JEE MAIN-2014

CHEMISTRY

21. Sol. (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 halfcell 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. Sol.

The required reactions are as follows:

(a) Reaction of Na with excess $\mathrm{NH_3}$:

$$\mathrm{Na(s)} + (x+\mathrm{y})\mathrm{NH_3}(e) \rightarrow \mathrm{Na}(\mathrm{NH_3})_x^y + (\mathrm{QG}) + \mathrm{e} - (\mathrm{NH_3})_\mathrm{y}(\mathrm{QG})$$

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

(b) Reaction of K with excess of $\mathrm{O_2}$:

$$\mathrm{K(S)} + \mathrm{O_2(Q)} \rightarrow \mathrm{KO_2}$$

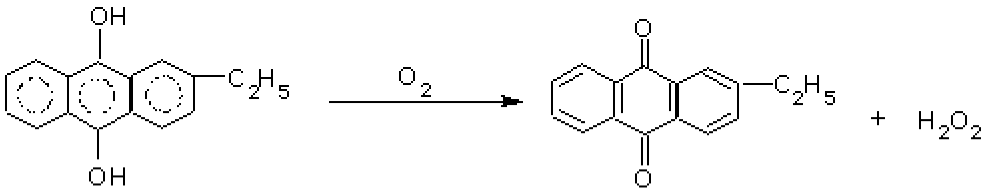
Potassium superoxide is paramagnetic in character.

(c) Reaction of Cu with HNO_3:

$$3Cq(s)+8HnC_3(qg)\rightarrow 3Cq(NC_3)_2(qg)+2No(g)+4H_2O(R)$$

NO is paramagnetic.

(d) Reaction of O_2 with 2 – ethylanthorquinol:



Hydrogen peroxide is diamagnetic.

23. Sol. (A), (B), (D)

The reaction would be given by:

$$2I^- + ClO_3^- + 6H_2SO_4 \rightarrow Cl^- + 6H_2SO_4^- + I_2 + 3H_2O$$

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. Sol. (B), (C), (D)

The reactions go as follows:

(a) $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

(b) $CuSO_4 + Cu_2S \rightarrow 3Cu + 2SO_2$

(c) $2CuO + Cu_2S \rightarrow 4Cu + SO_2$

25. Sol. (A), (B), (C), (D)

The reaction goes as follows: $B(OH)_3(aq) + 2H_2O \rightarrow B(OH)_4^- + H_3O^+$

	HBO	$\rightleftharpoons$	H_3O^+	$+BO^-$
Initial Cone}	C_{HA}		O	O
Change	$-x$		$+x$	$+x$
Equilitaion	$C_{HA} - x$		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,

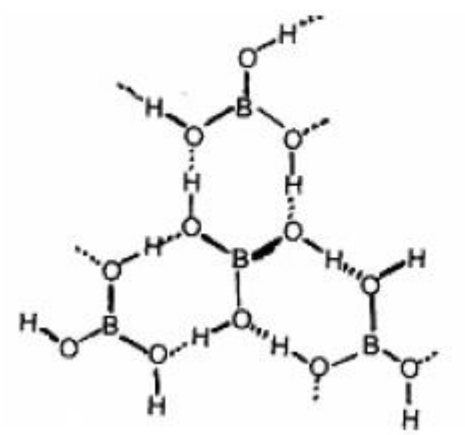
$$pH = -\log x = -\log\left(\frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}\right)$$

And the conditions of ionization would be given by:

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

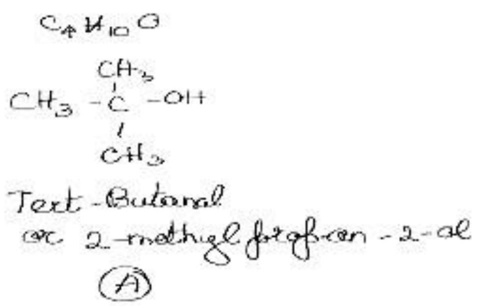
This results into a small value of the degree of ionization and hence it has a weak reactivity in water. Also, its acidity would increase with an addition of ethylene glycol.

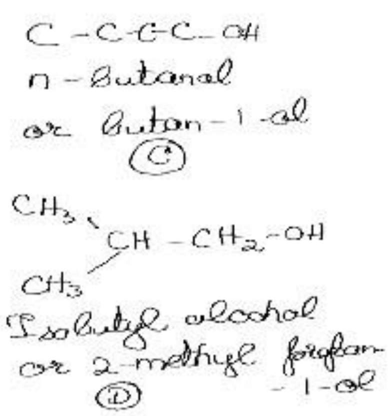
The structure of orthoboric acid is:



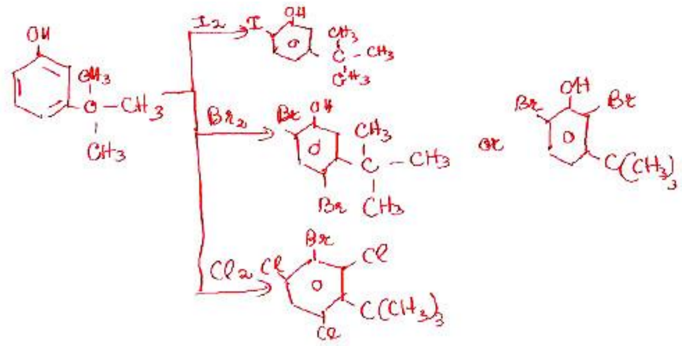
This forms this structure because of the presence of hydrogen bond.

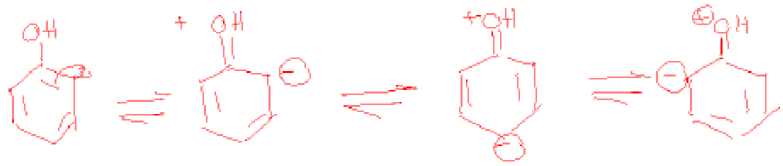
26. Sol.





27. **Sol.**





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. **Sol. (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. **Sol. (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.

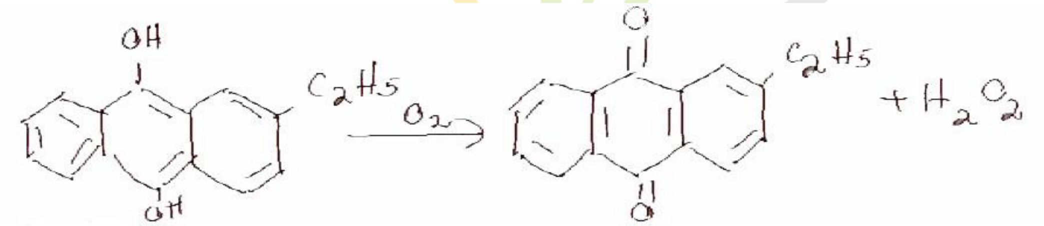
(B) All of the amines are more basic than ammonia, but primary and secondary amines are the most basic. The effect of the third alkyl group is another instance of steric inhibition of solvation. The presence of three alkyl groups sharply diminishes the ability of the solvent to stabilize the corresponding 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. Sol. (A), (C)

The reaction goes as follows:



This is the major product.

31. Sol. 2

The reaction goes as:

$$\underset{1}{MX_2} \rightarrow \underset{0}{M^{2+}} + \underset{0}{2X^-}$$

Here the initial number of moles of MX_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

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

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. Sol. (6)

We would have the following cases:

$n = 4$

$\Rightarrow$ contains 4 sub shells

$l = 0;\ m_l = 0$

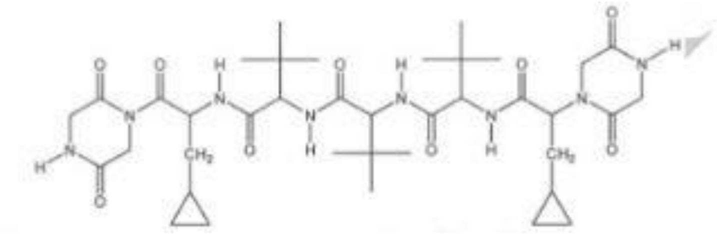
$l = 1;\ m_l = -1, 0, 1$
$\Uparrow \quad \Uparrow$

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

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

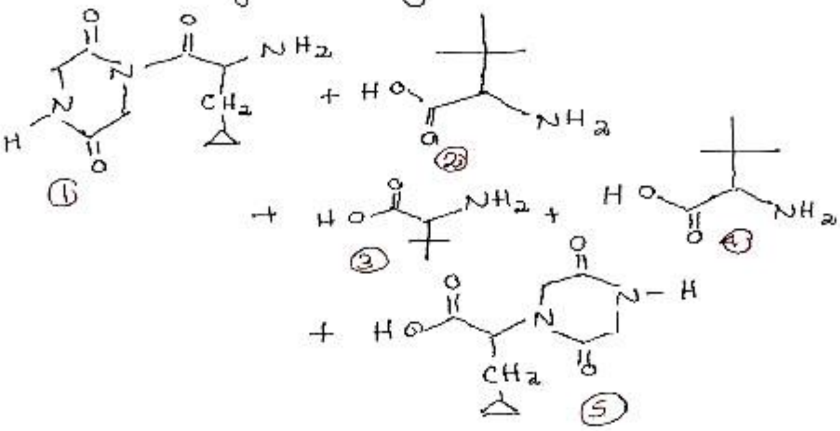
Thus the number of electrons $=2+2+2=6$.

33. Sol. (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. Sol. (4)

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

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:

$$R = kN_A = 6.023\times10^{23}\times1.38\times10^{-23} = 8.311740$$

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

35. Sol. (8)

We know that the molarity of the solution is given by:

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

$$Molarity = \frac{Number\ of\ moles\ of\ the\ solute}{Mass\ of\ solution\ in\ Kg}$$

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:

$$Molarity = \frac{Number\ of\ moles\ of\ the\ solute}{Mass\ of\ solution\ in\ Kg} = \frac{Number\ of\ moles\ of\ the\ solute}{Density\ of\ solvent\times Colume\ of\ solvent}$$

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

36. Sol. (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:

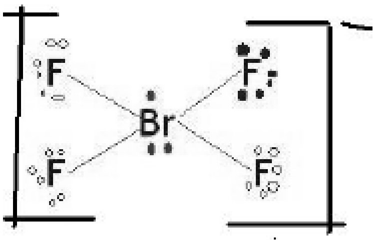
(a) When we rotate Br and Cl , in that there would be two structures possible.

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

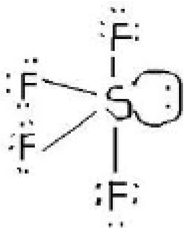
Thus, in all there are 4 stable conformers possible which have non - zero dipole moment.

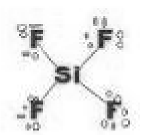
37. Sol. (4)

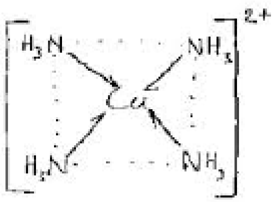
The structures are as follows:



This has a square planar shape.







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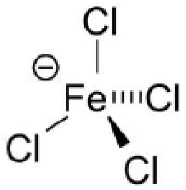
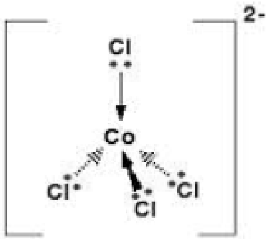
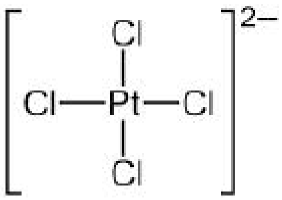
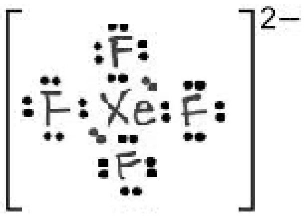






This has a square planar shape.



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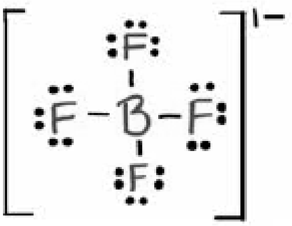


38. Sol. (6)

The reactions are:

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

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

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

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

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

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

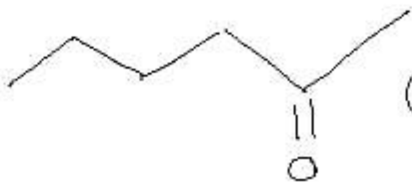
$FeCl_3 + 3I^- \rightarrow FeI_3 + 3Cl^-$

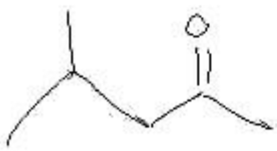
$HNO_3 + Agl \rightarrow HI + AgNO_3$

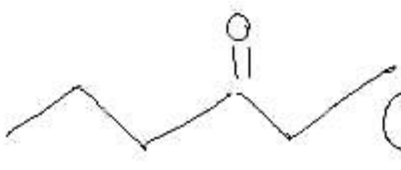
$S_2O_3^{2-} + 2l_3^- \rightarrow S_4O_6^{2-} + 3I^-$

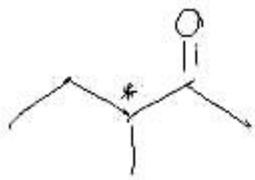
39. Sol. (5)

Given that the molar $\text{mass} = 100$. So, the possible compounds are

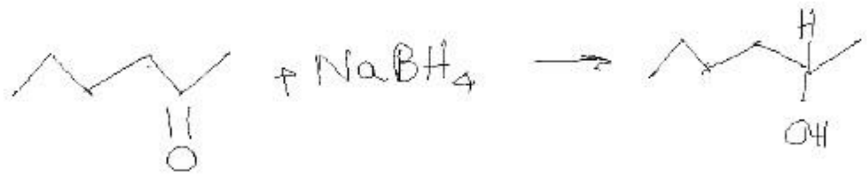

(1)


(3)


(2)


(4)

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



The $\left(4^{th}\right)$ compounds will have two stereo isomers, and hence there would be in all 5 isomers which would give 5 racemic mixtures.

40. Sol. (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