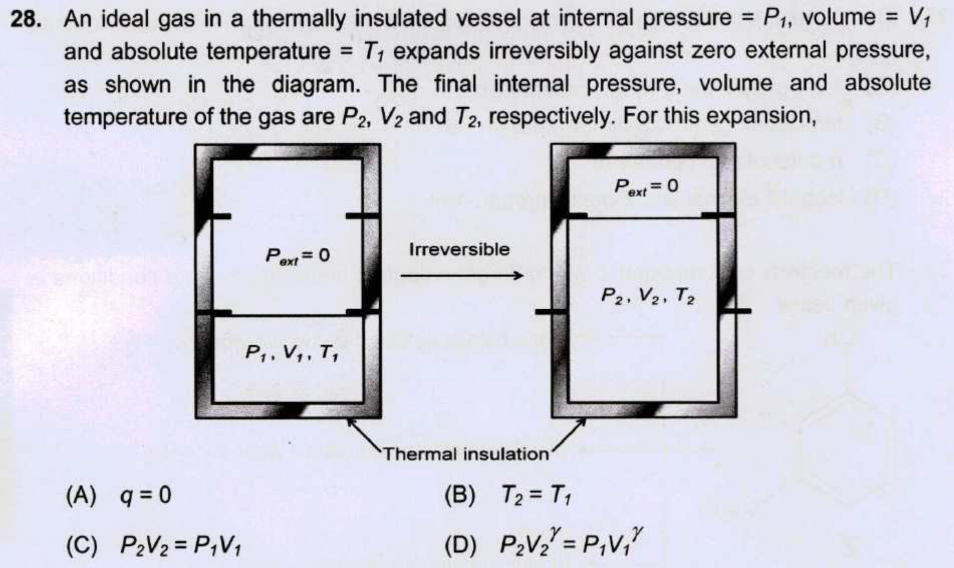
Solution:





We know that OH group is electron donating. SO it directs the electrophile to the ortho/para position. But the methyl group is bulky, so it presents electrophile substitution near to it due to steric hindrance.

Since I_2 is bigger only the mono halogenated product is formed. But Br_2 is relatively smaller than I_2. Thus, di halogenated product will be formed. But electron donating effect of Tri methyl group doesn't play any role.



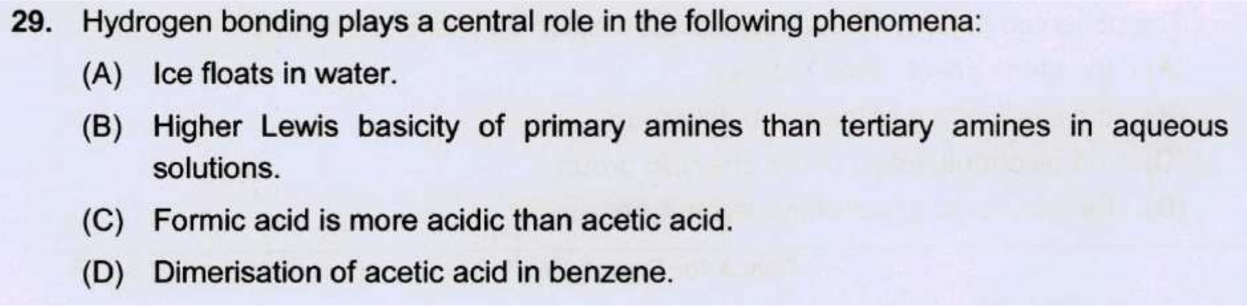
28. An ideal gas in a thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion,

(A) $q = 0$ (B) $T_2 = T_1$

(C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

Solution: (A), (D)

Since the system is insulated from surroundings, so there is not going to be any heat exchange taking place thereby resulting into an adiabatic situation. So the answers are Q=0 and $P_2V_2^{\gamma} = P_1V_1^{\gamma}$.



29. Hydrogen bonding plays a central role in the following phenomena:

(A) Ice floats in water.

(B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.

(C) Formic acid is more acidic than acetic acid.

(D) Dimerisation of acetic acid in benzene.

Solution: (A) (D)

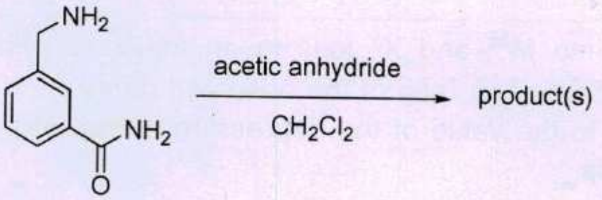
(A) The structure of ice is formed by the hydrogen bond formation between the water molecules which results into a cage like structure. The density of ice therefore is less than that of water so ice floats on water.

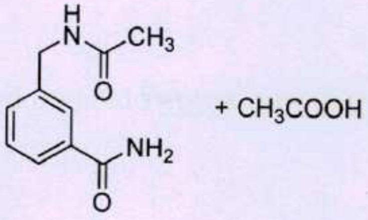
(B) All of the amines are more basic than ammonia, but primary and secondary amines are the most basic. The effect of the third alkyl group is another instance of steric inhibition of solvation. The presence of three alkyl groups sharply diminishes the ability of the solvent to stabilize the corresponding ammonium ion, thus causing a reversal in the tendency of the alkyl groups to decrease acidity and increase basicity.

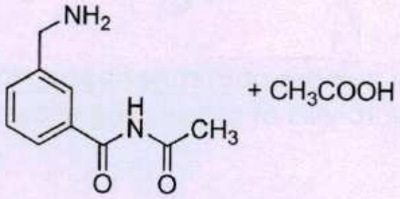
(C) Acetic acid is a CH_3 substituted formic acid. $CH_3 -$ is electron-donating relative to hydrogen, so it donates electrons to the carboxyl group, making it more negative.

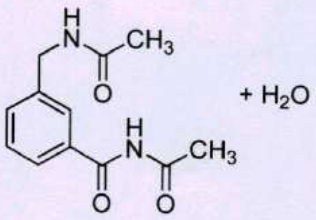
(D) A dimer forms by dimerization of acetic acid in benzene, in order to decrease the dipole moment of the acid to zero, making it much more soluble in benzene. The two molecules join by two hydrogen bonds, carboxylate group to carboxylate group.

30. In the reaction shown below, the major product(s) formed is/are



(A)


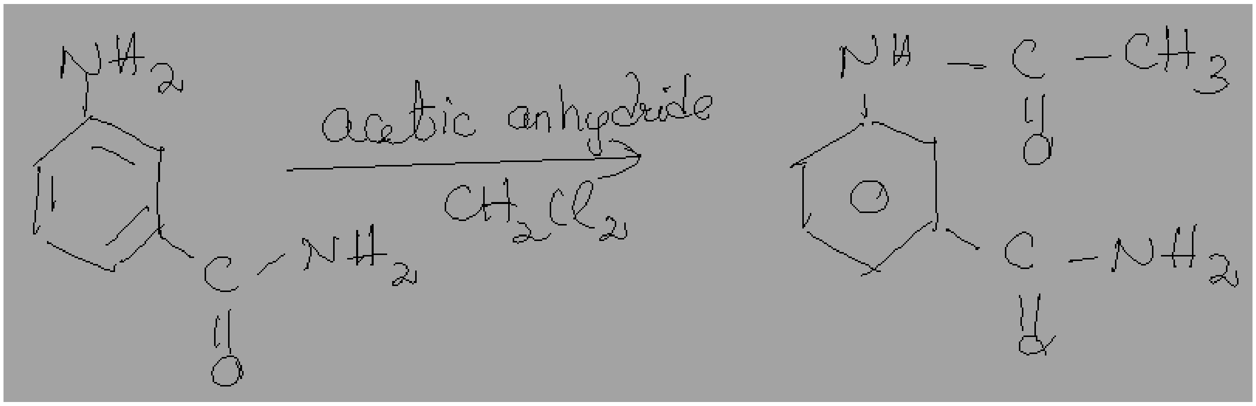
(B)


(C)


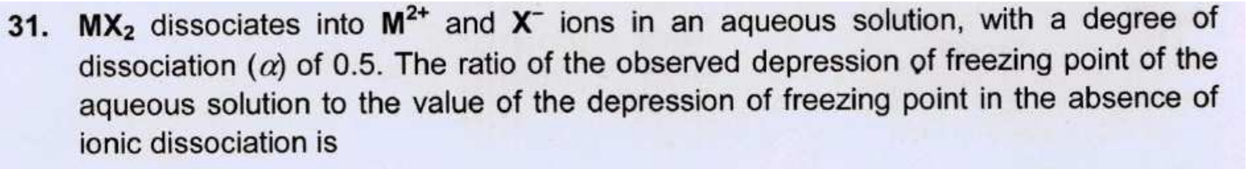
(D)


Solution: (A), (C)

The reaction goes as follows:



This is the major product.



31. **MX_2** dissociates into **M^{2+}** and **X^-** ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is

Solution: 2

The reaction goes as:

$$\begin{array}{ccc} X_2 & M^{2+} & 2X^- \\ & 0 & 0 \end{array}$$

Here the initial number of moles of [illegible]$_2$ be 1 and those of the products be 0. SO, before dissociation, the number of moles are equal to 1.

After the reaction is over, we would have

$$\begin{array}{ccccc} MX_2 & & M^{2+} & & 2X^- \\ 1-\alpha & \rightarrow & \alpha & + & 2\alpha \\ 0.5 & & 0.5 & & 1 \end{array}$$

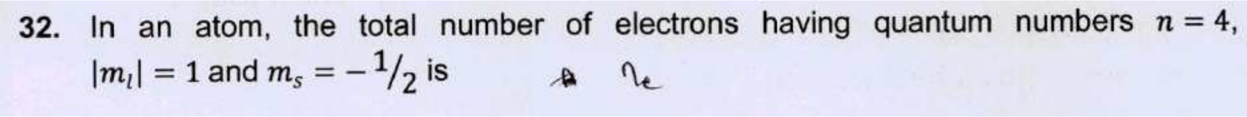
The number of moles after the dissociation would be equal to 0.5+0.5+1=2

Now the depression in the freezing point would be given by

$$\Delta T_f = iK_f m$$

So, the required ratio would be equal to:

$$\frac{(\Delta T_f)_{after\ dissociation}}{(\Delta T_f)_{in\ absence\ of\ dissociation}} = \frac{Number\ of\ moles\ after\ dissociation}{Number\ of\ moles\ before\ dissociation} = \frac{2}{1}$$



32. In an atom, the total number of electrons having quantum numbers $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is

Solution: (6)

We would have the following cases:

$n = 4$

$\Rightarrow$ contains 4 subshells

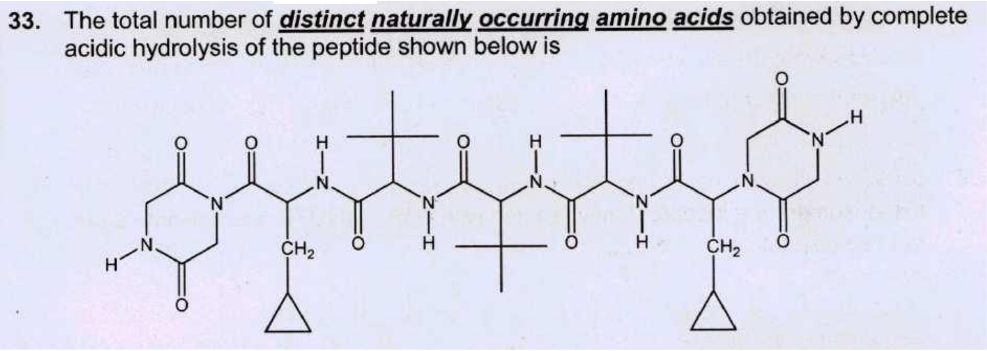
$l = 0;\quad m_l = 0$

$l = 1;\quad m_l = \underset{\Uparrow}{-1}, 0, \underset{\Uparrow}{1}$

$l = 2;\quad m_l = -2, \underset{\Uparrow}{-1}, 0, \underset{\Uparrow}{1}, 2$

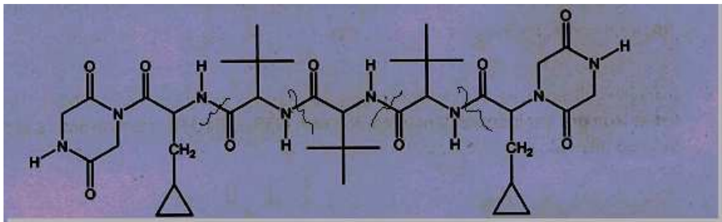
$l = 3;\quad m_l = -3, -2, \underset{\Uparrow}{-1}, 0, \underset{\Uparrow}{1}, 2, 3$

Thus the number of electrons = 2+2+2=6.



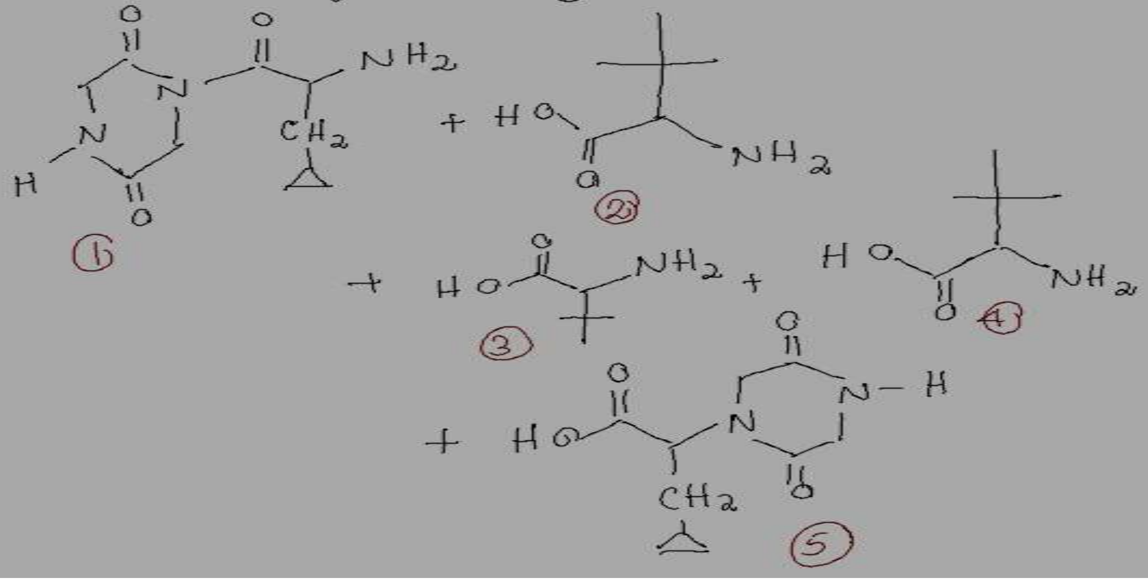
33. The total number of ***distinct naturally occurring amino acids*** obtained by complete acidic hydrolysis of the peptide shown below is

Solution: (1)



In acid hydrolysis of peptide, amine and carboxylic acid are formed.

Thus the products formed are given by



Though as can be seen, (2), (3) and (4) are similar products and hence the total number of distinct products are 3. In the products (1) and (5) glycine would be formed which is naturally occurring.

34. If the value of Avogadro number is 6.023×10^{23} mol^{-1} and the value of Boltzmann constant is $1.380 \times 10^{-23} J K^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is

Solution: (4)

We know that the Avogadro's number is given by: $N_A = 6.023 \times 10^{23}\ mol^{-1}$.

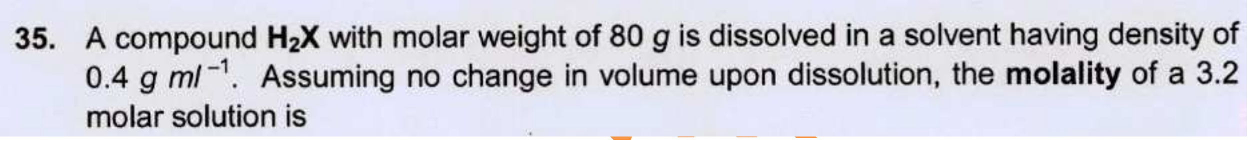
The Boltzmann Constant is given by: $k = 1.38 \times 10^{-23}$

Number of significant digits in N_A are 4 and so would be in k.

The number of significant digits in an answer should equal the least number of significant digits in ant of the numbers being multiplied. Hence the gas constant would be given by:

$$R = kN_A = 6.023 \times 10^{23} \times 1.38 \times 10^{-23} = 8.311740.$$

So, by applying the above rule, we get: $R = 8.311$ having 4 significant digits.



35. A compound **H_2X** with molar weight of 80 *g* is dissolved in a solvent having density of 0.4 *g ml*$^{-1}$. Assuming no change in volume upon dissolution, the **molality** of a 3.2 molar solution is

Solution: (8)

We know that the molarity of the is given by:

$$Molarit = \frac{Number\ of\ moles\ of\ the\ solute}{of\ solution\ in\ litre}$$

$$lity = \frac{Number\ of\ moles\ of\ the\ solute}{Mass\ of\ solvent\ in\ Kg}$$

Let us assume the volume of the solvent be equal to 1 litre.

Since there is no change in the volume on dissolution, we can say that the volume of solvent = volume of solution = 1 litre.

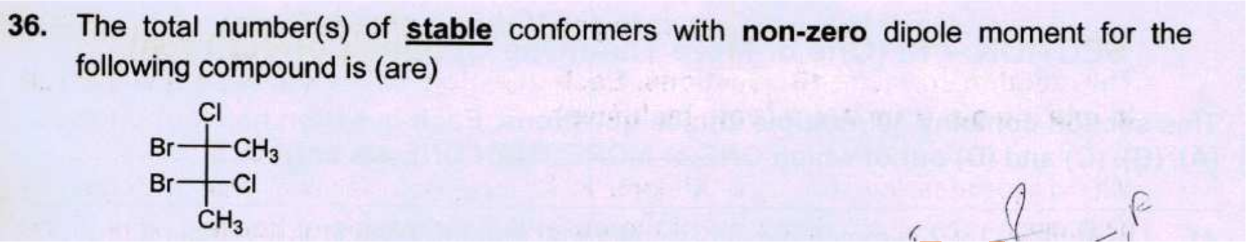
So, we get:

$$\frac{Number\ of\ moles\ of\ the\ solute}{1} = 3.2$$

So, the Molality would be given by:

$$Molality = \frac{Number\ of\ moles\ of\ the\ solute}{Mass\ of\ solvent\ in\ Kg} = \frac{Number\ of\ moles\ of\ the\ solute}{Density\ of\ solvent \times Volume\ of\ solvent}$$

$$= \frac{3.2}{0.4} = 8$$



36. The total number(s) of **stable** conformers with **non-zero** dipole moment for the following compound is (are)

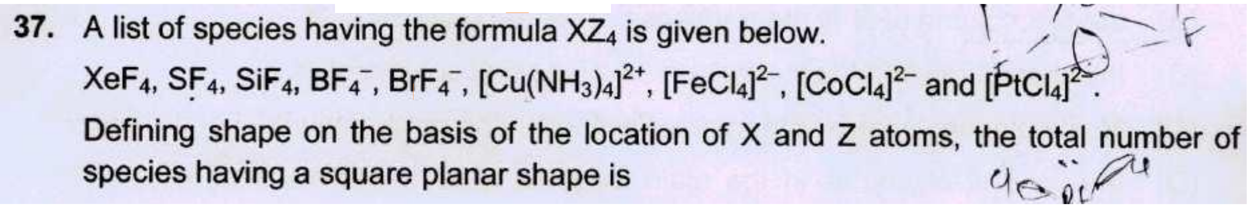
Solution: (4)

When we have the chiral groups in the same plane, in that case, the net dipole moment would be zero But when they are not in the same plane, in that case, we have the following cases:

(a) When we rotate Br and Cl, in that there would be two structures possible.

(b) Similarly if we rotate methane with Br and Cl, then 2 more structures would be possible.

Thus, in all there are 4 stable conformers possible which have non – zero dipole moment.



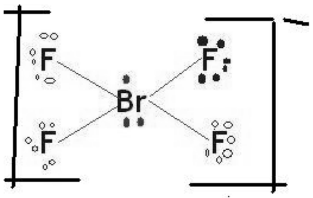
37. A list of species having the formula XZ_4 is given below.

XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.

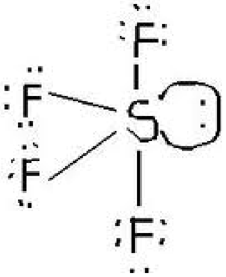
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

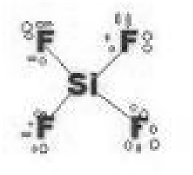
Solution: (4)

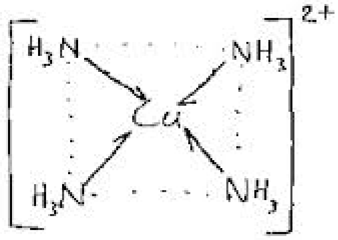
The structures are as follows:



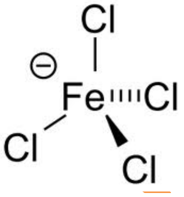
This has a square planar shape.

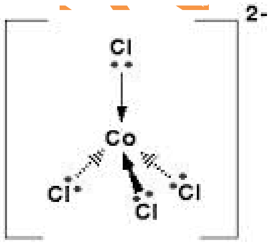


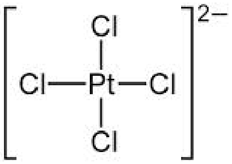




This has a square planar shape.







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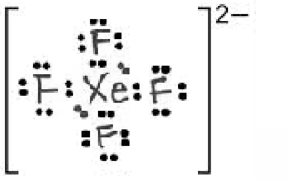
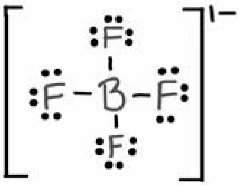
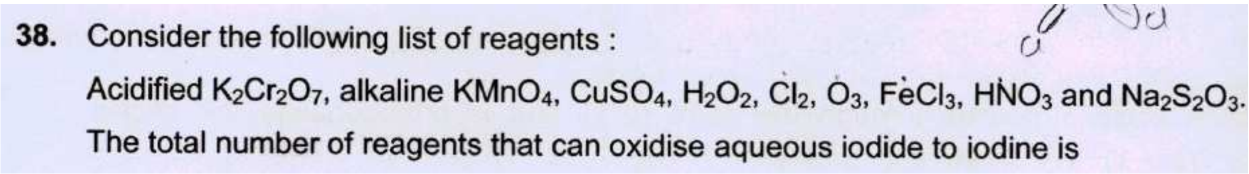


This has a square planar shape.





38. Consider the following list of reagents :

Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$.

The total number of reagents that can oxidise aqueous iodide to iodine is

Solution: (6)

The reactions are:

$$6I^- + Cr_2O_7^- + 14H^+ \rightarrow 3I_2 + 7H_2O + 2Cr^{3+}$$

$$Mn^{3+} + I^- \rightarrow 2Mn^{2+} + I_2$$

$$Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$$

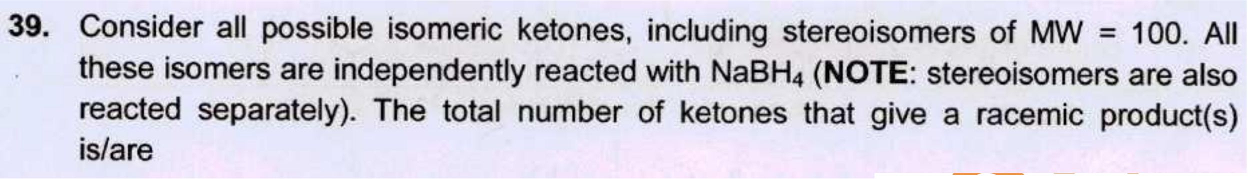
$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

$$2H^+ + O_3 + 2I^- \rightarrow I_2 + O_2 + H_2O$$

$$FeCl_3 + 3I^- \rightarrow FeI_3 + 3Cl^-$$

$$HNO_3 + AgI \rightarrow HI + AgNO_3$$

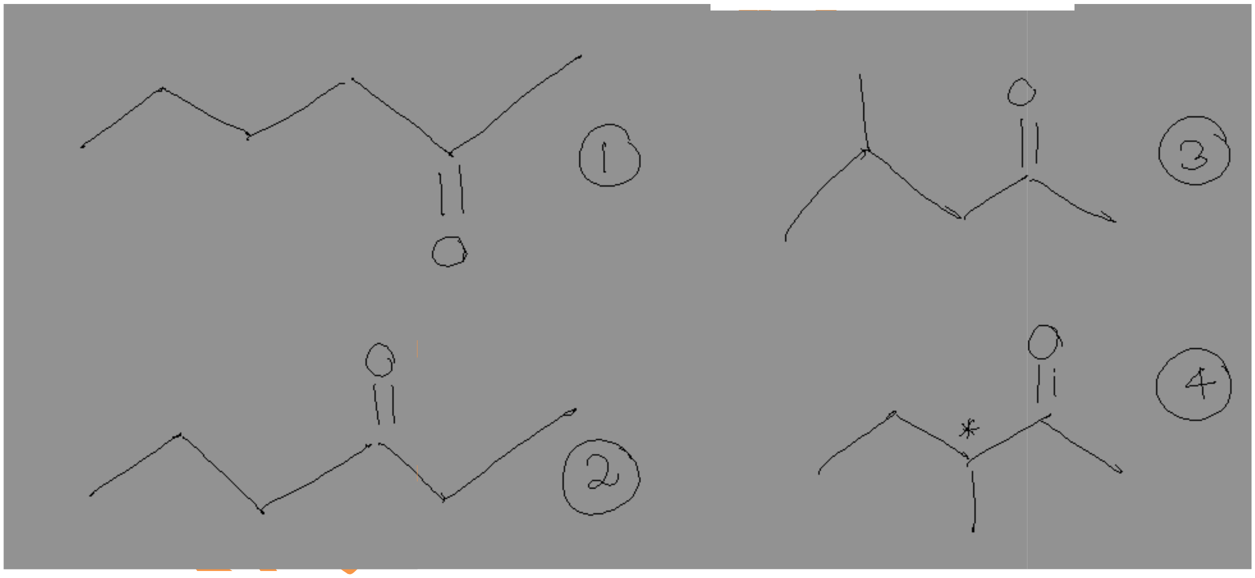
$$S_2O_3^{2-} + 2I_3^- \rightarrow S_4O_6^{2-} + 3I^-$$



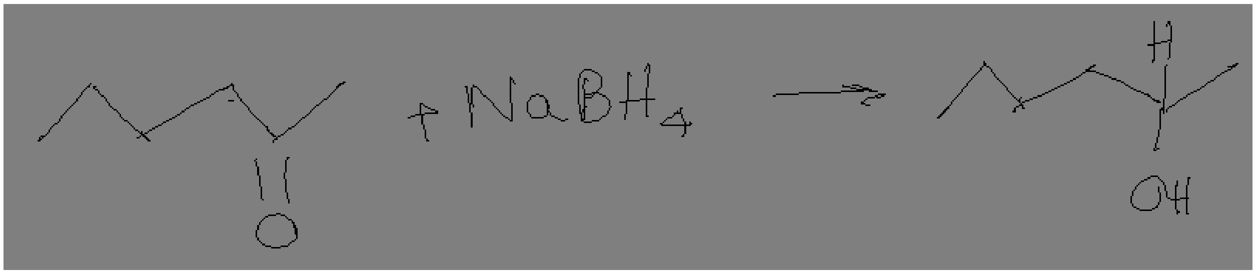
39. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (**NOTE**: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are

Solution: (5)

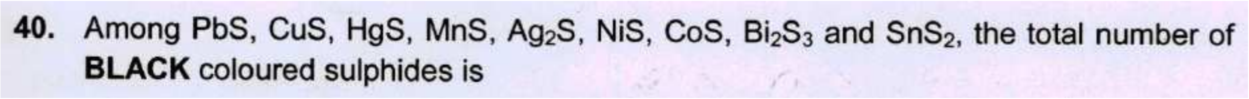
Given that the molar mass = 100. So, the possible compounds are



The structure (3) will give the following product with sodium boro hydride:



The (4th) compounds will have two stereo isomers, and hence there would be in all 5 isomers which would give 5 racemic mixtures.



40. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of **BLACK** coloured sulphides is

Solution: (5)

The colors are as follows:

Sulphide	**Color of Sulphide**
PbS	***Black***
CuS	***Black***
HgS	Brick Red
MnS	Green
Ag_2S	***Black***
NiS	***Black***
CoS	***Black***
Bi_2S_3	Brown
SnS_2	Brown