
LIVE BATCH
CSIR NET
Life Sciences
TARGET
June 2025
Starts: 1 Mar, 25 | 10 am - 5 pm


FOUNDATION BATCH
LIFE SCIENCES
Exam (CSIR, GATE, DBT, BARC, ICMR, ICAR)
Starts: 10, Mar | 10 am to 5 pm

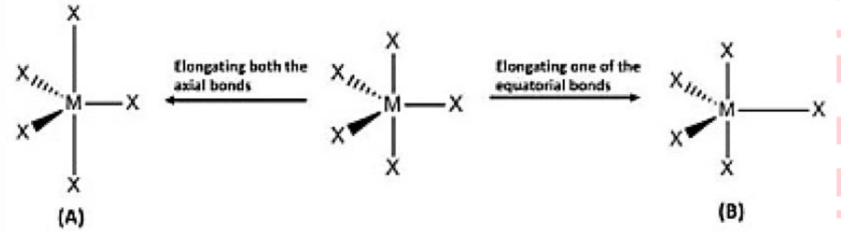
CSIR NET Chemical Science Questions Answers with Solutions

Q1. The difference in the second ionization energies of Li/Na, Be/Mg, B/Al and N/P are X_1, X_2, X_3 and X_4, respectively. The correct order of the difference in the second ionization energies is
(a) $X_1 > X_4 > X_3 > X_2$
(b) $X_1 > X_2 > X_3 > X_4$
(c) $X_4 > X_3 > X_1 > X_2$
(d) $X_1 > X_3 > X_4 > X_2$

Q2. The total number of six membered rings in the polycyclic compounds $P_4\,(NMe)_6$ and $P_2\,(N_2Me_2)_3$ is
(a) 7
(b) 6
(c) 5
(d) 4

Q3. Magnetic moment of $Yb^{3+}(f^{13})$ is
(a) 4.54BM
(b) 1.73BM
(c) 2.83BM
(d) 3.87BM

Q4. The molecule MX_5 belongs to the point group D_{3h}. Elongation of both the axial M-X bonds yields A and elongation of one of the M-X equatorial bonds yields B.



The point groups of A and B, respectively, are
(a) C_{3v} and D_{3h}
(b) D_{3h} and C_{3v}
(c) C_{3v} and C_{2v}
(d) D_{3h} and C_{2v}

Q5. According to VSEPR theory, the geometries of FClO and F_5IO, respectively, are
(a) linear and octahedral
(b) tetrahedral and octahedral
(c) tetrahedral and capped octahedral
(d) trigonal bipyramidal and capped octahedral

Q6. Molecule B is twice as heavy as molecule A. The ratio of the thermal de Broglie wavelength of the molecule A to that of the molecule B is

(a) $\sqrt{2}:1$
(b) $2:1$
(c) $1:2$
(d) $1:\sqrt{2}$

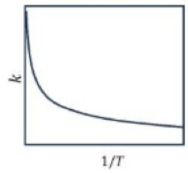
Q7. The number of skeletal electron pairs (SEP) and the cluster type of $[B_{10}H_{10}]^{2-}$ and $[B_6H_9]^-$, respectively, are

(a) 11, *closo* and 8, *nido*
(b) 11, *nido* and 8, *nido*
(c) 10, *closo* and 6, *arachno*
(d) 10, *closo* and 8, *nido*

Q8. The calculated magnetic moment of $Eu^{3+}(4f^6)$ is 0 (zero) BM. The experimental value is 3.4- 3.6 BM at 298 K. The deviation is due to the

(a) mixing of 4f and 4d orbitals
(b) large spin-orbit coupling constant (λ)
(c) large orbital angular momentum
(d) populated ground and the excited states

Q9. According to Arrhenius equation, the plot that correctly describes the temperature (T) dependence of the rate constant (k) is

(a)


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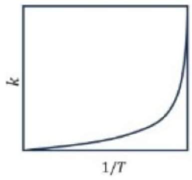

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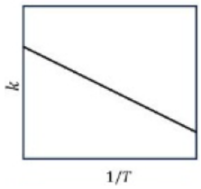

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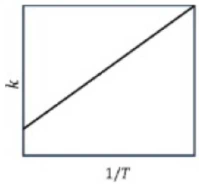
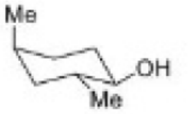
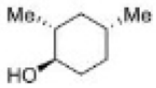


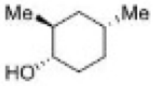
Q10. For face centered cubic (FCC) packing of a monoatomic solid, the number of tetrahedral and octahedral holes within the unit cell, respectively, are

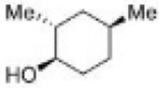
(a) 8 and 4
(b) 4 and 2
(c) 16 and 16
(d) 6 and 6

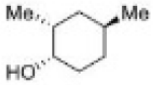
Q11. The structure that corresponds to the following compound is



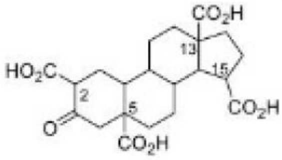
(a) 

(b) 

(c) 

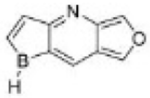
(d) 

Q12. The given steroid molecule undergoes facile monodecarboxylation on heating. The carboxylic acid group lost is at



(a) C15
(b) C13
(c) C5
(d) C2

Q13. Based on Hückel rule, the following species is



(a) aromatic
(b) antiaromatic
(c) nonaromatic
(d) homoaromatic

Q14. e^{ikx} is an eigenfunction of the linear momentum operator, $\hat{p}_x$, with the eigenvalue of

(a) $\hbar^2 k$

(b) $\hbar k$

(c) $\hbar k^2$

(d) $\hbar^2 k^2$

Q15. In a flame photometric analysis of a blood serum sample for K^+ ion, a band is obtained at 766 nm. This band is due to

(a) absorption by K^+ ion only.

(b) absorption by K atom only.

(c) emission by K^+ ion only.

(d) emission by K atom only.

Q16. If $H = \frac{p_x^2}{2m} + V(x)$, then $[H, p_x]$ is

(a) $i\hbar \frac{dV}{dx}$

(b) 0

(c) $-i\hbar$

(d) $-\frac{i\hbar p_x}{m}$

Q17. The following two molecules are

(a) Enantiomers

(b) Diastereomers

(c) Homomers(identical)

(d) Constitutional isomers

Q18. For 0.001 M aqueous solutions of $AlCl_3, CaCl_2$ and KCl at 25°C, the correct order of Debye length is

(a) $AlCl_3 < CaCl_2 < KCl$

(b) $KCl < CaCl_2 < AlCl_3$

(c) $CaCl_2 < KCl < AlCl_3$

(d) $AlCl_3 < KCl < CaCl_2$

Q19. The correct option for the oxidation state(s) of Nb in the cluster $Na_4[Nb_6Cl_{18}]$ is

(a) two are in +3 state and four are in +2 state

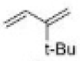
(b) all are in +2 state

(c) all are in +3 state

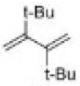
(d) three are in +2 state and three are in +3 state

Q20. The correct order of reactivity for the following dienes with maleic anhydride is


M



N



O

(a) M > N > O

(b) N > M > O

(c) N > O > M

(d) O > N > M

Solutions

S1. Ans.(a)

Sol. Ionization energy (IE) is the minimum energy required to remove the most loosely bound electron of an isolated gaseous atom, positive ion, or molecule. The first ionization energy is quantitatively expressed as

$X(g) + \text{energy} \longrightarrow X^+(g) + e^-$

where X is any atom or molecule, X^+ is the resultant ion when the original atom was stripped of a single electron, and e^- is the removed electron. Ionization energy is positive for neutral atoms, meaning that the ionization is an endothermic process. Roughly speaking, the closer the outermost electrons are to the nucleus of the atom, the higher the atom's ionization energy.

Ionization energy is usually expressed as the energy to ionize a mole of atoms or molecules, usually as kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol).

1st ionization energy is the energy that enables the reaction $X \longrightarrow X^+ + e^-$

2nd ionization energy is the energy that enables the reaction $X^+ \longrightarrow X^{2+} + e^-$

3rd ionization energy is the energy that enables the reaction $X^{2+} \longrightarrow X^{3+} + e^-$

Comparison of ionization energies of atoms in the periodic table reveals two periodic trends which follow the rules of Coulombic attraction:

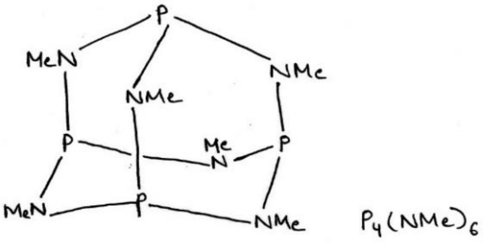
Ionization energy generally increases from left to right within a given period (that is, row). As the nuclear charge of the nucleus increases across the period, the electrostatic attraction increases between electrons and protons, hence the atomic radius decreases, and the electron cloud comes closer to the nucleus because the electrons, especially the outermost one, are held more tightly by the higher effective nuclear charge.

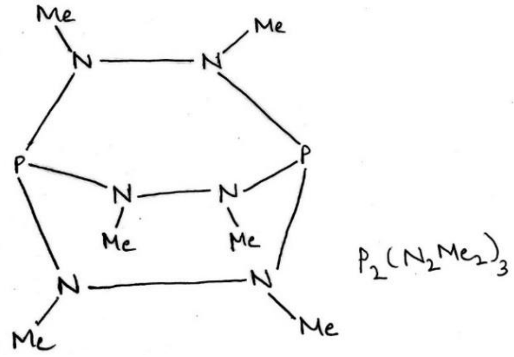
Ionization energy generally decreases from top to bottom in a given group (that is, column). On moving downward within a given group, the electrons are held in higher-energy shells with higher principal quantum number n, further from the nucleus and therefore are more loosely bound so that the ionization energy decreases. The effective nuclear charge increases only slowly so that its effect is outweighed by the increase in n.
Generally, the (*N*+1) th ionization energy of a particular element is larger than the *N*th ionization energy (it may also be noted that the ionization energy of an anion is generally less than that of cations and neutral atom for the same element). When the next ionization energy involves removing an electron from the same electron shell, the increase in ionization energy is primarily due to the increased net charge of the ion from which the electron is being removed. Electrons removed from more highly charged ions experience greater forces of electrostatic attraction; thus, their removal requires more energy. In addition, when the next ionization energy involves removing an electron from a lower electron shell, the greatly decreased distance between the nucleus and the electron also increases both the electrostatic force and the distance over which that force must be overcome to remove the electron. Both of these factors further increase the ionization energy.

X_1=7298 (Li)-4562(Na)=2736
X_2=1757 (Be)-1451(Mg)=306
X_3=2427(B)-1817(Al)=610
X_4=2856(N)-1907(P)=949

S2. Ans.(a)

Sol. The range of PN compounds is extensive, and includes cyclic and polymeric phosphazenes, $(PX_2N)_n$; phosphazenes form highly flexible elastomers.
Phosphazenes refer to classes of organophosphorus compounds featuring phosphorus(V) with a double bond between P and N.
Polyphosphazenes include a wide range of hybrid inorganic-organic polymers with a number of different skeletal architectures with the backbone P-N-P-N-P-N-.In nearly all of these materials two organic side groups are attached to each phosphorus center. Linear polymers have the formula $(N{=}PR^1R^2)_n$, where R^1 and R^2 are organic. Other architectures are cyclolinear and cyclomatrix polymers in which small phosphazene rings are connected together by organic chain units. Other architectures are available, such as block copolymer, star, dendritic, or comb-type structures. More than 700 different polyphosphazenes are known, with different side groups (R) and different molecular architectures.





S3. Ans.(a)

Sol. The magnetic moment μ of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution.

In a free atom or ion, both the orbital and the spin angular momenta give rise to a magnetic moment and contribute to the paramagnetism. When the atom or ion is part of a complex, any orbital angular momentum is normally quenched, or suppressed, as a result of the interactions of the electrons with their nonspherical environment. However, if any electrons are unpaired the net electron spin angular momentum survives and gives rise to spin-only paramagnetism, which is characteristic of many d-metal complexes.

For orbital angular momentum to contribute, and hence for the paramagnetism to differ significantly from the spin-only value, there must be one or more unfilled or half-filled orbitals similar in energy to the orbitals occupied by the unpaired spins and of the appropriate symmetry (one that is related to the occupied orbital by rotation round the direction of the applied field). If that is so, the applied magnetic field can force the electrons to circulate around the metal ion by using the low-lying orbitals and hence it generates orbital angular momentum and a corresponding orbital contribution to the total magnetic moment.

For the lanthanoids, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. Therefore, the magnetic moment must be expressed in terms of the total angular momentum quantum number *J*:

$$\mu = g_J\{J(J+1)\}^{1/2}\mu_B$$

where the Landé *g*-factor is

$$g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

and μ_B is the Bohr magneton.

Information Booster

A term symbol is an abbreviated description of the total spin and orbital angular momentum quantum numbers of the electrons in a multi-electron atom.

The usual atomic term symbols assume LS coupling (also known as Russell–Saunders coupling), in which the atom's total spin quantum number *S* and the total orbital angular momentum quantum number *L* are "good quantum numbers". The spin-orbit interaction then couples the total spin and orbital moments to give the total electronic angular momentum quantum number *J*. Atomic states are then well described by term symbols of the form:

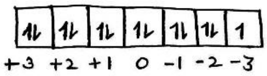
$^{2S+1}L_J$

where

- *S* is the total spin quantum number for the atom's electrons. The value 2*S* + 1 written in the term symbol is the spin multiplicity, which is the number of possible values of the spin magnetic quantum number M_S for a given spin *S*.
- *J* is the total angular momentum quantum number for the atom's electrons. *J* has a value in the range from |*L* − *S*| to *L* + *S*. The value of J for the ground state is given by (L-S) for a sub-shell that is less than half-filled, and by (L+S) for a sub-shell that is more than half-filled.

L is the total orbital quantum number in spectroscopic notation, in which the symbols for *L* are: "S", "P", "D", or "F" which represent *L* = 0, 1, 2, or 3 respectively.

Yb^{3+} (f^{13})



$L = +3+3+2+2+1+1+0-1-1-2-2-3 = 3$

$S = \frac{1}{2}$

$2S+1 = 2\times\frac{1}{2}+1 = 2$

$J = |L+S| = |3+\frac{1}{2}| = \frac{7}{2}$

$$g_J = 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) + \frac{7}{2}(\frac{7}{2}+1) - 3(3+1)}{2\times\frac{7}{2}(\frac{7}{2}+1)}$$

$g_J = 1.1428$

$\mu = g_J\{J(J+1)\}^{1/2}$ BM

$\mu = 1.1428\,\{\frac{7}{2}(\frac{7}{2}+1)\}^{1/2}$ BM

$\mu = 1.1428 \times 3.9686$

$\mu = 4.53$ BM.

S4. Ans.(d)

Sol. The systematic discussion of symmetry is called group theory. An action that leaves an object looking the same after it has been carried out is called a symmetry operation. Typical symmetry operations include rotations, reflections, and inversions. There is a corresponding symmetry element for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed.

The classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged gives rise to the point groups.

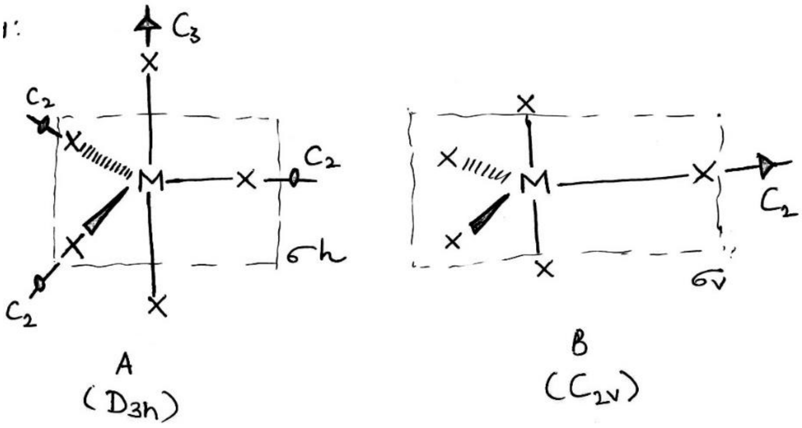
The identity, E, consists of doing nothing; the corresponding symmetry element is the entire object.

An n-fold rotation (the operation) about an n-fold axis of symmetry, C_n (the corresponding element) is a rotation through 360°/n. If a molecule possesses several rotation axes, then the one (or more) with the greatest value of n is called the principal axis.

A reflection (the operation) in a mirror plane, σ (the element), may contain the principal axis of a molecule or be perpendicular to it. If the plane is parallel to the principal axis, it is called 'vertical' and denoted σ_v. A vertical mirror plane that bisects the angle between two C_2 axes is called a 'dihedral plane' and is denoted σ_d. When the plane of symmetry is perpendicular to the principal axis it is called 'horizontal' and denoted σ_h.

If in addition to the identity and a C_n axis a molecule has n vertical mirror planes σ_v, then it belongs to the group C_{nv}.

A molecule that has an n-fold principal axis and *n* twofold axes perpendicular to C_n belongs to the group D_n. A molecule belongs to D_{nh} if it also possesses a horizontal mirror plane.



A (D3h)

B (C2v)

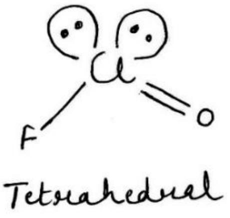
S5. Ans.(b)

Sol. The primary assumption of the VSEPR model is that regions of enhanced electron density, by which we mean bonding pairs, lone pairs, or the concentrations of electrons associated with multiple bonds, take up positions as far apart as possible so that the repulsions between them are minimized. For instance, four such regions of electron density will lie at the corners of a regular tetrahedron, five will lie at the corners of a trigonal bipyramid, and so on.

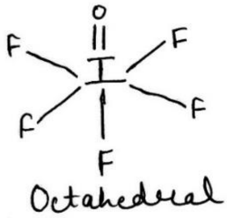
Although the arrangement of regions of electron density, both bonding regions and regions associated with lone pairs, governs the shape of the molecule, the *name* of the shape is determined by the arrangement of *atoms*, not the arrangement of the regions of electron density.

To apply the VSEPR model systematically, we first write down the Lewis structure for the molecule or ion and identify the central atom. Next, we count the number of atoms and lone pairs carried by that atom because each atom (whether it is singly or multiply bonded to the central atom) and each lone pair counts as one region of high electron density. To achieve lowest energy, these regions take up positions as far apart as possible, so we identify the basic shape they adopt.

Central atom should be large in size and less in number.

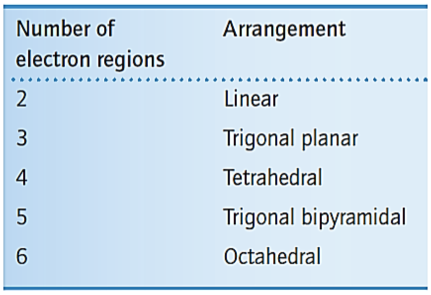


Tetrahedral



Octahedral

The basic arrangement of regions of electron density according to the VSEPR model



Number of electron regions	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

S6. Ans.(a)

Sol. The thermal de Broglie wavelength (λ_{th}, sometimes also denoted by Λ)is a measure of the uncertainty in location of a particle of thermodynamic average momentum in an ideal gas. It is roughly the average de Broglie wavelength of particles in an ideal gas at the specified temperature.

The average interparticle spacing in the gas to be approximately $(V/N)^{1/3}$ where V is the volume and N is the number of particles. When the thermal de Broglie wavelength is much smaller than the interparticle distance, the gas can be considered to be a classical or Maxwell–Boltzmann gas. Maxwell–Boltzmann statistics describes the distribution of classical material particles over various energy states in thermal equilibrium. On the other hand, when the thermal de Broglie wavelength is on the order of or larger than the interparticle distance, quantum effects will dominate and the gas must be treated as a Fermi gas or a Bose gas, depending on the nature of the gas particles. A Fermi gas is an idealized model, an ensemble of many non-interacting fermions. Fermions are particles that obey Fermi–Dirac statistics, like electrons, protons, and neutrons, and, in general, particles with half-integer spin. An ideal Bose gas is a quantum-mechanical phase of matter, analogous to a classical ideal gas. It is composed of bosons, which have an integer value of spin. The critical temperature is the transition point between these two regimes, and at this critical temperature, the thermal wavelength will be approximately equal to the interparticle distance.

For massive, non-interacting particles, the thermal de Broglie wavelength can be derived from the calculation of the partition function. Assuming a 1-dimensional box of length L, the partition function (using the energy states of the 1D particle in a box) is

$$Z = \sum_n \exp\left(-\frac{E_n}{k_B T}\right) = \sum_n \exp\left(-\frac{h^2 n^2}{8mL^2 k_B T}\right)$$

Since the energy levels are extremely close together, we can approximate this sum as an integral:

$$Z = \int_0^\infty \exp\left(-\frac{h^2 n^2}{8mL^2 k_B T}\right) dn = \sqrt{\frac{2\pi m k_B T}{h^2}} L \equiv \frac{L}{\lambda_{\mathrm{th}}}$$

Hence,

$$\lambda_{\mathrm{th}} = \frac{h}{\sqrt{2\pi m k_B T}},$$

where h is the Planck constant, m is the mass of a gas particle, k_B is the Boltzmann constant, and T is the temperature of the gas.

This can also be expressed using the reduced Planck constant $\hbar = \frac{h}{2\pi}$ as

$$\lambda_{\mathrm{th}} = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}.$$

Given, $m_B = 2m_A$

$$\frac{m_B}{m_A} = 2$$

$$\lambda = \frac{h}{\sqrt{2\pi m K_B T}}$$

$$\lambda \propto \frac{1}{\sqrt{m}}$$

$$\frac{\lambda_A}{\lambda_B} = \sqrt{\frac{m_B}{m_A}} = \sqrt{\frac{2}{1}} = \sqrt{2} : 1$$

S7. Ans.(a)

Sol. High nuclearity carbonyl clusters have metal atoms ≥ 5, each forming atleast one M-M bond. The first HNCC was discovered to be $Rh_6(CO)_{16}$.

Electron Counting in Carbonyl Clusters

Many carbonyl clusters have structures and are electron deficient similar to higher boranes $B_nH_n^{2-}$. Therefore, the approach used to describe the bonding, structure and electron count for higher boranes can be used for carbonyl clusters and other clusters. Wade gave the method for electron counting in HNCC. The structure of the cluster is decided purely by the number of cluster electrons (called skeletal electrons), not by any other factor.

It is a general feature of closo- $B_nH_n^{2-}$ anions that there are no $B—H—B$ or BH_2 group and each B-H bond is a normal 2e bond requiring one electron from B and one electron from H. As boron starts with three electrons, it has two electrons left to contribute to the cluster and these electrons are regarded as skeletal or framework electrons. Thus, $B_nH_n^{2-}$ anions have 2n + 2 skeletal electrons (the 2n electrons from nB atoms and the 2 electrons from the anionic charge). In borane clusters, each BH unit has a sp orbital that points directly towards the centre of the cluster and the other two p_x and p_y orbitals that point along the surface of the cluster.

The nB atoms have 4n atomic orbitals which are always distributed as follows:

n in the n(B-H$_t$) bonding orbitals, (n + 1) in cluster bonding molecular orbitals, (2n - 1) in non-bonding and antibonding cluster molecular orbitals.

In B_nH_n cluster, there are (n + 1) cluster bonding molecular orbitals and 2n electrons contributed by n B-H units, two additional electrons are required for $B_nH_n^{2-}$ ion. This is the reason why the $B_nH_n^{2-}$ ions are more stable than B_nH_n itself.

Since the shape of the cluster depends only on the number of skeletal electrons, it is possible (conceptually) to remove a vertex group, BH$_t$ from the cluster leaving two skeletal electrons that the vertex BH$_t$ group was contributing. This is possible only if BH^{2+} is removed instead of a BH$_t$ unit leaving one vertex of the cluster empty. If BH^{2+} unit is removed from $B_6H_6^{2-}$ then $B_5H_5^{4-}$ ion is obtained. This will have the same polyhedral structure because the electron count has not changed but one vertex is now unoccupied. The neutral B_5H_9 borane can be obtained by adding the appropriate number of protons (four protons in this case), this does not alter the number of electrons in the system because protons (H^+) are the zero electron species. Hence all the bonding molecular orbitals are just filled. The protons bridge the faces of polyhedron which include the missing vertex. In general, the number of skeletal electron pairs in $B_nH_n^{2-}$ will be equal to $\frac{1}{2}(2n+z)$ and the number of vertices (V) is $\left[\frac{1}{2}(2n+z)-1\right]$

The boranes are classified as: closo, nido, arachno, hypho and klado boranes.

The boranes in which each corner is occupied by B atoms are called closo boranes. These have the formula $B_nH_n^{2-}$. The number of vertices and skeletal electron pairs are respectively n and (n + 1). This indicates that the vertices in a closo borane will be one less than the number of skeletal electron pairs.

If one B atom is removed from a vertex of a closo structure, a nido (Latin: nest like) structure will result. The nido boranes have the formula $B_nH_n^{4-}$ or B_nH_{n+4}. The number of vertices will be (n - 1) of an n cornered polyhedron and the number of skeletal electron pairs is (n + 2).

If two vertex B atoms are removed, an arachno (Greek: spider's web like) borane will result. With two vertices missing, the structure is even more open than in the nido structure. Arachno boranes have the formula $B_nH_n^{6-}$ or B_nH_{n+6}. The number of vertices will be (n - 2) of an n cornered polyhedron and the number of skeletal electron pairs is (n + 3).

The hypho (Greek: net like) boranes have the formula $B_nH_n^{8-}$ or B_nH_{n+8}.They have (n - 3) vertices leaving three vertices unoccupied of an n cornered polyhedron and the number of skeletal electron pairs is (n + 4).

The klado (Greek: branched) boranes have the formula $B_nH_n^{10-}$ or B_nH_{n+10}.They have (n - 4) vertices leaving four vertices unoccupied of an n cornered polyhedron. The number of skeletal electron pairs is (n + 5).

The method for calculation of skeletal electron pairs is called the Wade's rule.

* $[B_{10}H_{10}]^{2-}$

Number of skeletal electron pairs $= \frac{10\times2+2}{2}$

$= \frac{22}{2} = 11$

As $n = 10$, therefore, $10+1 = 11$

$[B_{10}H_{10}]^{2-}$ is a closo borane

* $[B_6H_9]^- \longrightarrow [B_6H_6]^{4-}$

Number of skeletal electron pairs $= \frac{6\times2+4}{2}$

$= \frac{16}{2} = 8$

As $n = 6$, therefore $6+2 = 8$

$[B_6H_6]^{4-}$ is a nido borane

S8. Ans.(d)

Sol. The magnetic moment μ of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution.

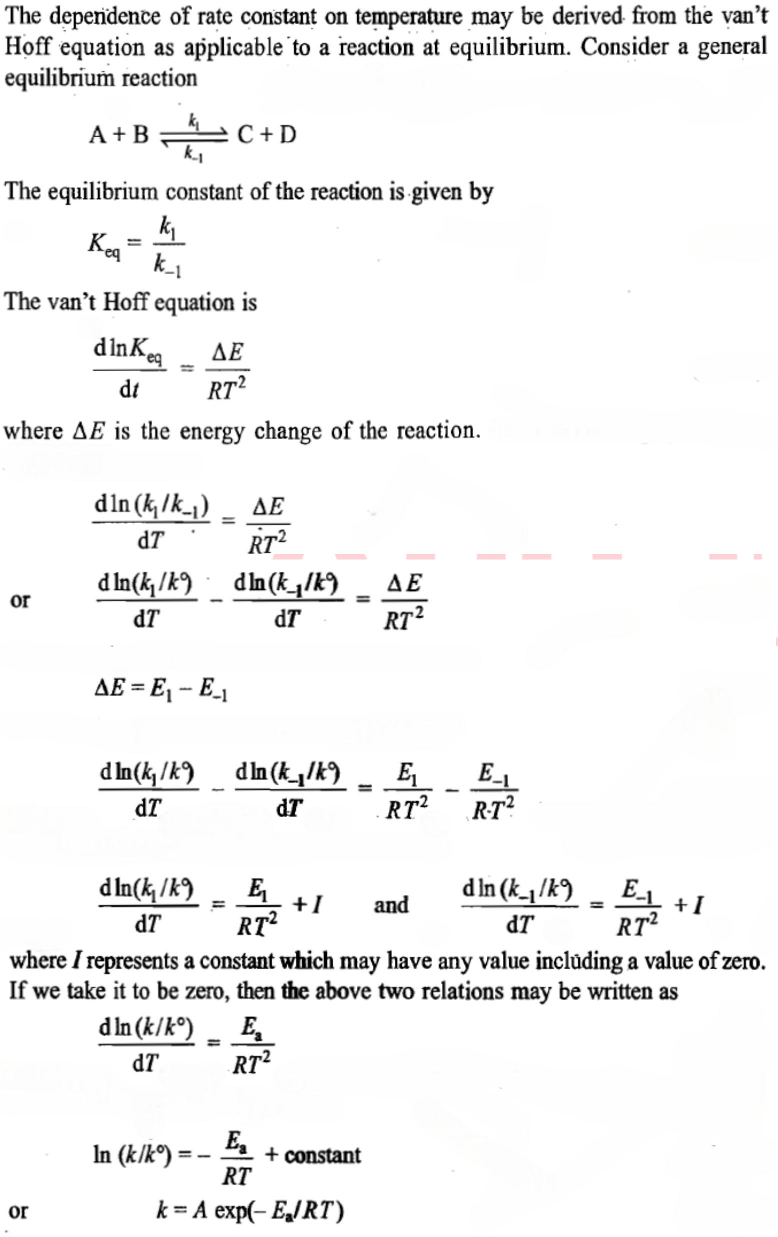
In a free atom or ion, both the orbital and the spin angular momenta give rise to a magnetic moment and contribute to the paramagnetism. When the atom or ion is part of a complex, any orbital angular momentum is normally quenched, or suppressed, as a result of the interactions of the electrons with their nonspherical environment. However, if any electrons are unpaired the net electron spin angular momentum survives and gives rise to spin-only paramagnetism, which is characteristic of many d-metal complexes.

For orbital angular momentum to contribute, and hence for the paramagnetism to differ significantly from the spin-only value, there must be one or more unfilled or half-filled orbitals similar in energy to the orbitals occupied by the unpaired spins and of the appropriate symmetry (one that is related to the occupied orbital by rotation round the direction of the applied field). If that is so, the applied magnetic field can force the electrons to circulate around the metal ion by using the low-lying orbitals and hence it generates orbital angular momentum and a corresponding orbital contribution to the total magnetic moment.

For the lanthanoids, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. In general, theoretical values of the magnetic moment of the ground states of the Ln^{3+} ions agree well with experimental data. This is based on the assumption of large spin–orbit coupling constants, as a consequence of which only the states of lowest J value are populated. This is not true for Eu^{3+}. For $Eu^{3+}(f^6)$, the spin–orbit coupling constant λ is $\approx 300\ \text{cm}^{-1}$, only slightly greater than $kT\ (\approx 200\ \text{cm}^{-1})$. The ground state of the f^6 ion is $^7F_0$ (which is diamagnetic, since J=0), but the states $^7F_1$ and $^7F_2$ are also populated to some extent and give rise to the observed magnetic moment. As expected, at low temperatures, the moment of Eu^{3+} approaches zero.

S9. Ans.(a)

Sol.



The dependence of rate constant on temperature may be derived from the van't Hoff equation as applicable to a reaction at equilibrium. Consider a general equilibrium reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

The equilibrium constant of the reaction is given by

$$K_{eq} = \frac{k_1}{k_{-1}}$$

The van't Hoff equation is

$$\frac{d\ln K_{eq}}{dt} = \frac{\Delta E}{RT^2}$$

where ΔE is the energy change of the reaction.

$$\frac{d\ln(k_1/k_{-1})}{dT} = \frac{\Delta E}{RT^2}$$

or $$\frac{d\ln(k_1/k^\circ)}{dT} - \frac{d\ln(k_{-1}/k^\circ)}{dT} = \frac{\Delta E}{RT^2}$$

$$\Delta E = E_1 - E_{-1}$$

$$\frac{d\ln(k_1/k^\circ)}{dT} - \frac{d\ln(k_{-1}/k^\circ)}{dT} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2}$$

$$\frac{d\ln(k_1/k^\circ)}{dT} = \frac{E_1}{RT^2} + I \quad \text{and} \quad \frac{d\ln(k_{-1}/k^\circ)}{dT} = \frac{E_{-1}}{RT^2} + I$$

where I represents a constant which may have any value including a value of zero. If we take it to be zero, then the above two relations may be written as

$$\frac{d\ln(k/k^\circ)}{dT} = \frac{E_a}{RT^2}$$

$$\ln(k/k^\circ) = -\frac{E_a}{RT} + \text{constant}$$

or $$k = A\exp(-E_a/RT)$$

The main characteristics of Arrhenius equation are described below.

1.Larger the activation energy, smaller the value of rate constant.

2.Larger the activation energy, greater the effect of a given temperature rise on k.

3.At lower temperatures, increase in temperature causes more change in the value of k than that at higher temperatures.

$$k = A\exp\left(\frac{-E_a}{RT}\right)$$

Let, $\frac{E_a}{R} = n$ (constant) $\frac{1}{T} = x$

$$\frac{E_a}{R}\left(\frac{1}{T}\right) = nx$$

$$k = Ae^{-nx}$$

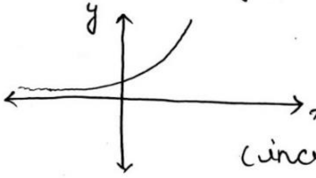
Exponential graph

$e^{-\infty} = 0 \qquad e^{0} = 1 \qquad e^{\infty} = \infty$

① $y = e^{x}$

$x \propto y$

x	0	$-\infty$	∞
y	1	0	∞

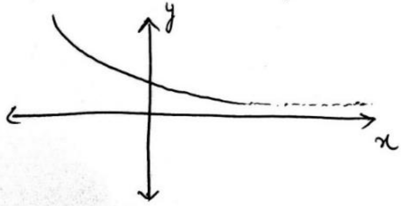


(increasing graph)

② $y = e^{-x}$

$y \propto \frac{1}{x}$

x	0	$-\infty$	∞
y	1	∞	0

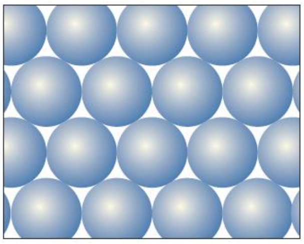


(decreasing graph)

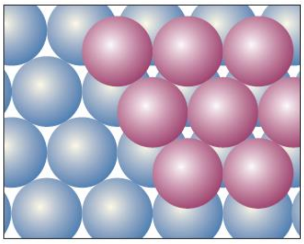
S10. Ans.(a)

Sol. A crystal is built up from regularly repeating 'structural motifs', which may be atoms, molecules, or groups of atoms, molecules, or ions. A space lattice is the pattern formed by points representing the locations of these motifs. The unit cell is an imaginary parallelepiped (parallel-sided figure) that contains one unit of the translationally repeating pattern. A unit cell is commonly formed by joining neighbouring lattice points (A lattice in the sense of a 3-dimensional array of regularly spaced points coinciding with e.g. the atom or molecule positions in a crystal) by straight lines. Such unit cells are called primitive. A primitive unit cell (with lattice points only at the corners) is denoted P. A face-centred unit cell (F) has lattice points at its corners and also at the centres of its six faces.

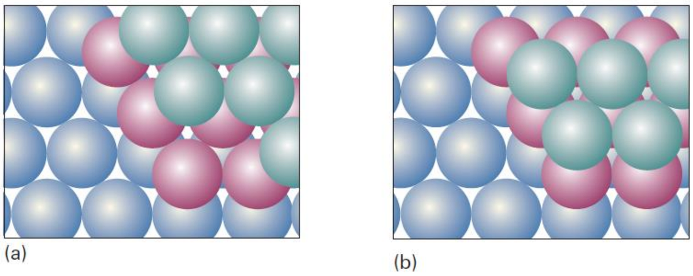
A close-packed layer of identical spheres, one with maximum utilization of space. A close-packed three-dimensional structure is obtained by stacking such close-packed layers on top of one another. In all polytypes, the spheres of second close-packed layer lie in the depressions of the first layer. The third layer may be added in either of two ways. In one, the spheres are placed so that they reproduce the first layer, to give an ABA pattern of layers. Alternatively, the spheres may be placed over the gaps in the first layer, so giving an ABC pattern. Two polytypes are formed if the two stacking patterns are repeated in the vertical direction. If the ABA pattern is repeated, to give the sequence of layers ABABAB..., the spheres are hexagonally close-packed(hcp). Alternatively, if the ABC pattern is repeated, to give the sequence ABCABC..., the spheres are cubic close-packed (ccp). The ccp structure gives rise to a face-centred unit cell, so may also be denoted cubic F (or fcc, for face-centred cubic). Strictly speaking, ccp refers to a close-packed arrangement whereas fcc refers to the lattice type of the common representation of ccp. However, this distinction is rarely made.



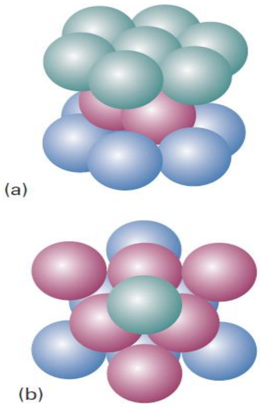
[illegible] The first layer of close-packed spheres used to build a three-dimensional close-packed structure.



[illegible] The second layer of close-packed spheres occupies the dips of the first layer. The two layers are the AB component of the close-packed structure.



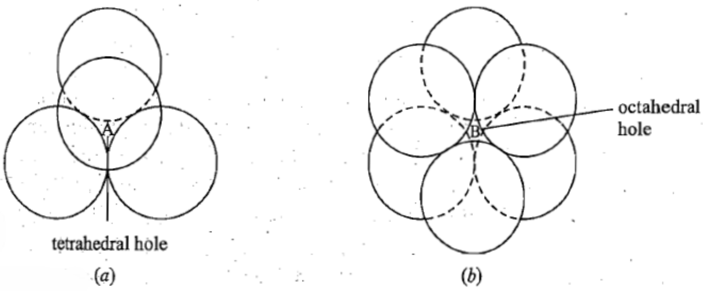
[illegible] (a) The third layer of close-packed spheres might occupy the dips lying directly above the spheres in the first layer, resulting in an ABA structure, which corresponds to hexagonal close-packing. (b) Alternatively, the third layer might lie in the dips that are not above the spheres in the first layer, resulting in an ABC structure, which corresponds to cubic close-packing



[illegible] A fragment of the structure shown in [illegible] revealing the (a) hexagonal (b) cubic symmetry.

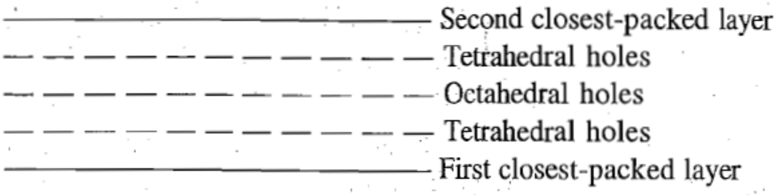
In closest-packing two types of holes are observed: (i) tetrahedral hole, and (ii) octahedral hole.

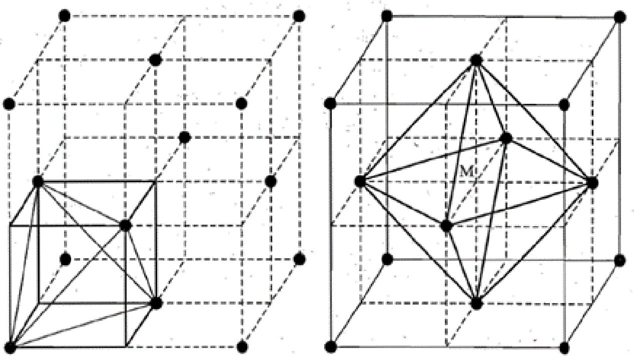
The tetrahedral hole is formed when a sphere fits into the depression formed by three other spheres closest-packed (forming an equilateral triangle) in two dimensions. In two closest-packed layers, there is such a hole above each atom in the first layer and below each atom in the second layer. In a multilayered closest-packed structure, there is a tetrahedral hole above and below each atom; hence there are twice as many tetrahedral holes as there are closest-packed atoms. The octahedral hole is formed when the three closest-packed spheres of one layer (forming an equilateral triangle) is put over three closest-packed spheres of the second layer, their positions being inverted with respect to each other.



(a) Tetrahedral hole shown by position A and (b) octahedral hole shown by position B

In a closest-packed structure, the number of octahedral holes is equal to the number of atoms present and they are located midway between the two closest-packed layers. The positions of these two holes relative to those of the two closest-packed layers are shown below:





Tetrahedral hole in closed-packed atoms

Octahedral hole in closed-packed atoms

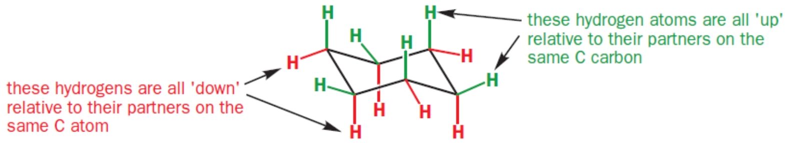
The atoms in one small cube actually touch one another. Since these atoms are at alternate corners of the cube they form a tetrahedron with a hole in the centre. The entire unit cell contains eight tetrahedral holes, one in each small cube. Since there are four atoms per cubic unit cell, there will be two tetrahedral holes per closest-packed atom.

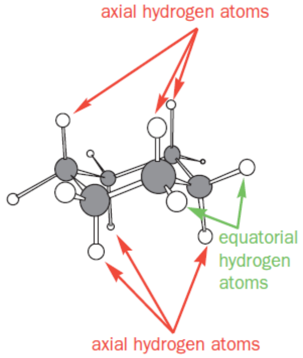
The intersections of the lines at M are not occupied by an atom and this is surrounded by six atoms at the corners of an octahedron. This intersection becomes an octahedral hole when the atoms just touch one another: Besides the intersection M, there are twelve more intersections at the centres of the edges. Since each edge is common to four-unit cells, there are only three intersections (holes) from edges that belong completely to one unit cell. Thus, in all we have four octahedral holes in one unit cell and hence one octahedral hole per closest-packed atom.

S11. Ans.(c)

Sol. In the chair conformation of cyclohexane, all six carbon atoms are identical, but there are two types of protons-one type stick either vertically up or down and are called axial hydrogen atoms; the other sort stick out sideways and are called equatorial hydrogen atoms.

As you go round the ring, notice that each of the CH_2 groups has one hydrogen sticking up and one sticking down. However, all the ‘up’ ones alternate between axial and equatorial, as do all the ‘down’ ones.





In a monosubstituted cyclohexane, there can exist two different chair conformers: one with the substituent axial, the other with it equatorial. When there are two or more substituents on the ring, stereoisomerism is possible.

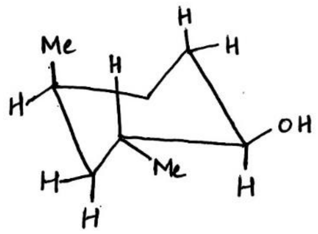
substituent equatorial

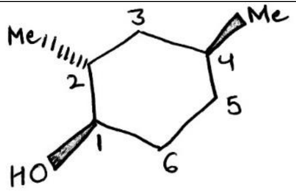
substituent axial

In the given chair conformation, the Me groups are trans to each other. The OH group is trans to the adjacent methyl group while cis to the methyl group present on the fourth position.

Remember, the ‘*cis*’ and ‘*trans*’ prefixes merely indicate that both groups are on the same ‘side’ of the cyclohexane ring. Whether the substituents are both axial/equatorial or one axial and the other equatorial depends on the substitution pattern. Each time you meet a molecule, draw the conformation or make a model to find out which bonds are axial and equatorial.

It is not always easy to decide if an equatorial substituent is ‘up’ or ‘down’. The key is to compare it with its axial partner on the same C atom-axial substituents very clearly point ‘up’ or ‘down’. If the axial partner is ‘up’, the equatorial substituent must be ‘down’ and vice versa.





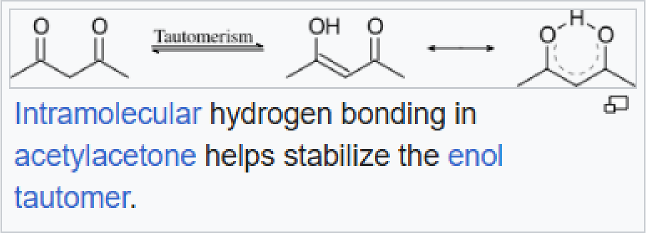
S12. Ans.(d)

Sol. Decarboxylation is a chemical reaction that removes a carboxyl group and releases carbon dioxide (CO_2). Usually, decarboxylation refers to a reaction of carboxylic acids, removing a carbon atom from a carbon chain.

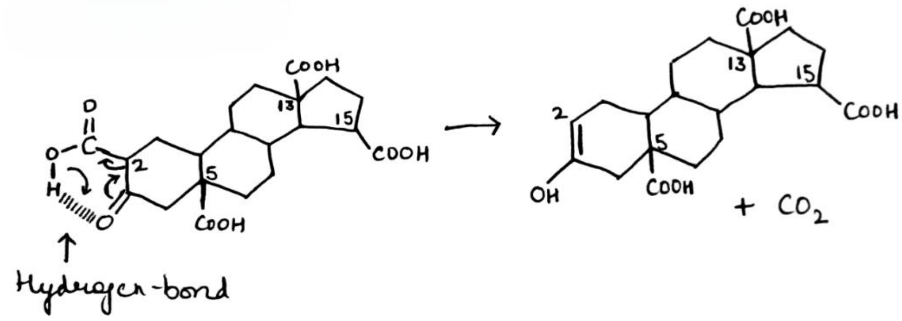
In chemistry, a hydrogen bond (or H-bond) is primarily an electrostatic force of attraction between a hydrogen (H) atom which is covalently bonded to a more electronegative "donor" atom or group (Dn), and another electronegative atom bearing a lone pair of electrons—the hydrogen bond acceptor (Ac). Such an interacting system is generally denoted Dn−H···Ac, where the solid line denotes a polar covalent bond, and the dotted or dashed line indicates the hydrogen bond. The most frequent donor and acceptor atoms are the period 2 elements nitrogen (N), oxygen (O), and fluorine (F).

Hydrogen bonds can be intermolecular (occurring between separate molecules) or intramolecular (occurring among parts of the same molecule).

In a hydrogen bond, the electronegative atom not covalently attached to the hydrogen is named the proton acceptor, whereas the one covalently bound to the hydrogen is named the proton donor. The hydrogen of the donor is protic and therefore can act as a Lewis acid and the acceptor is the Lewis base. Hydrogen bonds are represented as H···Y system, where the dots represent the hydrogen bond. Liquids that display hydrogen bonding (such as water) are called associated liquids.



Intramolecular hydrogen bonding in acetylacetone helps stabilize the enol tautomer.



S13. Ans.(b)

Sol. Aromatic compounds

Aromatic compounds or arenes are organic compounds "with a chemistry typified by benzene" and "cyclically conjugated." Aromatic compounds are now defined as cyclic compounds satisfying Hückel's Rule.

In organic chemistry, Hückel's rule predicts that a planar ring molecule will have aromatic properties if it has $4n + 2$ π-electrons, where n is a non-negative integer. A cyclic ring molecule follows Hückel's rule when the number of its π-electrons equals $4n + 2$, although clearcut examples are really only established for values of $n = 0$ up to about $n = 6$.

Criteria for simple aromatics are:

1. the molecule must have $4n + 2$ (a so-called "Hückel number") π electrons (2, 6, 10, ...) in a conjugated system of p orbitals (usually on sp^2-hybridized atoms, but sometimes sp-hybridized);
2. the molecule must be (close to) planar (p orbitals must be roughly parallel and able to interact, implicit in the requirement for conjugation);
3. the molecule must be cyclic (as opposed to linear);
4. the molecule must have a continuous ring of p atomic orbitals (there cannot be any sp^3 atoms in the ring, nor do exocyclic p orbitals count).

Antiaromatic compounds

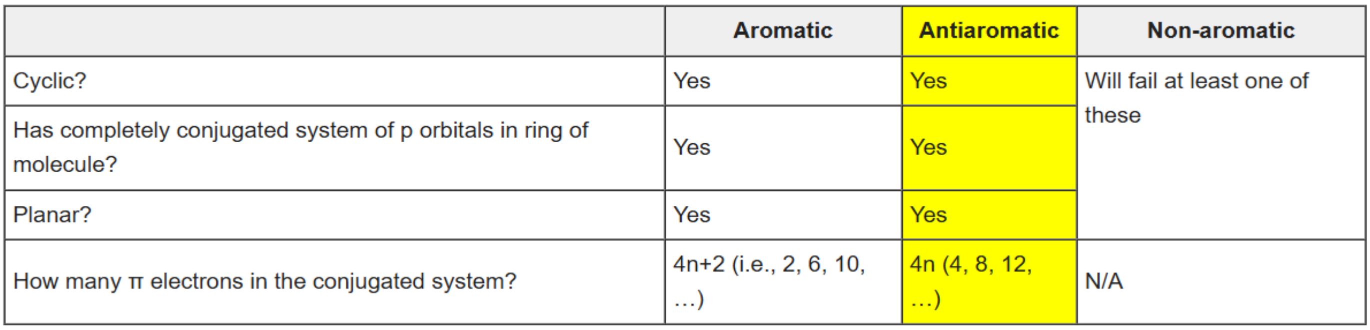
Antiaromaticity is a chemical property of a cyclic molecule with a π electron system that has higher energy, i.e., it is less stable due to the presence of 4n delocalised (π or lone pair) electrons in it, as opposed to aromaticity. Unlike aromatic compounds, which follow Hückel's rule ([$4n$+2]π electrons) and are highly stable, antiaromatic compounds are highly unstable and highly reactive.

The term 'antiaromaticity' was first proposed as "a situation in which a cyclic delocalization of electrons is destabilising". The IUPAC criteria for antiaromaticity are as follows:

1. The molecule must be cyclic.
2. The molecule must be planar.
3. The molecule must have a complete conjugated π-electron system within the ring.
4. The molecule must have $4n$ π-electrons where n is any integer within the conjugated π-system.

This differs from aromaticity only in the fourth criterion: aromatic molecules have $4n + 2$ π-electrons in the conjugated π system and therefore follow Hückel's rule. Non-aromatic molecules are either noncyclic, nonplanar, or do not have a complete conjugated π system within the ring.

Comparing aromaticity, antiaromaticity and non-aromaticity



	Aromatic	Antiaromatic	Non-aromatic
Cyclic?	Yes	Yes	Will fail at least one of these
Has completely conjugated system of p orbitals in ring of molecule?	Yes	Yes	
Planar?	Yes	Yes	
How many π electrons in the conjugated system?	4n+2 (i.e., 2, 6, 10, …)	4n (4, 8, 12, …)	N/A

Homoaromatic Compounds

Homoaromatic compound, which may be defined as a compound that contains one or more sp^3-hybridized carbon atoms in an otherwise conjugated cycle. In order for the orbitals to overlap most effectively so as to close a loop, the sp^3 atoms are forced to lie almost vertically above the plane of the aromatic atoms.

The given compound contains 12 pi electrons. Hence, the compound is antiaromatic.

S14. Ans.(b)

Sol. A problem that we frequently encounter in physical chemistry is the following: Given $\hat{A}$, find a function $\phi(x)$ and a constant *a* such that

$$\hat{A}\phi(x) = a\phi(x)$$

Note that the result of operating on the function $\phi(x)$ by $\hat{A}$ is simply to give $\phi(x)$ back again, only multiplied by a constant factor. Clearly, $\hat{A}$ and $\phi(x)$ have a very special relationship to each other. The function $\phi(x)$ is called an *eigenfunction* of the operator $\hat{A}$, and a is called an *eigenvalue*. The problem of determining $\phi(x)$ and a for a given $\hat{A}$ is called an *eigenvalue problem*.

An operator is a symbol that tells you to do something to whatever follows the symbol.

x component of the linear momentum can be represented in quantum mechanics by an operator of the form

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$$

We apply $\hat{P}_x$ to e^{ikx} and find

$$\hat{P}_x e^{ikx} = -i\hbar\frac{\partial}{\partial x}e^{ikx} = \hbar k e^{ikx}$$

and so we see that e^{ikx} is an eigenfunction and $\hbar k$ is the eigenvalue of the operator $\hat{P}_x$.

The momentum operator in three dimensions is

$$\hat{\mathbf{P}} = -i\hbar\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right)$$

S15. Ans.(d)

Sol. Flame photometry is a type of atomic emission spectroscopy. It is also known as flame emission spectroscopy. A photoelectric flame photometer is an instrument used in inorganic chemical analysis to determine the concentration of certain metal ions, among them sodium, potassium, lithium, and calcium. Group 1 (alkali metals) and Group 2 (alkaline earth metals) are quite sensitive to flame *photometry* due to their low excitation energies.

In principle, it is a controlled flame test with the intensity of the flame color quantified by photoelectric circuitry. The intensity of the color will depend on the energy that had been absorbed by the atoms that was sufficient to vaporise them. The sample is introduced to the flame at a constant rate. Filters select which colours the photometer detects and exclude the influence of other ions. Before use, the device requires calibration with a series of standard solutions of the ion to be tested.

The basis of flame photometric working is that, the species of alkali metals (Group 1) and alkaline earth metals (Group II) metals are dissociated due to the thermal energy provided by the flame source. Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques. The subsequent loss of energy will result in the movement of excited atoms to the low energy ground state with emission of some radiations, which can be visualized in the visible region of the spectrum. The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques while the emitting radiation intensity is measured using the emission techniques. The wavelength of emitted light is specific for specific elements.

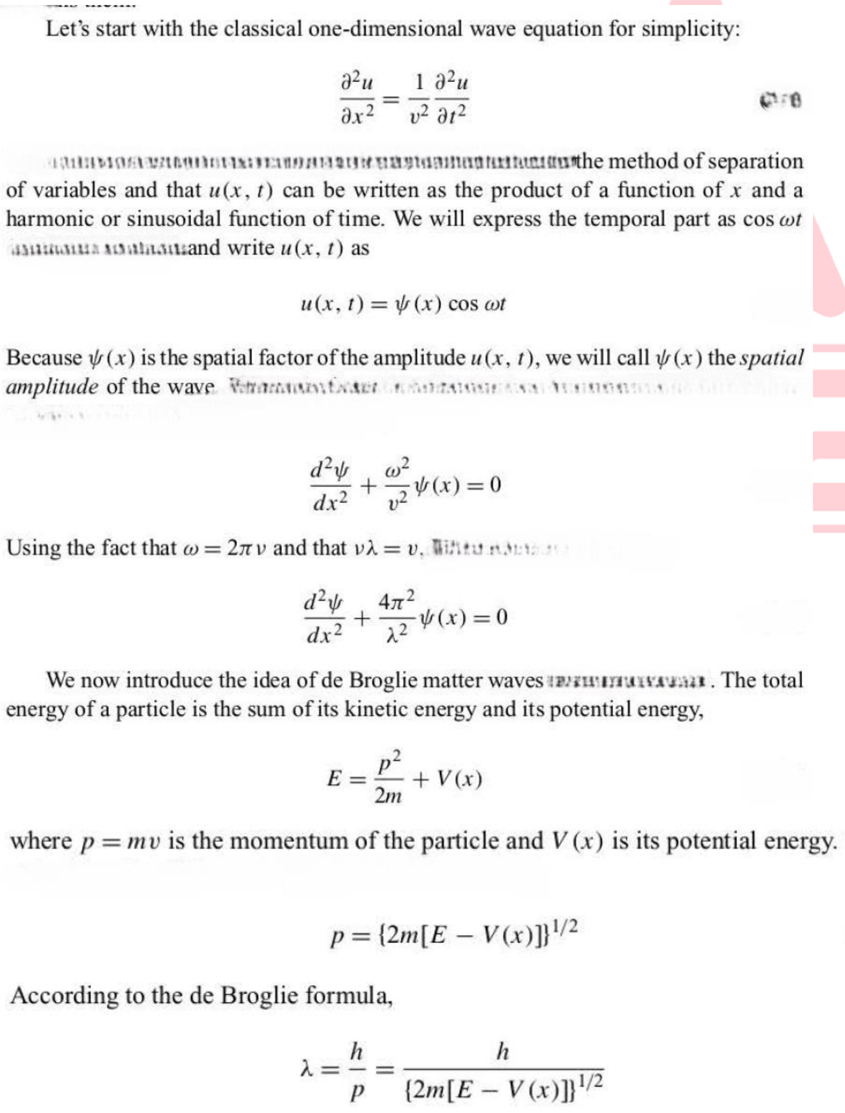
The band at 766 nm in flame photometry is due to the emission from neutral potassium atoms. When a potassium ion (e.g., from a blood serum sample) is introduced into the flame, the heat causes the potassium ions to convert into neutral potassium atoms. These neutral atoms are then excited to a higher energy state due to the thermal energy of the flame. As they return to their ground state, they emit light at specific characteristic wavelengths, one of which is 766 nm. This emission is used to detect potassium in flame photometric analysis.

Name of the element	Emitted wavelength range (nm)	Observed colour of the flame
Potassium (K)	766	 Violet

S16. Ans.(a)

Sol. An operator is a symbol that tells you to do something to whatever follows the symbol.

The Schrodinger equation is fundamental equation of quantum mechanics. The solutions to the Schrodinger equation are called wave functions.



Let's start with the classical one-dimensional wave equation for simplicity:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$$

[illegible] the method of separation of variables and that $u(x, t)$ can be written as the product of a function of x and a harmonic or sinusoidal function of time. We will express the temporal part as $\cos \omega t$ [illegible] and write $u(x, t)$ as

$$u(x, t) = \psi(x) \cos \omega t$$

Because $\psi(x)$ is the spatial factor of the amplitude $u(x, t)$, we will call $\psi(x)$ the *spatial amplitude* of the wave. [illegible]

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0$$

Using the fact that $\omega = 2\pi\nu$ and that $\nu\lambda = v$, [illegible]

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

We now introduce the idea of de Broglie matter waves [illegible]. The total energy of a particle is the sum of its kinetic energy and its potential energy,

$$E = \frac{p^2}{2m} + V(x)$$

where $p = mv$ is the momentum of the particle and $V(x)$ is its potential energy.

$$p = \{2m[E - V(x)]\}^{1/2}$$

According to the de Broglie formula,

$$\lambda = \frac{h}{p} = \frac{h}{\{2m[E - V(x)]\}^{1/2}}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0$$

where $\hbar$ (called h-bar) $= h/2\pi$.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

The Schrodinger equation, a differential equation whose solution, $\psi(x)$,describes a particle of mass m moving in a potential field described by $V(x)$.The exact nature of $\psi(x)$ is vague at this point, but in analogy to the classical wave equation, it is a measure of the amplitude of the matter wave and is called the wave function of the particle.

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

If we denote the operator in brackets by $\hat{H}$, then [illegible]

$$\hat{H}\psi(x) = E\psi(x)$$

We have formulated the Schrödinger equation as an eigenvalue problem. The operator $\hat{H}$,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

is called the *Hamiltonian operator*. The wave function is an eigenfunction, and the energy is an eigenvalue of the Hamiltonian operator. This suggests a correspondence between the Hamiltonian operator and the energy. [illegible]

If $V(x) = 0$ [illegible], the energy is all kinetic energy and so we define a kinetic energy operator according to

$$\hat{T}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

(Strictly speaking, the derivative here should be a partial derivative, but we will consider only one-dimensional systems for the time being.) Furthermore, classically, $T = p^2/2m$, and so we conclude that

$$\hat{P}_x^2 = -\hbar^2\frac{d^2}{dx^2}$$

When two operators act sequentially on a function, as in $\hat{A}\hat{B}f(x)$, we apply each operator in turn, working from right to left

$$\hat{A}\hat{B}f(x) = \hat{A}[\hat{B}f(x)] = \hat{A}h(x)$$

where $h(x) = \hat{B}f(x)$. An important difference between operators and ordinary algebraic quantities is that operators do not necessarily *commute*. If

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x) \qquad \text{(commutative)}$$

for arbitrary $f(x)$, then we say that $\hat{A}$ and $\hat{B}$ *commute*. If

$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x) \qquad \text{(noncommutative)}$$

for arbitrary $f(x)$, then we say that $\hat{A}$ and $\hat{B}$ do not commute. For example, if $\hat{A} = d/dx$ and $\hat{B} = x$ (multiply by x), then

$$\hat{A}\hat{B}f(x) = \frac{d}{dx}[xf(x)] = f(x) + x\frac{df}{dx}$$

and

$$\hat{B}\hat{A}f(x) = x\frac{d}{dx}f(x) = x\frac{df}{dx}$$

Therefore, $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$, and $\hat{A}$ and $\hat{B}$ do not commute. In this particular case, we have

$$\hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = f(x)$$

or

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = \hat{I}f(x)$$

where we have introduced the identity operator $\hat{I}$, which simply multiplies $f(x)$ by unity. [illegible]

$$\hat{A}\hat{B} - \hat{B}\hat{A} = \hat{I}$$

Realize that an operator equality like this is valid only if it is true for all $f(x)$. The combination of $\hat{A}$ and $\hat{B}$ [illegible] occurs often and is called the *commutator*, $[\hat{A}, \hat{B}]$, of $\hat{A}$ and $\hat{B}$:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $[\hat{A}, \hat{B}]f(x) = 0$ for all $f(x)$ on which the commutator acts, then we write that $[\hat{A}, \hat{B}] = 0$ and we say that $\hat{A}$ and $\hat{B}$ commute.

$$\left[\left(\frac{p_x^2}{2m}+V\right), p_x\right] = \frac{1}{2m}[p_x^2, p_x] + [V, p_x]$$

$$[p_x^2, p_x] = 0$$

$$p_x = -i\hbar\frac{d}{dx}$$

$$[H, p_x]\psi = V, p_x\psi - p_x V\psi$$

$$= V(-i\hbar)\frac{d\psi}{dx} - (-i\hbar)\frac{d}{dx}(V\psi)$$

$$= \cancel{-i\hbar V\frac{d\psi}{dx}} + i\hbar\left(\psi\frac{dV}{dx}\right) + \left(\cancel{i\hbar V\frac{d\psi}{dx}}\right)$$

$$[H, p_x]\psi = i\hbar\frac{dV}{dx}\psi$$

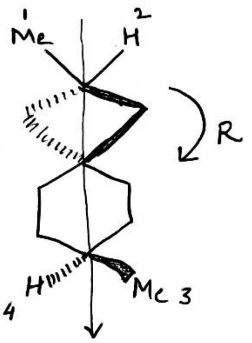
S17. Ans.(c)

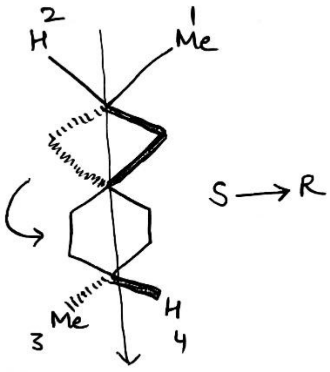
Sol. The *R*/*S* system is an important nomenclature system for denoting enantiomers. This approach labels each chiral center *R* or *S* according to a system by which its substituents are each assigned a *priority*, according to the Cahn–Ingold–Prelog priority rules (CIP), based on atomic number. When the center is oriented so that the lowest-priority substituent of the four is pointed away from the viewer, the viewer will then see two possibilities: if the priority of the remaining three substituents decreases in clockwise direction, it is labeled *R* (for Latin: *rectus* – right); if it decreases in counterclockwise direction, it is *S* (for Latin: *sinister* – left).

The Cahn–Ingold–Prelog (CIP) sequence rules are a standard process to completely and unequivocally name a stereoisomer of a molecule. The purpose of the CIP system is to assign an *R* or *S* descriptor to each stereocenter.

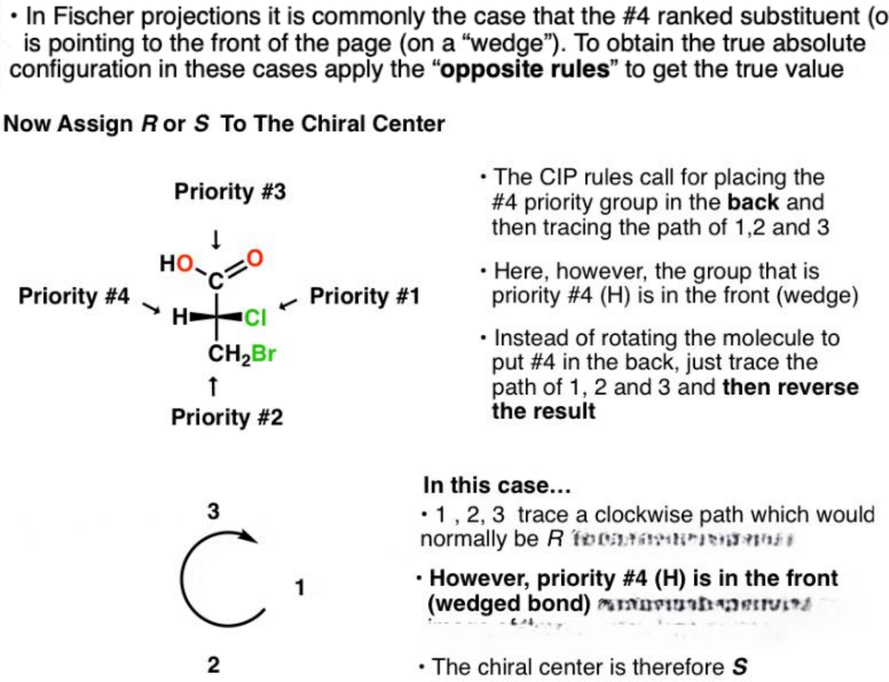
1. Compare the atomic number (*Z*) of the atoms directly attached to the stereocenter; the group having the atom of higher atomic number Z receives higher priority (i.e. number 1).
2. If there is a tie, the atoms at distance 2 from the stereocenter have to be considered: a list is made for each group of further atoms bonded to the one directly attached to the stereocenter. Each list is arranged in order of decreasing atomic number Z. Then the lists are compared atom by atom; at the earliest difference, the group containing the atom of higher atomic number Z receives higher priority.

Identical compounds (homomers) are those in which all of the atoms are arranged in the same spatial orientation.





Information Booster



- In Fischer projections it is commonly the case that the #4 ranked substituent (often H) is pointing to the front of the page (on a “wedge”). To obtain the true absolute configuration in these cases apply the “**opposite rules**” to get the true value

Now Assign *R* or *S* To The Chiral Center

- The CIP rules call for placing the #4 priority group in the **back** and then tracing the path of 1,2 and 3
- Here, however, the group that is priority #4 (H) is in the front (wedge)
- Instead of rotating the molecule to put #4 in the back, just trace the path of 1, 2 and 3 and **then reverse the result**

In this case…

- 1 , 2, 3 trace a clockwise path which would normally be *R*
- **However, priority #4 (H) is in the front (wedged bond)**
- The chiral center is therefore ***S***

Additional Knowledge

Enantiomers

An enantiomer is one of a pair of molecular entities which are mirror images of each other and non-superposable. Enantiomer molecules are like right and left hands: one cannot be superposed onto the other without first being converted to its mirror image. It is solely a relationship of chirality and the permanent three-dimensional relationships among molecules or other chemical structures: no amount of re-orientation of a molecule as a whole or conformational change converts one chemical into its enantiomer.

A common naming conventions for specifying one of the two enantiomers (the absolute configuration) of a given chiral molecule: the R/S system is based on the geometry of the molecule. A pair of enantiomers have opposite configurations.

Diastereomers

In stereochemistry, diastereomers are a type of stereoisomer. Diastereomers are defined as non-mirror image, non-identical stereoisomers. Hence, they occur when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereocenters and are not mirror images of each other. When two diastereoisomers differ from each other at only one stereocenter, they are epimers. Each stereocenter gives rise to two different configurations and thus typically increases the number of stereoisomers by a factor of two.

Diastereomers differ from enantiomers in that the latter are pairs of stereoisomers that differ in all stereocenters and are therefore mirror images of one another. Enantiomers of a compound with more than one stereocenter are also diastereomers of the other stereoisomers of that compound that are not their mirror image (that is, excluding the opposing enantiomer).

Constitutional isomers

In chemistry, a structural isomer (or constitutional isomer in the IUPAC nomenclature) of a compound is another compound whose molecule has the same number of atoms of each element, but with logically distinct bonds between them.

For example, butanol $H_3C{-}(CH_2)_3{-}OH$, methyl propyl ether $H_3C{-}(CH_2)_2{-}O{-}CH_3$, and diethyl ether $(H_3CCH_2{-})_2O$ have the same molecular formula $C_4H_{10}O$ but are three distinct structural isomers.

S18. Ans.(a)

Sol. The standard half-cell potentials are employed for calculating accurate values of various quantities such as equilibrium constant of a weak acid and ionic product of water. It is, therefore, essential to know their accurate values. For this purpose, the method of extrapolation is employed. To illustrate the method, we consider the following cell.

$$\mathrm{Pt} \mid \mathrm{H_2(1\ bar)} \mid \mathrm{HCl}(a) \mid \mathrm{AgCl(s)} \mid \mathrm{Ag}$$

The cell reaction is

$$\mathrm{AgCl} + \tfrac{1}{2}\mathrm{H_2} \rightarrow \mathrm{Ag} + \mathrm{Cl^-} + \mathrm{H^+}$$

and the cell potential is given by

$$E = E^\circ - \frac{RT}{F} \ln \frac{(a_{\mathrm{H^+}})(a_{\mathrm{Cl^-}})}{(f_{\mathrm{H_2}}/f^\circ)^{1/2}}$$

Assuming ideal behaviour for the gas, we get

$$E = E^\circ - \frac{RT}{F} \ln (a_{\mathrm{H^+}})(a_{\mathrm{Cl^-}})$$

Since individual ionic activities cannot be determined, we express $a_{\mathrm{H^+}}$ and $a_{\mathrm{Cl^-}}$ in terms of mean activity $a_\pm$ of hydrochloric acid by the relation

$$a_\pm^2 = (a_{\mathrm{H^+}})(a_{\mathrm{Cl^-}})$$

Now the mean activity may be expressed in terms of mean molality $m_\pm$ of the ions and the mean activity coefficient $\gamma_\pm$ by the relation

$$a_\pm = m'_\pm \, \gamma_\pm$$

For HCl solution

$$m'_\pm = m' = m/m^\circ$$

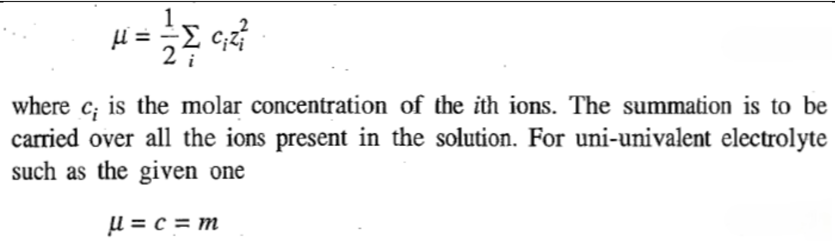
where m is the molality of the solution.

$$E = E^\circ - \frac{2\,RT}{F} \ln m' - \frac{2\,RT}{F} \ln \gamma_\pm$$

If the measurements are done in dilute solutions, than $\gamma_\pm$ can be expressed in terms of the ionic strength of the solution using the Debye-Hückel limiting law[††]

$$\log \gamma_\pm = -A z_+ |z_-| \mu^{1/2}$$

where A is equal to 0.514 $(\mathrm{mol\ dm^{-3}})^{-1/2}$, z_+ and z_- are the charge numbers of ions, and μ is the ionic strength of the solution. The latter is defined as

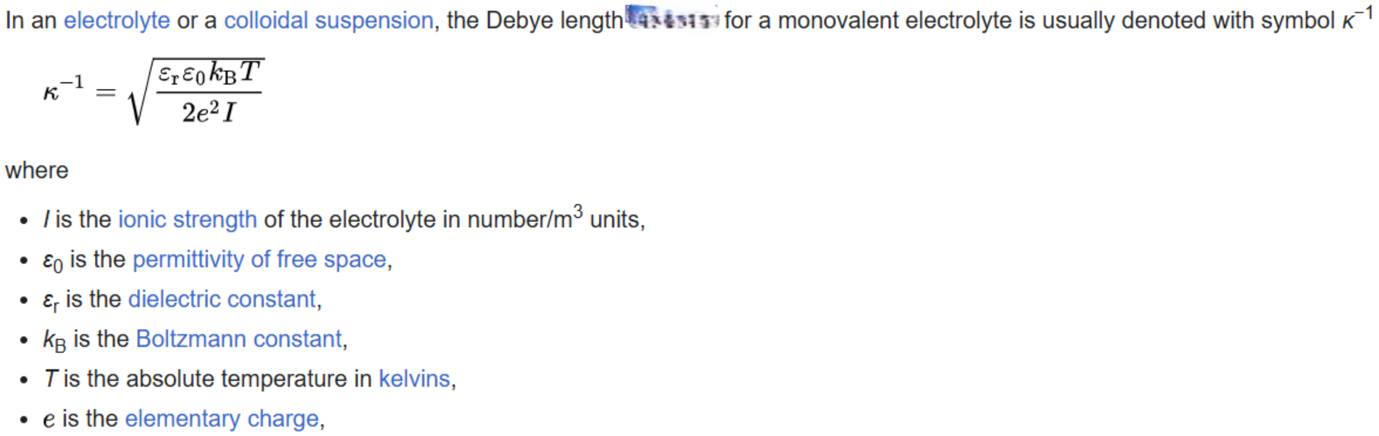


$$\mu = \frac{1}{2}\sum_i c_i z_i^2$$

where c_i is the molar concentration of the ith ions. The summation is to be carried over all the ions present in the solution. For uni-univalent electrolyte such as the given one

$$\mu = c = m$$

In plasmas and electrolytes, the Debye length λ_D (Debye radius or Debye–Hückel screening length), is a measure of a charge carrier's net electrostatic effect in a solution and how far its electrostatic effect persists. With each Debye length the charges are increasingly electrically screened and the electric potential decreases in magnitude by 1/e. A Debye sphere is a volume whose radius is the Debye length.

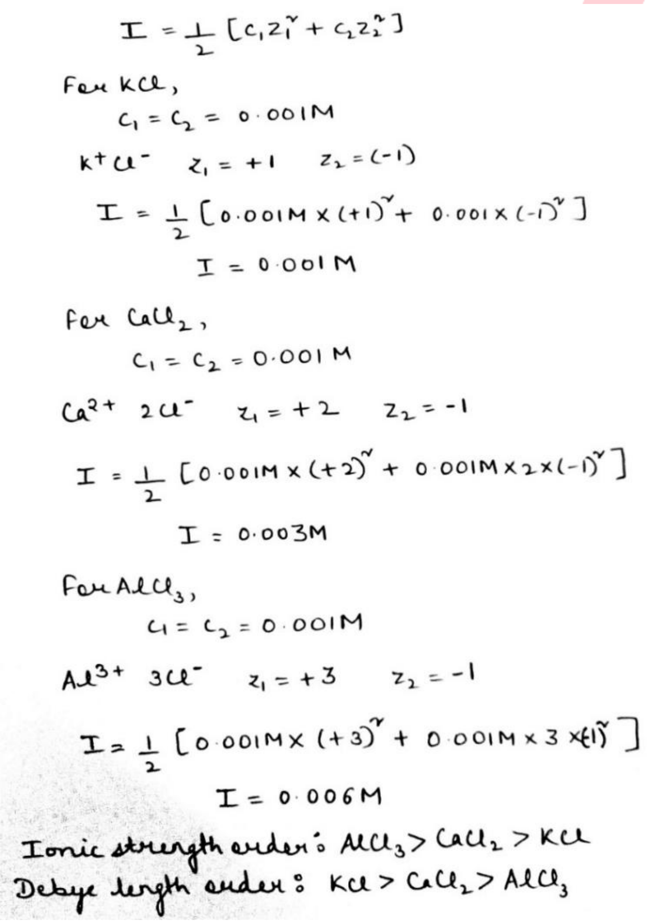


In an electrolyte or a colloidal suspension, the Debye length [illegible] for a monovalent electrolyte is usually denoted with symbol κ^{-1}

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2e^2 I}}$$

where

- I is the ionic strength of the electrolyte in number/m^3 units,
- ε_0 is the permittivity of free space,
- ε_r is the dielectric constant,
- k_B is the Boltzmann constant,
- T is the absolute temperature in kelvins,
- e is the elementary charge,



$$I = \frac{1}{2}[c_1 z_1^2 + c_2 z_2^2]$$

For KCl,

$c_1 = c_2 = 0.001M$

$K^+ \; Cl^-$ $z_1 = +1$ $z_2 = (-1)$

$$I = \frac{1}{2}[0.001M \times (+1)^2 + 0.001 \times (-1)^2]$$

$$I = 0.001M$$

For $CaCl_2$,

$c_1 = c_2 = 0.001M$

$Ca^{2+} \; 2Cl^-$ $z_1 = +2$ $z_2 = -1$

$$I = \frac{1}{2}[0.001M \times (+2)^2 + 0.001M \times 2 \times (-1)^2]$$

$$I = 0.003M$$

For $AlCl_3$,

$c_1 = c_2 = 0.001M$

$Al^{3+} \; 3Cl^-$ $z_1 = +3$ $z_2 = -1$

$$I = \frac{1}{2}[0.001M \times (+3)^2 + 0.001M \times 3 \times (-1)^2]$$

$$I = 0.006M$$

Ionic strength order: $AlCl_3 > CaCl_2 > KCl$

Debye length order: $KCl > CaCl_2 > AlCl_3$

S19. Ans.(a)

Sol. Metal cluster compounds are a molecular ion or neutral compound composed of three or more metals and featuring significant metal-metal interactions.

The halides of low-valent early metals often are clusters with extensive M-M bonding. The situation contrasts with the higher halides of these metals and virtually all halides of the late transition metals, where metal-halide bonding is replete.

Transition metal halide clusters are prevalent for the heavier metals: Zr, Hf, Nb, Ta, Mo, W, and Re.

$Na_4[Nb_6Cl_{18}] \Rightarrow 4Na^+ [Nb_6Cl_{18}]^{4-}$

Let the oxidation state of niobium be x

$[Nb_6Cl_{18}]^{4-} \Rightarrow 6x - 18 = -4$

$6x = 14$

Option a : $(2\times3) + (4\times2) = 6 + 8 = 14$

Option b : $(6\times2) = 12$

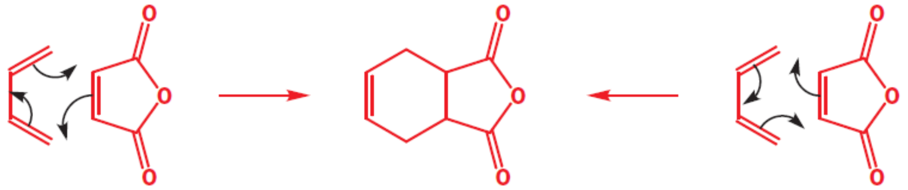
Option c : $(6\times3) = 18$

Option d : $(3\times2) + (3\times3) = 6 + 9 = 15$

S20. Ans.(b)

Sol. Electrons move round a circle and there are no positive or negative charges on any intermediates-indeed, there are no intermediates at all. This type of reaction is called pericyclic. The most famous example is the Diels–Alder reaction.

Each arrow leads directly to the next, and the last arrow connects to the first. We have drawn the electrons rotating clockwise, but it would make no difference at all if we drew the electrons rotating anticlockwise.

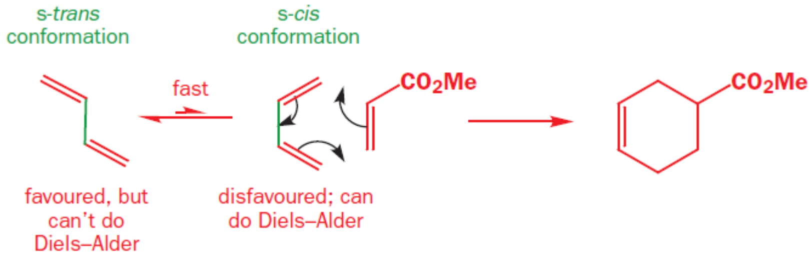


Both mechanisms are equally correct. The electrons do not really rotate at all. In reality two π bonds disappear and two σ bonds take their place by the electrons moving smoothly out of the π orbitals into the σ orbitals. Such a reaction is called a cycloaddition.

Diels–Alder reactions occur between a conjugated diene and an alkene, usually called the dienophile.

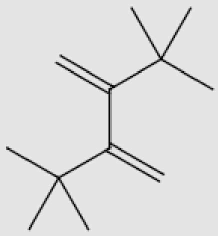
The diene component in the Diels–Alder reaction can be open-chain or cyclic and it can have many different kinds of substituents. There is only one limitation: it must be able to take up the conformation shown in the mechanism. Butadiene normally prefers the s-*trans* conformation with the two double bonds as far away from each other as possible for steric reasons. The barrier to rotation about the central σ bond is small (about 30 kJ mol^{-1} at room temperature) and rotation to the less favourable but reactive s-*cis* conformation is rapid.

The 's' in the terms 's-cis' and 's-trans' refers to a σ bond and indicates that these are conformations about a single bond and not configurations about a double bond. The diene must have the s-*cis* conformation. If the diene does not have, or cannot adopt, a *cisoid* conformation then no Diels–Alder cycloaddition reaction occurs.



Substituents in the butadiene molecule influence the rate of cycloaddition through their electronic nature and by a steric effect on the conformational equilibrium. The rate of the reaction is often increased by electron-donating substituents (e.g. NMe_2, OMe, Me) on the diene, as well as by electron-withdrawing substituents on the dienophile. Bulky substituents that discourage the diene from adopting the cisoid conformation hinder the reaction.

2,3-di-tertbutylbutadiene is completely unreactive in Diels-Alder reaction. Apparently 2,3-di-tert-butylbutadiene is prevented from attaining the necessary planar cisoid conformation by steric effects of the two bulky tert-butyl substituents.



2,3-di-*tert*-butylbutadiene

N is more reactive than M due to the +I effect of the t-butyl group.

In Organic chemistry, the inductive effect in a molecule is a local change in the electron density due to electron-withdrawing or electron-donating groups elsewhere in the molecule, resulting in a permanent dipole in a bond. It is present in a σ (sigma) bond.

The halogen atoms in an alkyl halide are electron withdrawing while the alkyl groups have electron donating tendencies. If the electronegative atom (missing an electron, thus having a positive charge) is then joined to a chain of atoms, typically carbon, the positive charge is relayed to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the -*I* effect. In short, alkyl groups tend to donate electrons, leading to the +*I* effect.

The effect of the sigma electron displacement towards the more electronegative atom by which one end becomes positively charged and the other end negatively charged is known as the inductive effect. The -*I* effect is a permanent effect & generally represented by an arrow on the bond.

However, some groups, such as the alkyl group, are less electron-withdrawing than hydrogen and are therefore considered as electron-releasing/ electron-donating groups. This is electron-releasing character and is indicated by the +*I* effect. In short, alkyl groups tend to give electrons, leading to the induction effect.