CHEMISTRY

SECTION 1 (Maximum Marks : 28)

- This section contains **SEVEN** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONE OR MORE THAN ONE** of these four options is (are) correct
- For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened

Partial Marks : +1 For darkening a bubble corresponding **to each correct option,** provided NO incorrect option is darkened

Zero Marks : 0 If none of the bubbles is darkened

Negative Marks : –2 In all other cases

- For example, if (A), (C) and (D) are all the correct options for a question, darkening all these three will get +4 marks; darkening only (A) and (D) will get +2 marks; and darkening (A) and (B) will get –2 marks, as a wrong option is also darkened.

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19. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to voilet down the group. This is due to :

(A) the physical state of X_2 at room temperature changes from gas to solid down the group

(B) decrease in HOMO-LUMO gap down the group

(C) decrease in $\pi^* - \sigma^*$ gap down the group

(D) decrease in ionization energy down the group

Ans. (B, C)

Sol. Colour of halogen is due to charge transfer from HOMO (π^*) -LUMO (σ^*).

20. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 \cdot 6H_2O$ **(X)** and NH_4Cl gives an octahedral complex **Y** in the presence of air. In aqueous solution, complex **Y** behaves as 1 : 3 electrolyte. The reaction of **X** with excess HCl at room temperature results in the formation of a blue coloured complex **Z**. The calculated spin only magnetic moment of **X** and **Z** is 3.87 B.M., whereas it is zero for complex **Y**.

Among the following options, which statement(s) is(are) correct ?

(A) The hybridization of the central metal ion in **Y** is d^2sp^3

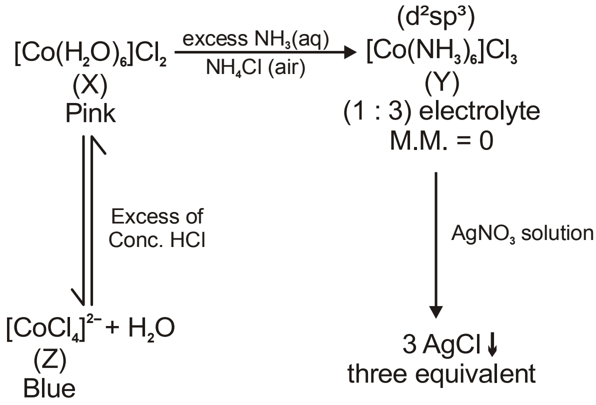
(B) When **X** and **Z** are in equilibrium at 0ºC, the colour of the solution is pink.

(C) **Z** is a tetrahedral complex

(D) Addition of silver nitrate to **Y** gives only two equivalents of silver chloride

Ans. (A, B, C)

Sol.



M.M = 3.87 B.M
Pink colour dominates because $[Co(H_2O)_6]Cl_2$ is more stable than $[CoCl_4]^{2-}$

21. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are) :

(A) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.

(B) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(C) The work done on the gas is maximum when it it compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1

(D) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

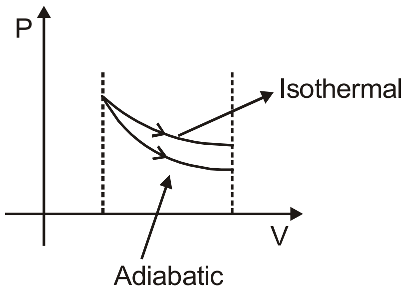
Ans. (A, B, C)

Sol. (A) In free expansion

$W = 0$

$q = \Delta U$

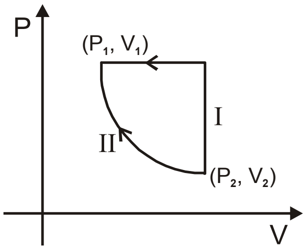
If $\Delta U = 0$ then q = 0 or vice-vesa.



(B) $|W_{adia}| < |W_{iso}|$:

(C) $W = -P_1(V_1 - V_2)$:

Area under the curve is maximum.



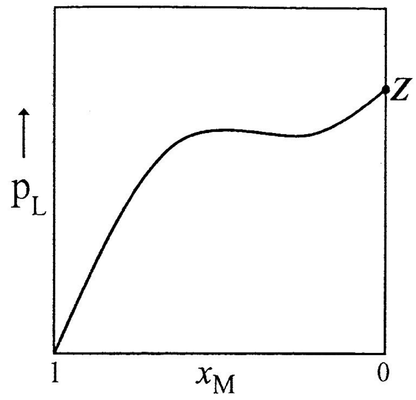
(D) $\Delta U = nC_V\Delta T = 0$ if $T_1 = T_2$

$\Delta U = nC_V\Delta T$

If adiabatic, expansion is done, temperature decreases and hence $\Delta T < 0 \Rightarrow \Delta U = 0$

So, wrong

22. For a solution formed by mixing liquids **L** and **M**, the vapour pressure of **L** plotted against the mole fraction of **M** in solution is shown in the following figure. Here x_L and x_M represent mole fractions of **L** and **M**, respectively, in the solution. The correct statement(s) applicable to the system is(are) :



(A) Attractive intermolecular interactions betweeen **L-L** in pure liquid **L** and **M-M** in pure liquid **M** are stronger than those between **L-M** when mixed in solution.

(B) The point **Z** represents vapour pressure of pure liquid **M** and Raoult's law is obeyed when $x_L \to 0$

(C) The point **Z** represents vapour pressure of pure liquid **M** and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

(D) The point **Z** represents vapour pressure of pure liquid **L** and Raoult's law is obeyed when $x_L \to 1$

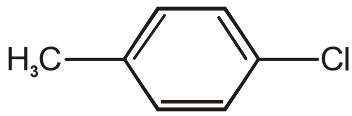
Ans. **(A, D)**

Sol. The given graph shows the (+ve) deviation from Raoult's law. So, **L-M** interaction < **L-L** and **M-M** interaction. thats why (A) is Correct.

Point **Z** represent vapour pressure of pure liquid **'L'**

When $x_M = 0$, $x_L = 1$ (pure L) and in this condition there is no deviation from ideal behaviour and thats why (D) is correct.

23. The IUPAC name(s) of the following compound is(are) :



(A) 1-chloro-4-methylbenzene

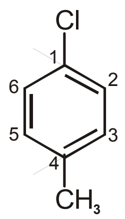
(B) 4-chlorotoluene

(C) 1-methyl-4-chlorobenzene

(D) 4-methylchlorobenzene

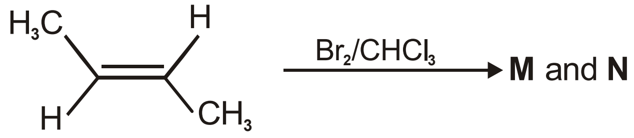
Ans. **(A, B)**

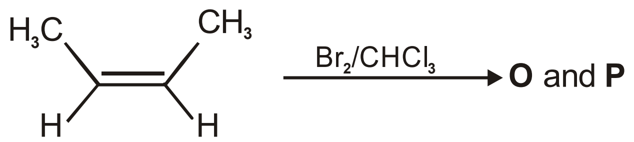
Sol.



1-chloro-4-methylbenzene and 4-chlorotoluene both are correct IUPAC name of the above compound.

24. The correct statement(s) for the following addition reactions is(are) :

(i) 

(ii) 

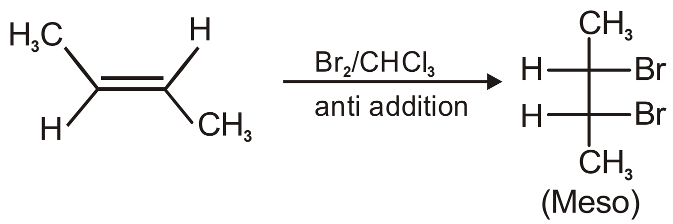
(A) **O** and **P** are identical molecules

(B) Bromination proceeds through *trans*-addition in both the reactions

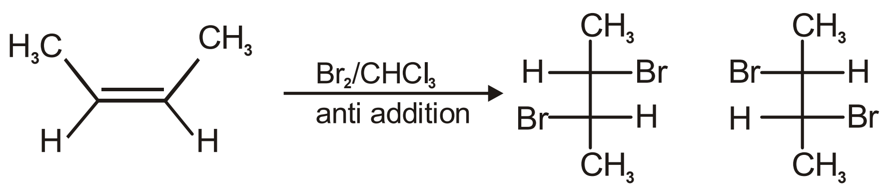
(C) (**M** and **O**) and (**N** and **P**) are two pairs of enantiomers

(D) (**M** and **O**) and (**N** and **P**) are two pairs of diastereomers

Ans. (B, D)

Sol. (i) 

M and **N** are identical

(ii) 

'O' **'P'**

both are enantiomers

M and O are diastereomers

N & P are diastereomers

25. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is (are) :

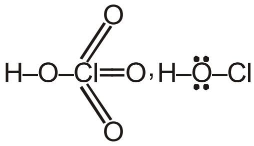
(A) The conjugate base of $HClO_4$ is weaker base than H_2O

(B) The central atom in both $HClO_4$ and HClO is sp^3 hybridized

(C) $HClO_4$ is formed in the reaction between Cl_2 and H_2O

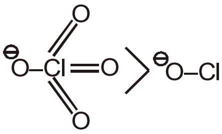
(D) $HClO_4$ is more acidic than HClO because of the resonance stabilization of its anion

Ans. (A, B, D)

Sol. *  (central atom is sp^3 hybridised)

* ClO_4^- is weaker base than H_2O

* $Cl_2 + H_2O \longrightarrow HCl + HOCl$

*  (stability due to resonance)

SECTION 2 (Maximum Marks : 15)

- This section contains **FIVE** questions
- The answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive
- For each question, darken the bubble corresponding to the correct integer in the ORS
- For each question, marks will be awarded in one of the following categories :

  Full Marks : +3 If only the bubble corresponding to the correct answer is darkened

  Zero Marks : 0 In all other cases

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26. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2. The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity $\left(\Lambda_m^0\right)$ of this weak monobasic acid in aqueous solution is $Z \times 10^2 \, S\,cm^{-1}\,mol^{-1}$. The value of Z is

Ans. **(6)**

Sol. $\kappa = (G)\left(\frac{\ell}{A}\right) = 5 \times 10^{-7} \times \frac{120}{1} = 60 \times 10^{-6} \, S\,cm^{-1}$

$$\Lambda_m = \frac{\kappa}{M} \times 1000 = \frac{60 \times 10^{-6}}{15 \times 10^{-4}} \times 1000 = 4 \times 10^1$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\infty} = \frac{4 \times 10^1}{Z \times 10^2} = \frac{4}{10Z}$$

Also, $[H^+] = C\alpha = 15 \times 10^{-4} \cdot \alpha$

$$10^{-4} = 15 \times 10^{-4} \cdot \alpha$$

$$\alpha = \frac{1}{15}$$

$$\frac{1}{15} = \frac{4}{10 \times Z}$$

$$Z = \frac{15 \times 4}{10} = 6$$

27. The sum of the number of lone pairs of electrons on each central atom in the following species is

$[TeBr_6]^{2-}, [BrF_2]^{+}, SNF_3, \text{and } [XeF_3]^{-}$

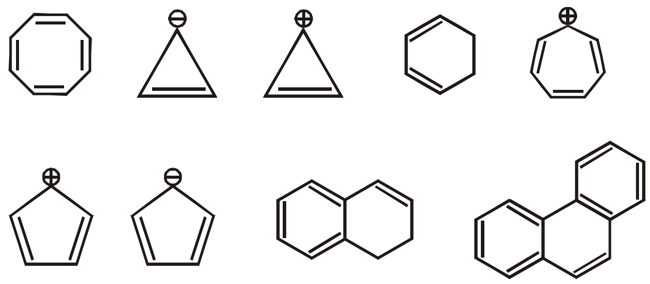
(Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

Ans. (6)

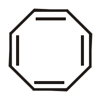
Sol.

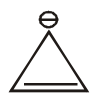
Molecule	L.P.
$[Te\ Br_6]^{2-}$	1
$[Br\ F_2]^{+}$	2
SN F_3. $\Rightarrow$ $F_3S\equiv N$	0
$[XeF_3]^{-}$	3
	Total = 6

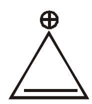
28. Among the following, the number of aromatic compound(s) is



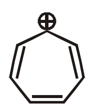
Ans. (5)

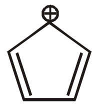
Sol.  This is nonplanar (tub shape), so nonaromatic

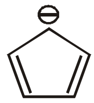
 $4\pi e^-$ delocalised, so anti-aromatic

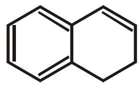
 2π electron delocalised so, aromatic

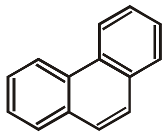
 Non planar & not fully conjugated so, non aromatic

 $6\pi\ e^-$ delocalised so, aromatic (Tropyllium ion)


$4\pi\ e^-$ delocalised so, anti-aromatic


$6\pi\ e^-$ delocalised so, aromatic


In left side ring $6\pi e^-$ delocalised so, aromatic


All three rings are aromatic($14\pi e^-$ delocalised).

Total five structures are aromatic.

29. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3}, then the number of atoms present in 256 g of the crystal is N × 10^{24}. The value of N is

Ans. **(2)**

Sol. In Fcc: a = 400 pm, Z = 4 × 10^{-8} cm

$d = 8\,g/CC$

no. of atoms in 256 g is N × 10^{24}, N =?

$$d = \frac{Z \times M}{N_A \times a^3}$$

$$8 = \frac{4 \times M}{6 \times 10^{23} \times (4 \times 10^{-8})^3}$$

$$M = \frac{8 \times 6 \times 10^{23} \times 4^3 \times 10^{-24}}{4} = 16 \times 8 \times 6 \times 10^{-1}\,g$$

no. of atoms = $\frac{m}{M} \times N_A$

$$= \frac{16}{16 \times 8 \times 6 \times 10^{-1}} \times 6 \times 10^{23} = 2 \times 10^{24}$$

N = 2

30. Among $H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^-$, and F_2, the number of diamagnetic species is

(Atomic numbers: H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9)

Ans. **(6)**

Sol. If number of unpaired electron = 0, then molecule is considered as DIAMAGNETIC. For $Z \le 14 \Rightarrow \sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x = 2p_y) < \sigma(2p_z) < \pi^*(2p_x = 2p_y) < \sigma^*(2p_z)$

H_2, Li_2, C_2, N_2, Be_2 and F_2 are diamagnetic.

SECTION 3 (Maximum Marks : 18)

- This section contains **SIX** questions of matching type
- This section contains **TWO** tables (each haivng 3 columns and 4 rows)
- Based on each table, there are **THREE** questions
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct
- For each question, darken the bubble corresponding to the correct option in the ORS
- For each question, marks will be awarded in one of the following categories :

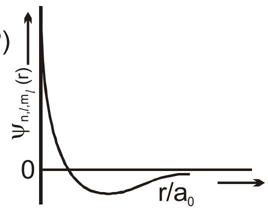
Full Marks : +3 If only the bubble corresponding to the correct option is darkened

Zero Marks : 0 If none of the bubbles is darkened

Negative Marks : –1 In all other cases

Answer Q.31, Q.32 and Q.33 by appropriately matching the information given in the three columns of the following table.

The wave function, ψ_{n,l,m_l} is a mathematical function whose value depends upon spherical polar coordinates (r,θ,ϕ) of the electron and characterized by the quantum numbers n, l and m_l. Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the Table, Z is atomic number and a_0 is Bohr radius.

Column 1	Column 2	Column 3
(I) 1s orbital	(i) $\psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\left(\frac{Zr}{a_0}\right)}$	(P) 
(II) 2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$
(III) $2p_z$ orbital	(iii) $\psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\left(\frac{Zr}{2a_0}\right)} \cos\theta$	(R) Probability density is maximum at nucleus
(IV) $3d_z^2$ orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from n = 2 state to n = 4 state is $\frac{27}{32}$ times the energy needed to excite electron from n = 2 state to n = 6 state

31. For He^{+} ion, the only **INCORRECT** combination is

[A] (I) (i) (R) [B] (II) (ii) (Q) [C] (I) (i) (S) [D] (I) (iii) (R)

Ans. (D)

Sol. (i) 1s-orbital has no angular dependence.

so, 1s-orbital can't have wave function containing θ or ϕ.

(I) does not correspond to (iii)

32. For the given orbital in Column 1, the only CORRECT combination for any hydrogen-like species is

[A] (I) (ii) (S) [B] (IV) (iv) (R) [C] (III) (iii) (P) [D] (II) (ii) (P)

Ans. (D)

Sol. 2s-orbital has 1 radial node with ψ vs r curves as given in P.

33. For hydrogen atom, the only CORRECT combination is

[A] (II) (i) (Q) [B] (I) (iv) (R) [C] (I) (i) (P) [D] (I) (i) (S)

Ans. (D)

Sol. $E_{2\to4} = 13.6\,Z^2\left(\frac{1}{4}-\frac{1}{16}\right) = \frac{3}{16}\times 13.6\,Z^2 \;\; ev$

$E_{2\to6} = 13.6\,Z^2\left(\frac{1}{4}-\frac{1}{36}\right) = \frac{8}{36}\times 13.6\,Z^2 \;\; ev$

$\frac{E_{2\to4}}{E_{2\to6}} = \frac{3/16}{8/36} = \frac{3}{16}\times\frac{36}{18} = \frac{27}{32}$

Answer Q.34, Q.35 and Q.36 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively

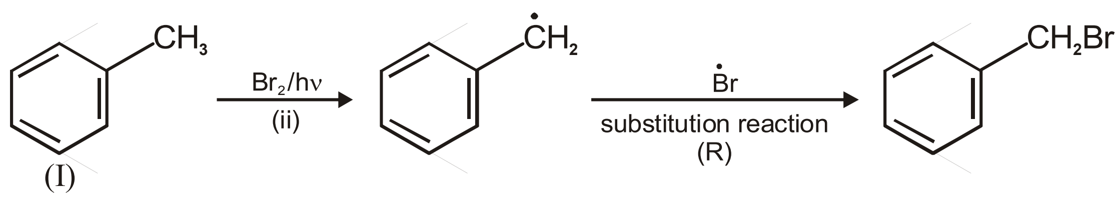
	Column 1		Column 2		Column 3
(I)	Toluene	(i)	$NaOH/Br_2$	(P)	Condensation
(II)	Acetophenone	(ii)	Br_2 / hν	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O/CH_3COOK$	(R)	Substitution
(IV)	Phenol	(iv)	$NaOH/CO_2$	(S)	Haloform

34. The only CORRECT combination in which the reaction proceeds through radical mechanism is :

[A] (II) (iii) (R) [B] (III) (ii) (P) [C] (IV) (i) (Q) [D] (I) (ii) (R)

Ans. (D)

Sol.

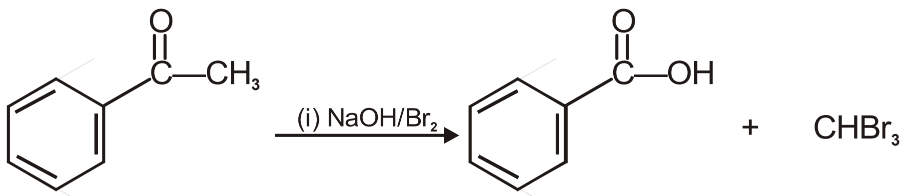


35. For the synthesis of benzoic acid, the only CORRECT combination is :

[A] (III) (iv) (R) [B] (IV) (ii) (P) [C] (II) (i) (S) [D] (I) (iv) (Q)

Ans. (C)

Sol.



(II)

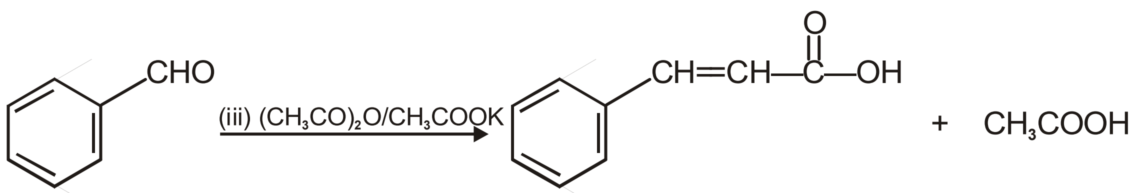
this is haloform reaction.
(S)

36. The only CORRECT combination that gives two different carboxylic acids is :

[A] (IV) (iii) (Q) [B] (I) (i) (S) [C] (III) (iii) (P) [D] (II) (iv) (R)

Ans. (C)

Sol.



(III)

this is Perkin reaction in which condensation occurs between two different molecules.
(P)