

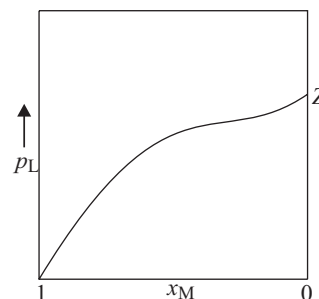
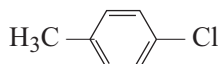
JEE ADVANCED—2017

CHEMISTRY PAPER-I

SECTION - I

This section contains **SEVEN** questions. Each question has **FOUR** options (a), (b), (c) and (d). **One or More Than One** of these four option(s) is/are correct.

- The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to
 - the physical state of the X_2 at room temperature changes from gas to solid down the group.
 - decrease in HOMO–LUMO gap down the group.
 - decrease in $\pi^* - \sigma^*$ gap down the group.
 - decrease in ionization energy down the group.
- Addition of excess ammonia to 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., where as it is zero for complex Y. Among the following options, which statement(s) is (are) correct?
 - The hybridization of the central metal ion in Y is d^2sp^3 .
 - When X and Z are in equilibrium at 0 °C, the colour of the solution is pink.
 - Z is a tetrahedral complex.
 - Addition of $AgNO_3$ in Y gives only two equivalents of silver chloride.
- 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)
 - If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.
 - 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
 - The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1 .
 - 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 under adiabatic conditions with $T_1 \neq T_2$.
- 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 this system is (are)
 - Attractive intermolecular interactions between L – L in pure liquid L and M – M in pure liquid M are stronger than those between L – M when mixed in solution.
 - The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$.
 - The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$.
 - The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$.
- The IUPAC name(s) of the following compound is (are)



CI.2 JEE (Advanced)—2017: Chemistry Paper-I

- (a) 1-chloro-4-methylbenzene (b) 4-chlorotoluene
 (c) 1-methyl-4-chlorobenzene (d) 4-methylchlorobenzene
6. The correct statement(s) for the following addition reactions is (are)



- (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
7. The correct statement(s) about the oxoacids, HClO₄ and HClO, is (are)
- (a) The conjugate base of HClO₄ is weaker base than H₂O.
 (b) The central atom in both HClO₄ and HClO is sp³ hybridized.
 (c) HClO₄ is formed in the reaction between Cl₂ and H₂O
 (d) HClO₄ is more acidic than HClO because of the resonance stabilization of its anion

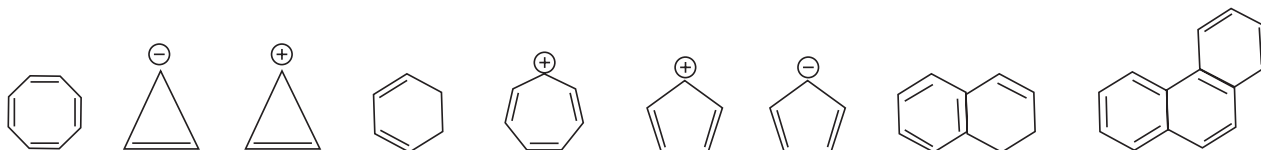
SECTION 2

This section contains **FIVE** questions. The answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive.

8. 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 cm². 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 (Λ_m^∞) of this weak monobasic acid in aqueous solution is $Z \times 10^2$ S cm⁻¹ mol⁻¹. The value of Z is _____.
9. The sum of the number of lone pairs of electrons on each central atom in the following species is _____.
 [TeBr₆]²⁻, [BrF₂]⁺, SNF₃ and [XeF₃]⁻

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

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

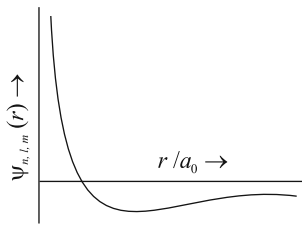


11. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm⁻³, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is _____.
12. Among H₂, He₂⁺, Li₂, Be₂, B₂, C₂, N₂, O₂⁻ and F₂, 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.)

SECTION 3

- This section contains **SIX** questions of matching type.
 - This section contains **TWO** tables (each having 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.
- Answer Q. 13, Q. 14 and Q. 15 by appropriately matching the information given in the three columns of the following table.

The wave function $\psi_{n,l,m}$ 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 coaltitude and ϕ is azimuth. In the mathematical functions given in the table, Z is atomic number and a_0 is Bohr radius.

Column I	Column 2	Column 3
I. 1s orbital	(i) $\psi_{n,l,m} \propto \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	(P) 
II. 2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto 1/a_0^3$
III. 2p _z orbital	(iii) $\psi_{n,l,m} \propto \left(\frac{Z}{a_0}\right)^{5/2} r e^{-(Zr/2a_0)} \cos \theta$	(R) Probability density is maximum at nucleus
IV. 3d _{z²} orbital	(iv) xy -plane is a nodal plane	(S) Energy needed to excite electron from $n = 2$ state to $n = 4$ state is 27/32 times the energy needed to excite electron from $n = 2$ state to $n = 6$ state.

13. For He⁺ ion, the only **INCORRECT** combination is:

- (a) (I), (i), (R) (b) (II), (ii), (Q) (c) (I), (i), (S) (d) (I), (iii), (R)

14. 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)

15. For hydrogen atom, the only **CORRECT** combination is:

- (a) (II), (i), (Q) (b) (I), (iv), (R) (c) (I), (i), (p) (d) (I), (iv), (S)

Answer Q 16, Q 17 and Q 18 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2, 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 ₃ CO) ₂ O/ CH ₃ COOK	(R) Substitution
(IV) Phenol	(iv) NaOH/CO ₂	(S) Haloform

16. 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)

17. 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)

18. The only **CORRECT** combination that gives two different carboxylic acid is:

- (a) (IV), (iii), (Q) (b) (I), (i), (S)
(c) (III), (iii), (P) (d) (II), (iv), (R)

ANSWERS

- | | | | | |
|-------------|------------------|------------------|-------------|-------------|
| 1. (b), (c) | 2. (a), (b), (c) | 3. (a), (b), (c) | 4. (a), (d) | 5. (a), (b) |
| 6. (b), (d) | 7. (a), (b), (d) | 8. (6) | 9. (6) | 10. (5) |
| 11. (2) | 12. (6) | 13. (d) | 14. (d) | 15. (d) |
| 16. (d) | 17. (c) | 18. (c) | | |

Solutions

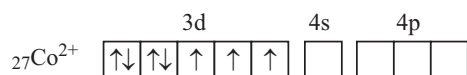
1. The molecular orbitals formed from p orbitals of halogens along with the occupancy of 10 electrons are shown in Fig. 1.

The highest occupied molecular orbital (HOMO) is π^*p orbital and the lowest unoccupied orbital (LUMO) is σ^*p . On descending the halogen group, the energy difference between π^* (i.e. HOMO) and σ^* (i.e. LUMO) is decreased. This is responsible for changing colour from yellow to violet. This is due to the electronic excitation from π^*p orbital to σ^*p orbital. Thus, the choices (b) and (c) are correct.

2. The compound X is $MCl_2 \cdot 6H_2O$, i.e. $[M(H_2O)_6]Cl_2$. The treatment of X with NH_4Cl in the presence of air gives 1 : 3 complex Y. This shows that M^{2+} in X is oxidised to M^{3+} in Y. The metal ion may be that of cobalt since Co(II) complexes are readily oxidised to Co(III) complexes in the presence of air. This is also supported by the spin only magnetic moment of X. Given value of 3.87 bohr magneton corresponds to 3 unpaired electrons:

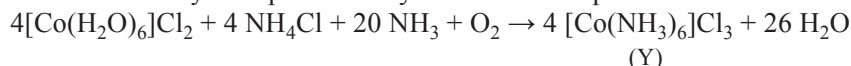
$$\sqrt{n(n+2)} = 3.87 \quad \text{i.e.} \quad n(n+2) = 15. \quad \text{Thus,} \quad n = 3$$

The electronic configuration of Co^{2+} confirms this fact.

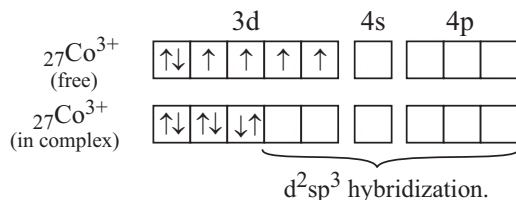


Thus, the compound X is $[Co(H_2O)_6]Cl_2$.

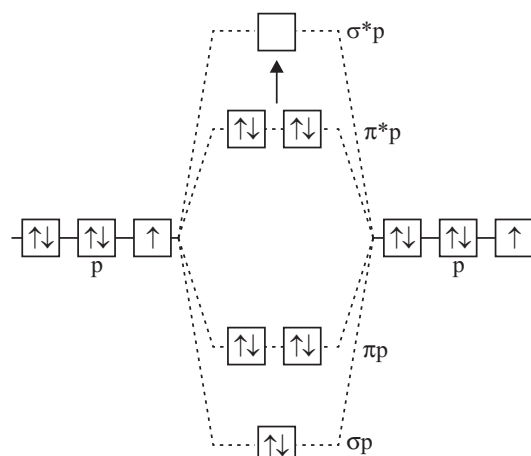
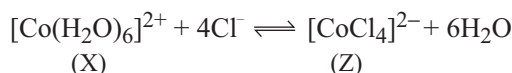
The conversion of X into Y may be represented by the chemical equation



Since NH_3 is a strong ligand, it is able to couple the unpaired electrons in Co^{3+} ion.

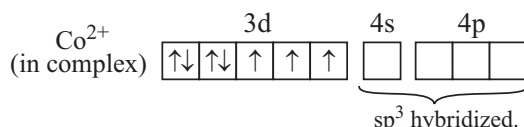


It is supported by zero spin magnetic moment. Cobalt, in the complex Y is d^2sp^3 hybridized. The reaction of X with excess of HCl at room temperature gives blue-coloured complex Z. The reaction corresponding to this is:


Fig. 1

The above reaction is an equilibrium reaction and is weakly endothermic, i.e. $\Delta_r H^\circ = \text{positive}$. At room temperature it lies more towards Z giving blue-coloured complex. At 0°C , the equilibrium lies more towards complex X giving pink colour of the complex.

The compound Z involves sp^3 hybridization and is thus tetrahedral in shape. This is due to the fact that Cl^- is a weak ligand and it is unable to couple the unpaired electrons in Co^{2+} ion.



This is supported by the spin-only magnetic moment of the complex which requires the presence of 3 unpaired electrons.

Addition of AgNO_3 to the complex Y will precipitate three equivalents of silver chloride.

Thus, the choices (a), (b) and (c) are correct.

3. (a) For free expansion, $p_{\text{ext}} = 0$

Thus, $w = -p_{\text{ext}} \Delta V = 0$

For an isothermal expansion, $\Delta T = 0$. Since the internal energy of an ideal gas depends only on temperature, it follows that $\Delta U = 0$. From the first law of thermodynamics ($\Delta U = q + w$), it follows that $q = 0$.

Thus, for an isothermal free expansion, we have $w = 0$, $q = 0$ and $\Delta U = 0$

For adiabatic free expansion, $q = 0$ as no heat is allowed to enter or leave from the system. Since $w = 0$, it follows that $\Delta U = 0$

Thus, for both isothermal and adiabatic free expansions, $q = 0$, $w = 0$ and $\Delta U = 0$

- (b) Since in adiabatic expansion, work is done at the expense of internal energy, the temperature T_2 in the final state will be lesser in adiabatic expansion as compared to that in isothermal expansion. Since $p \propto T$, it follows that p_2 in adiabatic expansion will be lesser than that in isothermal expansion. The variations of p versus V in the two expansions are shown in Fig. 2

Since work done is represented by the area under p - V curve, it follows that the work done under adiabatic condition will be lesser than that done under isothermal condition

- (c) Since the external pressure is equal to pressure of the gas after the gas has gone compression and it is maximum pressure which the external pressure can have. Thus, work done on the gas will be maximum. It is shown in Fig. 3.

- (d) Expansion under isothermal conditions, $T_1 = T_2$, Thus, $\Delta U = 0$

Under adiabatic conditions, $T_2 < T_1$, Thus, $\Delta U < 0$

Thus, the choices (a), (b) and (c) are correct.

4. (a) Since the pressure p_L in Fig. 4 is larger than that predicted by Raoult's law (represented by broken line in the figure), larger number of molecules of L are escaping from solution when compared with ideal solution.

This is possible when the molecular attractions $L \cdots M$ are weaker than those existing in $L \cdots L$ and $M \cdots M$

- (d) The point Z represents vapour pressure of pure liquid L where $x_L = 1$. The Raoult's law is applicable when $x_L \rightarrow 1$

5. The compound is named either as benzene derivative or by common name.

Thus, the IUPAC names are:

1-chloro-4-methylbenzene and 4-chlorotoluene

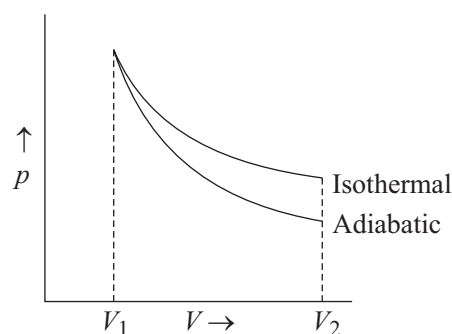


Fig. 2

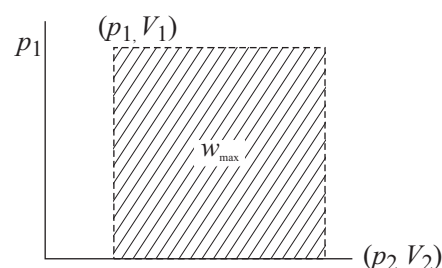


Fig. 3

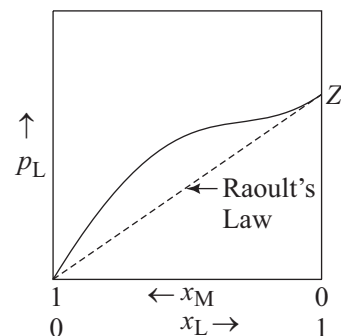
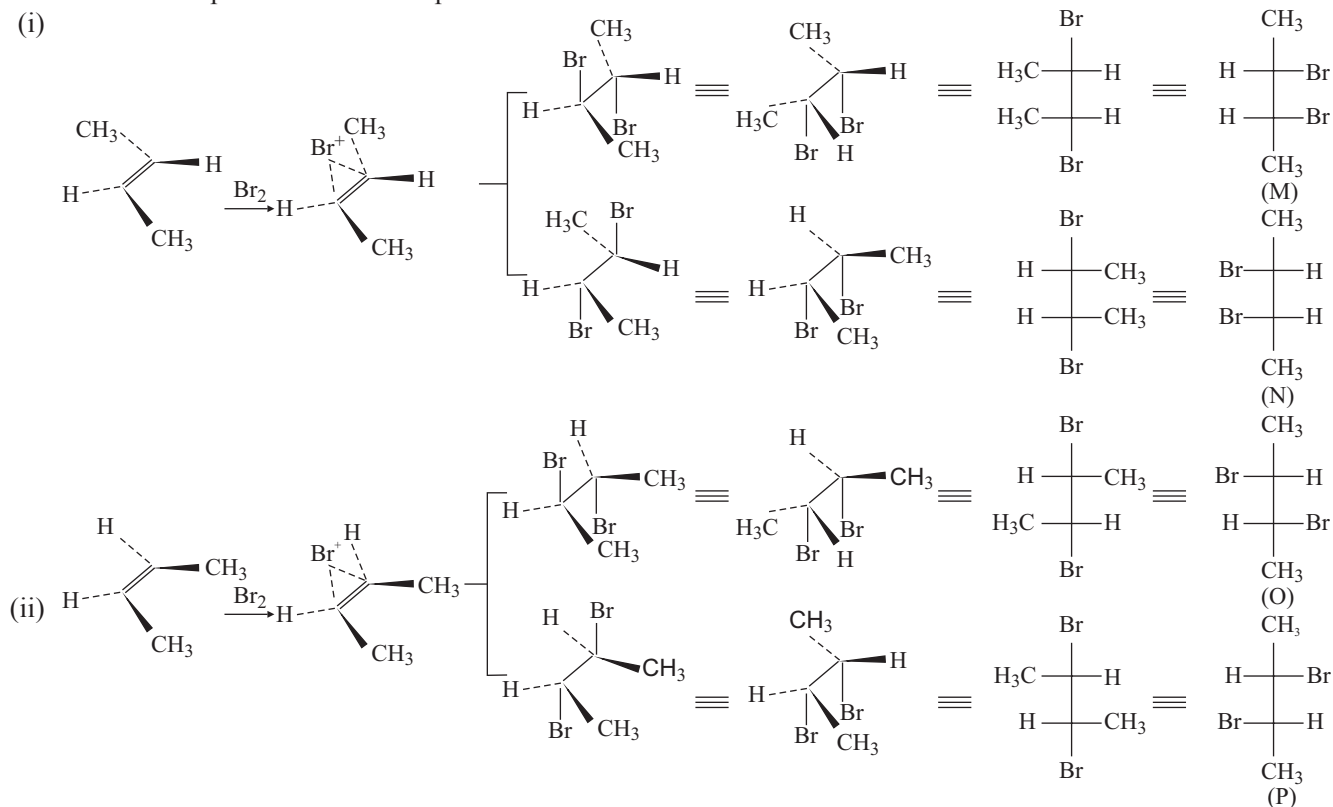


Fig. 4

6. Addition of bromine across double bond is *anti*-addition. The *cis*-alkene yields only racemic mixture whereas *trans*-alkene produces *meso* compound.



The compounds M and N are identical whereas O and P are enantiomers.

The compounds M and O and N and P are diastereomers.

The choices (b) and (d) are correct.

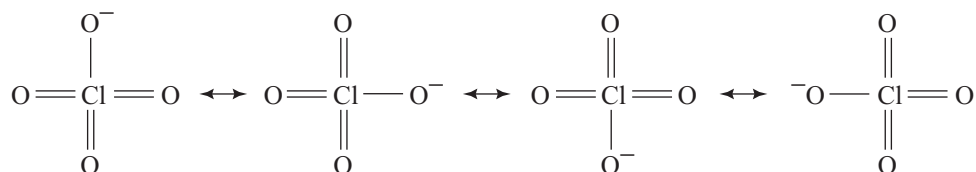
7. (a) The strength of oxoacids of chlorine follows the order: $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

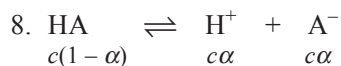
The strength of conjugate bases follow the reverse order: $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}^-$

(b) Molecule	Valence electrons	Lewis structure	Prediction
HClO_4	$1 + 7 + 4 \times 6 = 32$	$\begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \\ \\ \text{:}\ddot{\text{O}}-\text{Cl}-\ddot{\text{O}}\text{:} \\ \\ \text{:}\ddot{\text{O}}\text{:} \end{array}$	4 pairs of electrons around Cl, sp^3 hybridization
HClO	$1 + 7 + 6 = 14$	$\text{:}\ddot{\text{Cl}}-\ddot{\text{O}}-\text{H}$	4-pairs of electrons around Cl, sp^3 hybridization

(c) The reaction between Cl_2 and H_2O is $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$

(d) ClO_4^- is stabilized due to resonance structures





$$\alpha = \frac{\Lambda}{\Lambda^\infty} = \frac{\kappa/c}{\Lambda^\infty} \Rightarrow \Lambda^\infty = \frac{\kappa}{c\alpha} = \frac{G(l/a)}{[\text{H}^+]}$$

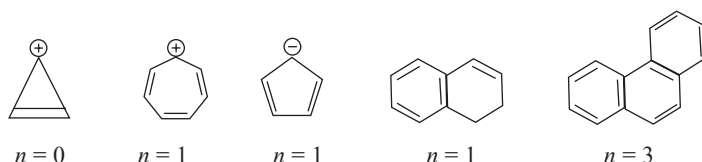
$$\text{Thus } \Lambda^\infty = \frac{(5 \times 10^{-7} \text{ S})(120 \text{ cm}/1 \text{ cm}^2)}{10^{-4} \text{ mol dm}^{-3}} = 0.6 \text{ S cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$$

$$= 0.6 \text{ S cm}^{-1} \text{ mol}^{-1} (10 \text{ cm})^3 = 6 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$$

Thus, the value of **Z** is **6**.

9. Species	Valence electrons	Lewis structure	Lone pairs
$[\text{TeBr}_6]^{2-}$	$6 + 7 \times 6 + 2 = 50$		1
$[\text{BrF}_2]^+$	$7 + 2 \times 7 - 1 = 20$		2
SNF_3	$6 + 5 + 3 \times 7 = 32$		0
$[\text{XeF}_3]^-$	$8 + 3 \times 7 + 1 = 30$		3
Total lone pairs =			6

10. Aromatic compounds have $(4n + 2)\pi$ electrons. The following compounds satisfy this requirement.



The number of aromatic compounds is **5**.

11. The expression of density is

$$\rho = \left(\frac{N}{a^3} \right) m$$

where $N = 4$, $a = 400 \text{ pm}$ and m is mass/atom of the solid. From this, use get

$$m = \frac{\rho a^3}{N} = \frac{(8 \text{ g cm}^{-3})(400 \times 10^{-10} \text{ cm})^3}{4} = 1.28 \times 10^{-22} \text{ g}$$

$$\text{Number of atoms in 256 g is } N' = \frac{256 \text{ g}}{1.28 \times 10^{-22} \text{ g}} = 2 \times 10^{24}$$

Thus, the value of N is **2**.

12. Species	Molecular electronic configuration	Conclusion
H ₂	(σ1s) ²	Diamagnetic
He ₂ ⁺	(σ1s) ² (σ*1s) ¹	Paramagnetic
Li ₂	KK(σ2s) ²	Diamagnetic
Be ₂	KK(σ2s) ² (σ*2s) ²	Diamagnetic
B ₂	KK(σ2s) ² (σ*2s) ² (π2p _x) ¹ (π2p _y) ¹	Paramagnetic
C ₂	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ²	Diamagnetic
N ₂	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ² (σ2p _z) ²	Diamagnetic
O ₂ ⁻	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ¹ (π*2p _y) ¹	Paramagnetic
F ₂	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ² (π*2p _y) ²	Diamagnetic

There are 6 diamagnetic species.

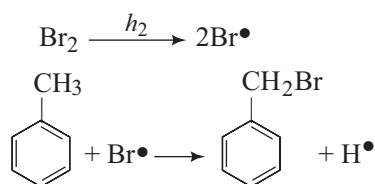
13. The choice (d) is incorrect. 1s orbital (I in column 1) has no directional characteristics (iii in column 2 contains $\cos \theta$).
14. The choice (d) is correct. 2s orbital (II in column 1) has one radial node ($= n - l - 1$) (ii in column 2) and the plot of $\psi_{n, l, m}(r)$ has the characteristic of P shown in column 3.
15. The choice (d) is correct. 1s orbital (I in column 1) has wave function dependence shown in (i) of column 2. The option S of column 3 is also correct as shown in the following.

$$\text{Transition from } n = 2 \text{ to } n = 4 \quad \Delta E_1 = R_\infty hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_\infty hc \left(\frac{1}{4} - \frac{1}{16} \right) = \frac{3}{16} R_\infty hc$$

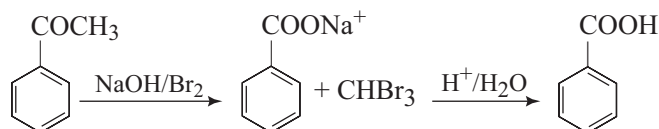
$$\text{Transition from } n = 2 \text{ to } n = 6 \quad \Delta E_2 = R_\infty hc \left(\frac{1}{4} - \frac{1}{36} \right) = \frac{8}{36} R_\infty hc$$

$$\frac{\Delta E_1}{\Delta E_2} = \frac{(3/16) R_\infty hc}{(8/36) R_\infty hc} = \frac{27}{32}$$

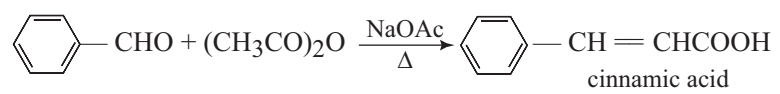
16. The combination Br₂/hν (choice ii in column 2) produces Br radicals. Of the two choices (b) and (d) which include (ii), the choice (d) is correct as bromination of toluene (choice I in column 1) involves substitution (choice S in column 3) in the methyl group as shown in the following.



17. The choice (c) is correct combination as C₆H₅COCH₃ (acetophenone, choice II in column 1) undergoes haloform reaction (choice S in column 3) with the use of reagents NaOH/Br (choice ii in column 2)



18. The choice (c) is correct. Heating of aromatic aldehyde (choice III in column 1) with acetic anhydride in the presence of sodium acetate (Choice ii in column 2) gives α, β-unsaturated carboxylic acid. This is known as Perkin reaction.



Cinnamic acid exists in two geometrical isomers due to the presence of a double bond.