Chapter 4: Chemical Bonding and Molecular Structure

Exercises — Exercises

Q1 Explain the formation of a chemical bond.

SOLUTION

A chemical bond is the attractive force that holds atoms or ions together in a molecule or compound. Bonds form because the resulting arrangement is more stable (lower in energy) than the separated atoms.

Kössel-Lewis approach: Atoms achieve stable noble-gas configurations by either transferring or sharing valence electrons.

Ionic bond: Formed by transfer of electrons from a metal (low ionisation enthalpy) to a non-metal (high negative electron-gain enthalpy). The oppositely charged ions attract each other electrostatically. Example: Na donates 1 electron to Cl, forming Na^+ and Cl^-, which combine to give NaCl.

Covalent bond: Formed by sharing of electron pairs between non-metal atoms so each attains an octet (or duplet for H). Example: Two Cl atoms each contribute 1 electron to form a shared pair in Cl_2.

Bond formation lowers the potential energy of the system; the minimum in the potential-energy curve corresponds to the equilibrium bond length and gives the bond dissociation enthalpy.

Answer: A chemical bond (ionic or covalent) forms because atoms lower their energy by attaining noble-gas configurations—either by electron transfer (ionic) or electron sharing (covalent).

Q2 Write Lewis dot symbols for atoms of the following elements: Mg, Na, B, O, N, Br.

SOLUTION

Lewis dot symbols show only the valence electrons as dots around the chemical symbol.

Mg (Group 2, 2 valence electrons): Mg with 2 dots (one on each of two sides)
Na (Group 1, 1 valence electron): Na with 1 dot
B (Group 13, 3 valence electrons): B with 3 dots
O (Group 16, 6 valence electrons): O with 6 dots (2 lone pairs + 2 unpaired)

N (Group 15, 5 valence electrons): N with 5 dots (1 lone pair + 3 unpaired)
Br (Group 17, 7 valence electrons): Br with 7 dots (3 lone pairs + 1 unpaired)

Answer: Mg: 2 dots; Na: 1 dot; B: 3 dots; O: 6 dots; N: 5 dots; Br: 7 dots (dots placed singly first, then paired).

Q3 Write Lewis symbols for the following atoms and ions: S and S^{2-}; Al and Al^{3+}; H and H^{-}

SOLUTION

S (Group 16, 6 valence electrons): symbol S with 6 dots
S^{2-} (gains 2 electrons -> 8 valence electrons): symbol $[S]^{2-}$ with 8 dots (4 lone pairs); resembles Ar configuration

Al (Group 13, 3 valence electrons): symbol Al with 3 dots
Al^{3+} (loses 3 electrons -> 0 valence electrons): symbol $[Al]^{3+}$ with no dots; resembles Ne configuration

H (1 valence electron): symbol H with 1 dot
H^{-} (gains 1 electron -> 2 valence electrons): symbol $[H]^{-}$ with 2 dots (1 lone pair); resembles He configuration

Answer: S: 6 dots; S^{2-}: 8 dots (closed shell); Al: 3 dots; Al^{3+}: no dots; H: 1 dot; H^{-}: 2 dots.

Q4 Draw the Lewis structures for the following molecules and ions: H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

SOLUTION

H_2S: S is central; 6 valence electrons on S, 1 from each H -> total 8e. S shares 1 pair with each H (two S-H single bonds), leaving 2 lone pairs on S. Geometry: bent (like H_2O). Structure: H-S-H with 2 lone pairs on S.

$SiCl_4$: Si is central; 4 valence electrons from Si, 7 from each Cl -> total 4+28=32e. Si forms 4 single bonds to Cl; each Cl has 3 lone pairs. Octet satisfied on all atoms. Geometry: tetrahedral.

BeF_2: Be is central; 2 valence electrons from Be, 7 from each F -> total 2+14=16e. Be forms 2 single bonds to F; each F has 3 lone pairs; Be has no lone pairs (incomplete octet—only 4 electrons on Be). Geometry: linear.

CO_3^{2-}: C is central; total electrons = 4 + 3(6) + 2 = 24e. One C=O double bond and two C-O single bonds, each O with lone pairs; three resonance structures. Formal charge: C=0 in the best structure. Geometry: trigonal planar, bond angle 120°.

HCOOH (formic acid): H-C(=O)-O-H. C has 4 bonds: one C-H, one C=O (double bond), one C-O (single bond to -OH). O of OH has 2 lone pairs. Total electrons: 1+4+6+6+1=18 valence electrons. Structure: H-C(=O)(-OH) with lone pairs on both oxygens.

Answer: H_2S: bent, 2 lone pairs on S; $SiCl_4$: tetrahedral, 3 lone pairs on each Cl; BeF_2: linear, 3 lone pairs on each F, incomplete octet on Be; CO_3^{2-}: trigonal planar with resonance (one C=O + two C-O bonds per canonical form); HCOOH: H-C(=O)(-O-H) with lone pairs on O atoms.

Q5 Define octet rule. Write its significance and limitations.

SOLUTION

Definition: The octet rule states that atoms tend to combine (by sharing or transferring electrons) so that each atom attains eight electrons in its valence shell, resembling the stable noble-gas configuration ($ns^2\ np^6$).

Significance:

1. Explains why atoms form specific numbers of bonds (valence).
2. Helps write correct Lewis structures for many organic and inorganic molecules (CH_4, H_2O, NH_3, CO_2, etc.).
3. Predicts ionic charges: Na loses 1e (Na^+), Cl gains 1e (Cl^-).

Limitations:

1. Incomplete octet: Some compounds have fewer than 8 electrons on the central atom: LiCl, BeH_2 (4e), BCl_3 (6e), $AlCl_3$.
2. Odd-electron molecules: NO and NO_2 have an odd number of electrons; the octet cannot be satisfied for all atoms.
3. Expanded octet: Third-period elements can accommodate more than 8 electrons using d orbitals: PCl_5 (10e on P), SF_6 (12e on S), H_2SO_4.
4. Does not explain molecular shapes.
5. Does not explain relative stability (energy) of molecules.
6. Noble gases like Xe and Kr can form compounds (XeF_2, KrF_2), contradicting the idea that the octet is uniquely stable.

Answer: Octet rule: atoms combine to achieve 8 valence electrons. Significance: explains valence and Lewis structures. Limitations: incomplete octet (BeH_2, BCl_3), odd-electron molecules (NO, NO_2), expanded octet (PCl_5, SF_6), no explanation of shape or stability.

Q6 Write the favourable factors for the formation of ionic bond.

SOLUTION

An ionic bond is formed by complete transfer of electrons from a metal to a non-metal. The favourable factors are:

1. Low ionisation enthalpy of the metal: The cation-forming atom should lose electrons easily (low energy required). Alkali metals (Li, Na, K) have low ionisation enthalpies.

2. High (negative) electron gain enthalpy of the non-metal: The anion-forming atom should readily accept electrons with large energy release. Halogens and oxygen have high negative electron-gain enthalpies.

3. High lattice enthalpy: The energy released when gaseous ions come together to form the crystalline lattice must be large enough to compensate for the energy spent in ionisation. High lattice enthalpy (due to high ionic charge and small ionic radii) strongly favours ionic bond stability.

4. Large difference in electronegativity between the two atoms: The greater the electronegativity difference, the more electron transfer is favoured (ionic rather than covalent bonding).

Example: In NaCl, ionisation enthalpy of Na = +495.8 kJ mol^{-1}, electron gain enthalpy of Cl = -348.7 kJ mol^{-1}, lattice enthalpy of NaCl = -788 kJ mol^{-1}; the lattice energy more than compensates the net endothermic ion-formation step.

Answer: Favourable factors: low ionisation enthalpy of metal, high negative electron gain enthalpy of non-metal, high lattice enthalpy, and large electronegativity difference between bonding atoms.

Q7 Discuss the shape of the following molecules using the VSEPR model: $BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

SOLUTION

VSEPR principle: electron pairs (bonding + lone) around the central atom arrange to minimise repulsion.

$BeCl_2$: Be has 2 bond pairs, 0 lone pairs -> 2 electron pairs -> linear geometry. Bond angle: 180°. Shape: linear.

BCl_3: B has 3 bond pairs, 0 lone pairs -> 3 electron pairs -> trigonal planar. Bond angle: 120°. Shape: trigonal planar.

$SiCl_4$: Si has 4 bond pairs, 0 lone pairs -> 4 electron pairs -> tetrahedral. Bond angle: 109.5°. Shape: tetrahedral.

AsF_5: As has 5 bond pairs, 0 lone pairs -> 5 electron pairs -> trigonal bipyramidal (sp^3d hybridisation). Bond angles: 120° (equatorial) and 90° (axial-equatorial). Shape: trigonal bipyramidal.

H_2S: S has 2 bond pairs + 2 lone pairs -> 4 electron pairs -> bent (V-shaped). The 2 lone pairs repel bond pairs more, compressing the bond angle below 109.5°. Bond angle: ~92°. Shape: bent.

PH_3: P has 3 bond pairs + 1 lone pair -> 4 electron pairs -> trigonal pyramidal. The lone pair repels bond pairs, reducing bond angle below 109.5°. Bond angle: ~93.5°. Shape: trigonal pyramidal.

Answer: $BeCl_2$: linear (180°); BCl_3: trigonal planar (120°); $SiCl_4$: tetrahedral (109.5°); AsF_5: trigonal bipyramidal; H_2S: bent (~92°); PH_3: trigonal pyramidal (~93.5°).

Q8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

SOLUTION

Both NH_3 and H_2O have sp^3 hybridised central atoms with tetrahedral electron-pair geometry, but lone pairs distort the ideal 109.5° angle.

NH_3: N has 3 bond pairs + 1 lone pair. The 1 lone pair exerts greater repulsion on the 3 N-H bond pairs, reducing the H-N-H angle from 109.5° to 107°. Shape: trigonal pyramidal.

H_2O: O has 2 bond pairs + 2 lone pairs. The 2 lone pairs exert even greater

repulsion (lp-lp repulsion > lp-bp repulsion) on the 2 O-H bond pairs, compressing the H-O-H angle further to 104.5°. Shape: bent (V-shaped).

Order of repulsion: lp-lp > lp-bp > bp-bp.
NH_3 has 1 lone pair causing moderate compression (107°), while H_2O has 2 lone pairs causing greater compression (104.5°).

Therefore, the bond angle in H_2O (104.5°) is smaller than in NH_3 (107°) because water has more lone pairs on the central atom, resulting in greater lone pair-bond pair repulsion.

Answer: H_2O has 2 lone pairs on O (vs 1 lone pair on N in NH_3); more lone pairs cause greater lp-lp and lp-bp repulsion, compressing the bond angle more: H-O-H = 104.5° < H-N-H = 107°.

Q9 How do you express the bond strength in terms of bond order?

SOLUTION

Bond order (b.o.) is defined as one-half the difference between the number of electrons in bonding molecular orbitals (Nb) and the number in antibonding molecular orbitals (Na):
b.o. = (1/2)(Nb - Na)

Relationship between bond order and bond strength (bond enthalpy):
Higher bond order -> stronger bond -> higher bond dissociation enthalpy -> shorter bond length.

Examples:
H_2: b.o. = 1 (single bond), bond enthalpy = 435.8 kJ mol^{-1}
O_2: b.o. = 2 (double bond), bond enthalpy = 498 kJ mol^{-1}
N_2: b.o. = 3 (triple bond), bond enthalpy = 946 kJ mol^{-1}

Thus, bond enthalpy increases and bond length decreases as bond order increases.

Answer: Bond strength increases with bond order: higher bond order means greater bond dissociation enthalpy and shorter bond length. b.o. = (1/2)(Nb - Na).

Q10 Define the bond length.

SOLUTION

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

It is determined experimentally by X-ray diffraction, electron diffraction, or spectroscopic methods.

For a covalent bond A-B: bond length R = rA + rB, where rA and rB are the covalent radii of atoms A and B respectively.

Key trends:
- Bond length decreases as bond order increases: C-C (154 pm) > C=C (133 pm) > C≡C (120 pm).
- Bond length increases as atomic size (covalent radius) increases: H-F (92 pm) < H-Cl (127 pm) < H-Br (141 pm) < H-I (160 pm).

Answer: Bond length is the equilibrium internuclear distance between two bonded atoms. It decreases with increasing bond order and increases with increasing atomic size.

Q11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

SOLUTION

Resonance is invoked when a single Lewis structure cannot adequately represent a molecule or ion. Multiple Lewis structures (canonical or resonance structures) with the same atomic positions but different electron distributions are written; the actual species is a resonance hybrid of all these structures.

For CO_3^{2-}:
Total valence electrons = 4 (C) + 3×6 (O) + 2 (charge) = 24 electrons.

Three canonical structures can be drawn, each with one C=O double bond and two C-O single bonds, with the double bond shifting to each of the three oxygen atoms in turn.

Experimental evidence: All three C-O bonds in CO_3^{2-} are equivalent with bond length 129 pm, which lies between C-O single bond (143 pm) and C=O double bond (121 pm). No single Lewis structure with unequal bonds can represent this.

Important aspects of resonance:
1. Canonical forms have no real existence; the molecule exists as a single

resonance hybrid.

2. The resonance hybrid has lower energy than any individual canonical form (resonance stabilisation).

3. Resonance averages the bond characteristics—all C-O bonds in CO_3^{2-} are equivalent (bond order = 4/3 ≈ 1.33).

4. There is no equilibrium between canonical forms; they are just representations.

Answer: CO_3^{2-} has 3 equivalent canonical structures (each with one C=O and two C-O bonds). The resonance hybrid has all three C-O bonds equal (bond length 129 pm, bond order 4/3), lower energy than any single structure.

Q12 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, give reasons for the same.

SOLUTION

Structure 1 of H_3PO_3: P is bonded to 3 OH groups and 1 H directly (H directly on P), with a P=O double bond. Formula: $HP(=O)(OH)_2$

Structure 2 of H_3PO_3: P is bonded to 3 OH groups and one =O, but no H directly on P. Formula: $P(=O)(OH)_3$

No, these two structures cannot be canonical forms of a resonance hybrid. The reasons are:

1. Different connectivity (skeletal structure): In structure 1, one hydrogen is directly bonded to phosphorus (P-H bond). In structure 2, all three hydrogens are bonded to oxygen (O-H bonds) with no P-H bond. Canonical resonance structures must have the same positions of all atoms (same connectivity/skeleton); only electron positions differ.

2. Different molecular formulas in terms of bonding: The two structures represent different compounds or different constitutional arrangements, not merely different electron distributions.

3. They are tautomers (constitutional isomers that interconvert), not resonance structures. Resonance structures differ only in the distribution of electrons, not in the atomic connectivity.

Therefore, structures 1 and 2 of H_3PO_3 are tautomers of each other, not canonical forms of a resonance hybrid.

Answer: No. The two structures have different atomic connectivities (structure 1 has a P-H bond; structure 2 has no P-H bond). Canonical forms must have the same skeleton with only electron positions differing. These are tautomers, not resonance structures.

Q13 Write the resonance structures for SO_3, NO_2 and NO_3^-.

SOLUTION

SO_3 (total valence electrons = 6+3×6 = 24):
Three canonical structures, each with one S=O double bond and two S-O single bonds (S has expanded octet). The double bond shifts to each O in turn. All S-O bonds are equivalent (bond order = 4/3). S is central; each structure has formal charges 0 on S, 0 on =O, -1 on single-bond O.

NO_2 (total valence electrons = 5+2×6 = 17, odd-electron molecule):
Two resonance structures with N at centre: one has N=O (double bond) to one O and N-O (single bond) to the other O with an unpaired electron on N; second structure reverses. The odd electron is on N. Bond angle ~134°. Both N-O bonds are equivalent.

NO_3^- (total valence electrons = 5+3×6+1 = 24):
Three canonical structures, each with one N=O double bond and two N-O single bonds, with the double bond shifting to each O. All three N-O bonds are equivalent (bond order = 4/3). N is central; bond angle 120°.

Answer: SO_3: 3 resonance structures (S=O shifts to each of 3 oxygens); NO_2: 2 resonance structures (N=O shifts to each O, odd electron on N); NO_3^-: 3 resonance structures (N=O shifts to each of 3 oxygens).

Q14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions: (a) K and S (b) Ca and O (c) Al and N.

SOLUTION

(a) K and S:
K has 1 valence electron; S has 6 valence electrons (needs 2 more for octet).
Two K atoms each transfer 1 electron to one S atom:
$2K \rightarrow 2K^+ + 2e^-$
$S + 2e^- \rightarrow S^{2-}$
Product: K_2S (2 K^+ and 1 S^{2-})

(b) Ca and O:
Ca has 2 valence electrons; O has 6 valence electrons (needs 2 more for octet).
One Ca atom transfers 2 electrons to one O atom:
$Ca \rightarrow Ca^{2+} + 2e^-$
$O + 2e^- \rightarrow O^{2-}$
Product: CaO (1 Ca^{2+} and 1 O^{2-})

(c) Al and N:
Al has 3 valence electrons; N has 5 valence electrons (needs 3 more for octet).
One Al atom transfers 3 electrons to one N atom:
$Al \rightarrow Al^{3+} + 3e^-$
$N + 3e^- \rightarrow N^{3-}$
Product: AlN (1 Al^{3+} and 1 N^{3-})

Answer: (a) $2K + S \rightarrow 2K^+ + S^{2-} \rightarrow K_2S$; (b) $Ca + O \rightarrow Ca^{2+} + O^{2-} \rightarrow CaO$; (c) $Al + N \rightarrow Al^{3+} + N^{3-} \rightarrow AlN$.

Q15 Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

SOLUTION

CO_2 (linear, $\mu = 0$):
CO_2 has two C=O polar bonds. Carbon is the central atom; the molecule is linear (sp hybridisation of C). The two C=O bond dipoles are equal in magnitude but point in exactly opposite directions (180° apart). They cancel vectorially, giving a net dipole moment $\mu = 0$. Because $\mu = 0$ (non-polar molecule), the geometry must be linear.

H_2O (bent, $\mu = 1.85$ D):
H_2O has two O-H polar bonds. Oxygen is the central atom with 2 lone pairs; the molecule is bent (sp^3 hybridisation of O, bond angle 104.5°). The two O-H bond dipoles do not cancel because they are not collinear—they make an angle of 104.5° with each other. Their vector sum gives a net dipole moment $\mu = 1.85$ D (non-zero). The lone pairs on O also add an orbital dipole in the same direction, increasing μ. A non-zero dipole moment confirms a non-linear (bent) structure.

Conclusion: The zero dipole moment of CO_2 implies that the two bond dipoles must cancel -> linear shape. The non-zero dipole moment of H_2O implies the

bond dipoles do not cancel -> bent shape.

Answer: CO_2 has $\mu = 0$ because the two C=O bond dipoles cancel (linear geometry); H_2O has $\mu = 1.85$ D because the two O-H bond dipoles do not cancel in a bent structure (bond angle 104.5°, with lone pairs also contributing).

Q16 Write the significance/applications of dipole moment.

SOLUTION

Dipole moment ($\mu = Q \times r$) is a vector quantity that measures the polarity of a bond or molecule.

Significance and applications:

1. Determining polarity of bonds and molecules: A non-zero dipole moment indicates a polar molecule; zero indicates a non-polar molecule.

2. Predicting geometry/shape of molecules: By comparing expected dipole moments for possible structures with experimental values, shapes can be confirmed. For example, the zero dipole moment of CO_2 confirms its linear geometry, while that of BF_3 confirms trigonal planar.

3. Determining percentage ionic character: Dipole moment data, combined with bond length, help estimate the extent of ionic character of a covalent bond.

4. Distinguishing isomers: cis and trans isomers, ortho/meta/para isomers have different dipole moments. For example, cis-1,2-dichloroethene has $\mu \neq 0$ while trans has $\mu = 0$.

5. Estimating lone pair contribution: Comparison of NH_3 ($\mu = 1.47$ D) and NF_3 ($\mu = 0.23$ D) shows how the direction of the lone-pair orbital dipole can either add to or oppose the bond dipoles.

6. Predicting physical properties: Polar molecules (high μ) have higher boiling points, higher solubility in polar solvents, and can form dipole-dipole interactions.

Answer: Dipole moment indicates molecular polarity, helps determine molecular geometry, distinguishes geometric/structural isomers, estimates ionic character, reveals lone-pair effects, and predicts physical properties such as boiling point and solubility.

Q17 Define electronegativity. How does it differ from electron gain enthalpy?

SOLUTION

Electronegativity: The tendency of a bonded atom to attract the shared electron pair (bonding electrons) towards itself in a covalent bond. It is a dimensionless relative scale (Pauling scale: F = 4.0 is the highest). Electronegativity is a property of an atom in a molecule, not of an isolated atom.

Electron gain enthalpy (Delta_eg H): The enthalpy change when a gaseous atom in its ground state gains one electron to form a gaseous anion. It is a thermodynamic quantity with units kJ mol^{-1}, measured for an isolated atom in the gaseous phase.

Key differences:

1. Electronegativity refers to the ability of a bonded atom to attract shared electrons in a covalent bond; electron gain enthalpy refers to energy released/absorbed when an isolated gaseous atom gains an electron.
2. Electronegativity is a dimensionless relative property; electron gain enthalpy has units of kJ mol^{-1}.
3. Electronegativity depends on the bonding environment; electron gain enthalpy is an intrinsic atomic property measured for the free atom.
4. Electronegativity applies to atoms in molecules; electron gain enthalpy is measured for isolated gaseous atoms.
5. Both increase across a period (left to right) and decrease down a group, but F has the highest electronegativity while Cl has the most negative electron gain enthalpy.

Answer: Electronegativity: relative tendency of a bonded atom to attract shared electrons (dimensionless, e.g., Pauling scale). Electron gain enthalpy: energy change when a free gaseous atom gains an electron (kJ mol^{-1}). Electronegativity is a bonding property; electron gain enthalpy is an intrinsic thermodynamic property of isolated atoms.

Q18 Explain with the help of a suitable example polar covalent bond.

SOLUTION

A polar covalent bond is formed between two atoms of different electronegativities. The shared electron pair is displaced towards the more electronegative atom, creating a partial negative charge (delta$^-$) on that atom and

a partial positive charge (delta$^+$) on the other atom.

Example: HF (hydrogen fluoride)
Electronegativity of H = 2.1; electronegativity of F = 4.0.
The shared pair is pulled towards F (more electronegative), so F acquires delta$^-$ and H acquires delta$^+$.
The bond is represented as: H^(delta+) - F^(delta-)
Dipole moment of HF = 1.78 D (large, confirming high polarity).

The greater the difference in electronegativity between the bonded atoms, the more polar the bond.
Scale: purely covalent (identical atoms, e.g., H_2) < polar covalent (e.g., HCl, HF, H_2O) < ionic (complete electron transfer, e.g., NaCl).

Answer: A polar covalent bond has unequal sharing of electrons due to electronegativity difference. Example: H-F, where the shared pair shifts towards the more electronegative F, creating H^(delta+)-F^(delta-) with dipole moment 1.78 D.

Q19 Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

SOLUTION

Ionic character of a bond depends on the difference in electronegativity between the bonded atoms. Greater the difference, greater the ionic character.

Electronegativity values (Pauling scale):
Li = 1.0, F = 4.0 -> Delta EN = 3.0 (Li-F bond in LiF)
K = 0.8, O = 3.5 -> Delta EN = 2.7 (K-O bond in K_2O)
N = 3.0, N = 3.0 -> Delta EN = 0 (N-N bond in N_2)
S = 2.5, O = 3.5 -> Delta EN = 1.0 (S-O bond in SO_2)
Cl = 3.0, F = 4.0 -> Delta EN = 1.0 (Cl-F bond in ClF_3)

Ordering:
N_2 (Delta EN = 0) < SO_2 approximately = ClF_3 (Delta EN ~1.0) < K_2O (Delta EN = 2.7) < LiF (Delta EN = 3.0)

Order of increasing ionic character: $N_2 < SO_2 \approx ClF_3 < K_2O < LiF$

Answer: Increasing ionic character: $N_2 < SO_2 \approx ClF_3 < K_2O < LiF$ (based on increasing electronegativity difference between bonded atoms).

Q20 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.

SOLUTION

Acetic acid (ethanoic acid): CH_3COOH, molecular formula $C_2H_4O_2$.
Total valence electrons = 2(4) + 4(1) + 2(6) = 8 + 4 + 12 = 24 electrons.

Correct Lewis structure:
The methyl carbon (CH_3^-): sp^3 hybridised, bonded to 3 H atoms and the carbonyl carbon by single bonds.
The carboxyl carbon (-COOH): sp^2 hybridised, forms one C=O double bond (carbonyl) and one C-O single bond (to the OH group) and one C-C single bond.
The hydroxyl oxygen: bonded to the carboxyl C and to H by single bonds; has 2 lone pairs.
The carbonyl oxygen: double-bonded to the carboxyl C; has 2 lone pairs.

Correct bonding: $H_3C\text{-}C(=O)\text{-}O\text{-}H$
The carboxyl C has: one C=O (double bond to O), one C-O (single bond to OH oxygen), one C-C (single bond to CH_3).
Common errors in skeletal structures: showing the C=O as a single bond, or the C-O of the OH as a double bond. Only the carbonyl oxygen has a double bond to C.

Answer: Correct Lewis structure: $H_3C\text{-}C(=O)\text{-}OH$. The carboxyl group has one C=O (double bond) to the carbonyl oxygen and one C-O (single bond) to the -OH oxygen. The methyl C makes four single bonds; the carboxyl C is sp^2 hybridised.

Q21 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar.

SOLUTION

Carbon in CH_4 has 4 bond pairs and 0 lone pairs. VSEPR theory predicts that 4 electron pairs arrange themselves to maximise separation, giving tetrahedral geometry (bond angles 109.5°) — not square planar (bond angles 90°).

Reasons why CH_4 is not square planar:

1. Energy: In tetrahedral geometry the 4 bond pairs are as far apart as possible (109.5°), minimising repulsion. In square planar geometry bond angles would be 90°, meaning greater electron-pair repulsion and higher energy — an unstable

arrangement.

2. Hybridisation: Carbon uses sp^3 hybridisation for CH_4, directing the four equivalent hybrid orbitals towards the corners of a tetrahedron. Square planar would require dsp^2 hybridisation, which needs a d orbital; carbon in its valence shell has no available d orbital.

3. Experimental: The H-C-H bond angle in CH_4 is 109.5°, confirmed by spectroscopy, consistent with tetrahedral and inconsistent with the 90° angle of square planar.

Therefore, CH_4 is tetrahedral and cannot be square planar.

Answer: CH_4 is not square planar because: (1) sp^3 hybridisation directs 4 bond pairs tetrahedrally (109.5°), minimising repulsion; (2) square planar (90° angles) has greater repulsion and higher energy; (3) square planar needs dsp^2 hybridisation, requiring a d orbital that C lacks.

Q22 Explain why BeH_2 molecule has a zero dipole moment although the Be-H bonds are polar.

SOLUTION

The Be-H bond is polar because Be (electronegativity ~1.5) and H (electronegativity ~2.1) have different electronegativities, so each Be-H bond has a bond dipole pointing towards H.

BeH_2 is a linear molecule (sp hybridisation of Be): the two Be-H bonds are oriented at exactly 180° to each other (opposite directions).

The two Be-H bond dipoles are equal in magnitude but point in exactly opposite directions. Vector sum of the two dipoles = 0.

Net dipole moment $\mu = \mu(Be\text{-}H) - \mu(Be\text{-}H) = 0$.

Therefore, despite having polar bonds, BeH_2 has zero net dipole moment due to the symmetric (linear) geometry in which the individual bond dipoles cancel each other.

Answer: BeH_2 is linear (180°); the two equal Be-H bond dipoles point in exactly opposite directions and cancel vectorially, giving a net dipole moment of zero, even though individual Be-H bonds are polar.

Q23 Which out of NH_3 and NF_3 has higher dipole moment and why?

SOLUTION

Both NH_3 and NF_3 are pyramidal molecules with N as the central atom having 1 lone pair and 3 bond pairs.

NH_3: N-H bonds are polar with the bond dipole pointing from H towards N (N is more electronegative). The lone pair on N has an orbital dipole pointing away from N (towards the 'top' of the pyramid). The bond dipoles and the lone-pair orbital dipole point in the SAME direction (both point from base towards lone pair). They add up, giving a large resultant dipole moment: $\mu(NH_3) = 1.47$ D.

NF_3: N-F bonds are polar with bond dipole pointing from N towards F (F is more electronegative). The lone pair orbital dipole on N points away from the base (upward). However, the bond dipoles point downward (towards F), while the lone-pair dipole points upward — they are in OPPOSITE directions. The lone pair partially cancels the resultant N-F bond dipoles, giving a much smaller dipole moment: $\mu(NF_3) = 0.23$ D.

Therefore, NH_3 has a higher dipole moment (1.47 D) than NF_3 (0.23 D).

Answer: NH_3 has higher dipole moment (1.47 D vs 0.23 D for NF_3). In NH_3, the lone-pair orbital dipole adds to the resultant N-H bond dipoles; in NF_3, the lone-pair orbital dipole opposes the resultant N-F bond dipoles (since F is more electronegative than N), reducing the net dipole.

Q24 What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp^2, sp^3 hybrid orbitals.

SOLUTION

Hybridisation: The process of intermixing of atomic orbitals of slightly different energies to form a new set of orbitals of equivalent energy, shape, and orientation. The hybrid orbitals are more effective in bonding than the pure atomic orbitals.

Key features: The number of hybrid orbitals = number of atomic orbitals mixed. They are equivalent in energy and shape, directed in specific orientations to minimise repulsion.

sp hybridisation: Mixing of 1 s orbital + 1 p orbital -> 2 sp hybrid orbitals.
Shape: Each sp orbital is asymmetric—large lobe on one side of the nucleus and

small lobe on the other. The two sp orbitals are directed at 180° (linear), i.e., along opposite directions. The orbitals have 50% s-character and 50% p-character. Example: $BeCl_2$ (linear).

sp^2 hybridisation: Mixing of 1 s orbital + 2 p orbitals -> 3 sp^2 hybrid orbitals.
Shape: Each sp^2 orbital is similar in shape to sp but with different proportions (33.3% s, 66.7% p). The three sp^2 orbitals lie in the same plane and are directed at 120° to each other (trigonal planar arrangement). One unhybridised p orbital remains perpendicular to this plane. Example: BCl_3 (trigonal planar).

sp^3 hybridisation: Mixing of 1 s orbital + 3 p orbitals -> 4 sp^3 hybrid orbitals.
Shape: Each sp^3 orbital has 25% s-character and 75% p-character. The four sp^3 orbitals are directed towards the four corners of a tetrahedron at bond angles of 109.5°. Example: CH_4 (tetrahedral).

Answer: Hybridisation mixes atomic orbitals of similar energy to give equivalent hybrid orbitals. sp: 2 orbitals at 180° (linear); sp^2: 3 orbitals at 120° in a plane (trigonal planar); sp^3: 4 orbitals at 109.5° (tetrahedral).

Q25 Describe the change in hybridisation (if any) of the Al atom in the following reaction: $AlCl_3 + Cl^- \rightarrow AlCl_4^-$

SOLUTION

In $AlCl_3$: Al has 3 bond pairs and 0 lone pairs. It uses sp^2 hybridisation (trigonal planar geometry, bond angles 120°). Al has an incomplete octet (6 electrons).

In $AlCl_4^-$: Al has 4 bond pairs and 0 lone pairs. It uses sp^3 hybridisation (tetrahedral geometry, bond angles 109.5°). Al now has a complete octet (8 electrons).

Change in hybridisation: sp^2 (in $AlCl_3$) -> sp^3 (in $AlCl_4^-$)

The Cl^- ion (Lewis base) donates a lone pair to the electron-deficient Al (Lewis acid) in $AlCl_3$. To accommodate the fourth bond, Al changes from sp^2 to sp^3 hybridisation, and the geometry changes from trigonal planar to tetrahedral.

Answer: Al changes from sp^2 hybridisation (trigonal planar) in $AlCl_3$ to sp^3 hybridisation (tetrahedral) in $AlCl_4^-$, as it accepts a Cl^- ion to complete its octet.

Q26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction? $BF_3 + NH_3 \rightarrow F_3B\text{-}NH_3$

SOLUTION

In BF_3 (before reaction): B has 3 bond pairs, 0 lone pairs -> sp^2 hybridisation (trigonal planar, 120°). B has an incomplete octet.

In $F_3B\text{-}NH_3$ (after reaction): B now has 4 bonds (3 B-F + 1 B-N coordinate/dative bond). B has 4 bond pairs, 0 lone pairs -> sp^3 hybridisation (tetrahedral). B now has a complete octet.
B: sp^2 -> sp^3 (change in hybridisation).

In NH_3 (before reaction): N has 3 bond pairs + 1 lone pair -> sp^3 hybridisation (trigonal pyramidal).

In $F_3B\text{-}NH_3$ (after reaction): N donates its lone pair to B. N now has 4 bond pairs (3 N-H + 1 N-B) + 0 lone pairs -> still sp^3 hybridisation (tetrahedral arrangement of bonds).
N: sp^3 -> sp^3 (no change in hybridisation; it was sp^3 before and remains sp^3 after).

Summary: B changes hybridisation from sp^2 to sp^3; N does not change (remains sp^3).

Answer: B changes from sp^2 (trigonal planar in BF_3) to sp^3 (tetrahedral in $F_3B\text{-}NH_3$). N remains sp^3 throughout (from trigonal pyramidal NH_3 to tetrahedral N in the adduct).

Q27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

SOLUTION

C_2H_4 (ethene) — Double bond:
Each C is sp^2 hybridised with three sp^2 orbitals and one unhybridised 2p orbital perpendicular to the molecular plane.
Sigma bond: One sp^2 orbital of each C overlaps axially (head-on) to form one C-C sigma bond.
Pi bond: The two unhybridised p orbitals (one from each C) overlap sidewise (laterally, above and below the C-C axis) to form one C-C pi bond.
Each C also forms two C-H sigma bonds (sp^2 of C with 1s of H).
Total C=C: 1 sigma + 1 pi bond (double bond).
Bond length of C=C: 134 pm; H-C-H angle: 117.6°; H-C-C angle: 121°.

C_2H_2 (ethyne) — Triple bond:
Each C is sp hybridised with two sp orbitals and two unhybridised p orbitals (2px and 2py) perpendicular to the C-C axis.
Sigma bond: One sp orbital of each C overlaps axially to form one C-C sigma bond.
Pi bonds: The 2px orbital of one C overlaps sidewise with 2px of the other -> one pi bond; the 2py of one C overlaps sidewise with 2py of the other -> a second pi bond.
Each C also forms one C-H sigma bond (sp of C with 1s of H).
Total C≡C: 1 sigma + 2 pi bonds (triple bond).
Bond length of C≡C: 120 pm; molecule is linear (180°).

Answer: C_2H_4: C=C = 1 sigma (sp^2-sp^2 head-on overlap) + 1 pi (sideways p-p overlap). C_2H_2: C≡C = 1 sigma (sp-sp head-on) + 2 pi bonds (sideways 2px-2px and 2py-2py overlap); molecule is linear.

Q28 What is the total number of sigma and pi bonds in the following molecules?
(a) C_2H_2 (b) C_2H_4

SOLUTION

(a) C_2H_2 (ethyne): H-C≡C-H
C-H bonds: 2 (one on each C) -> 2 sigma bonds
C≡C triple bond: 1 sigma + 2 pi bonds
Total sigma bonds = 2 (C-H) + 1 (C-C) = 3
Total pi bonds = 2

(b) C_2H_4 (ethene): $H_2C=CH_2$
C-H bonds: 4 (two on each C) -> 4 sigma bonds
C=C double bond: 1 sigma + 1 pi bond
Total sigma bonds = 4 (C-H) + 1 (C-C) = 5
Total pi bonds = 1

Answer: (a) C_2H_2: 3 sigma bonds + 2 pi bonds. (b) C_2H_4: 5 sigma bonds + 1 pi bond.

Q29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1s and 1s (b) 1s and 2px; (c) 2py and 2py (d) 1s and 2s.

SOLUTION

Sigma bonds require head-on (axial) overlap along the internuclear (x) axis and positive (constructive) overlap.

(a) 1s and 1s: Both are spherically symmetrical; they overlap along the x-axis with positive overlap -> forms sigma bond.

(b) 1s and 2px: The 1s is spherically symmetric; 2px has its lobes along the x-axis. The positive lobe of 2px overlaps constructively with 1s along the x-axis -> forms sigma bond.

(c) 2py and 2py: The 2py orbitals have lobes along the y-axis (perpendicular to the x internuclear axis). When the two atoms approach along x, the lobes are parallel. They can form a pi bond (sidewise overlap) but NOT a sigma bond (they do not have lobes directed towards each other along x). Answer: 2py and 2py do NOT form a sigma bond.

(d) 1s and 2s: The 2s orbital is also spherically symmetrical and can overlap with 1s along the x-axis -> forms sigma bond (though energy match is poorer).

Therefore, only (c) 2py and 2py will NOT form a sigma bond; they form a pi bond instead.

Answer: (c) 2py and 2py will NOT form a sigma bond: their lobes are perpendicular to the x internuclear axis, so they cannot overlap head-on along x. They would instead form a pi bond (sidewise overlap).

Q30 Which hybrid orbitals are used by carbon atoms in the following molecules? (a) CH_3-CH_3; (b) CH_3-CH=CH_2; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH

SOLUTION

(a) CH_3-CH_3 (ethane):
Both C atoms are sp^3 hybridised. Each C forms 4 single bonds (3 C-H + 1 C-C). All sigma bonds, no pi bonds.

(b) CH_3-CH=CH_2 (propene):
CH_3^- carbon: sp^3 (4 single bonds: 3 C-H + 1 C-C)
-CH= carbon: sp^2 (3 sigma bonds: 1 C-H + 1 C-C to CH_3 + 1 C=C sigma; 1 pi

bond in C=C)
=CH_2 carbon: sp^2 (3 sigma bonds: 2 C-H + 1 C=C sigma; 1 pi bond in C=C)

(c) CH_3-CH_2-OH (ethanol):
Both C atoms are sp^3 hybridised (all single bonds). The O atom is also sp^3.

(d) CH_3-CHO (ethanal/acetaldehyde):
CH_3^- carbon: sp^3 (3 C-H + 1 C-C, all single bonds)
-CHO carbon: sp^2 (2 sigma bonds: 1 C-H + 1 C-C; 1 C=O double bond with 1 sigma + 1 pi)

(e) CH_3COOH (acetic acid):
CH_3^- carbon: sp^3 (3 C-H + 1 C-C, all single bonds)
Carboxyl carbon (-COOH): sp^2 (3 sigma bonds: 1 C-C + 1 C=O sigma + 1 C-O sigma; 1 pi bond in C=O)

Answer: (a) Both C: sp^3. (b) CH_3: sp^3; -CH= and =CH_2: sp^2. (c) Both C: sp^3. (d) CH_3: sp^3; CHO carbon: sp^2. (e) CH_3: sp^3; carboxyl C: sp^2.

Q31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.

SOLUTION

Bond pairs (shared pairs): Pairs of electrons that are shared between two bonded atoms. They are responsible for holding the atoms together in a covalent bond.
Example: In H_2O, the two O-H bonds each consist of one bond pair (one electron from O and one from H), shared between O and H.

Lone pairs (non-bonding pairs): Pairs of valence electrons on an atom that are not shared with any other atom and do not participate in bonding. They remain localised on the atom.
Example: In H_2O, the oxygen atom has 2 lone pairs (4 electrons not involved in bonding) in addition to the 2 bond pairs.

Effect: Lone pairs occupy more space than bond pairs and cause greater repulsion. In H_2O, the 2 lone pairs compress the H-O-H bond angle from 109.5° to 104.5°.

Answer: Bond pairs: shared electron pairs between bonded atoms (e.g., O-H bonds in H_2O). Lone pairs: non-bonding electron pairs on an atom (e.g., 2 lone pairs on O in H_2O). Lone pairs exert greater repulsion and reduce bond angles.

Q32 Distinguish between a sigma and a pi bond.

SOLUTION

Sigma (sigma) bond:

1. Formed by head-on (axial/end-to-end) overlap of orbitals along the internuclear axis.
2. Electron density is concentrated between the two nuclei along the bond axis.
3. Can be formed by s-s, s-p, or p-p (axial) orbital overlap.
4. Stronger bond due to greater extent of orbital overlap.
5. Rotation about the sigma bond axis is possible (free rotation in simple molecules).
6. Every single bond is a sigma bond; first bond in a double/triple bond is sigma.

Pi (pi) bond:

1. Formed by sidewise (lateral) overlap of parallel p orbitals perpendicular to the internuclear axis.
2. Electron density is concentrated above and below the internuclear axis in two lobes (not between nuclei).
3. Formed only by p-p (lateral) orbital overlap.
4. Weaker bond due to lesser extent of lateral overlap.
5. Rotation about the pi bond is restricted (would break the pi bond).
6. Pi bonds are the second bond in a double bond and the second and third bonds in a triple bond; never exists alone without a sigma bond.

Answer: Sigma: axial (head-on) overlap, electron density along bond axis, stronger, allows rotation. Pi: lateral (sideways) p-p overlap, electron density above and below axis, weaker, restricts rotation. Every double bond = 1 sigma + 1 pi; every triple bond = 1 sigma + 2 pi.

Q33 Explain the formation of H_2 molecule on the basis of valence bond theory.

SOLUTION

Consider two hydrogen atoms A and B, each with one electron in its 1s orbital, approaching each other.

Attractive forces arise between: (i) nucleus NA and its own electron eA; (ii) nucleus NB and electron eB; (iii) nucleus NA and electron eB; (iv) nucleus NB and electron eA.

Repulsive forces arise between: (i) electrons eA and eB; (ii) nuclei NA and NB.

As the atoms approach, the new attractive forces (nucleus of one atom attracting electron of the other) exceed the new repulsive forces, so the system potential energy decreases.

As the separation decreases further, a minimum in potential energy is reached at the equilibrium bond length (74 pm). At this point, the two 1s orbitals undergo partial interpenetration (overlap) and the electrons (with opposite spins) pair up to form a bonding electron pair. This overlap is the sigma bond.

Any attempt to bring the nuclei closer than 74 pm increases repulsion sharply, raising the energy. Any attempt to separate them requires input of 435.8 kJ mol^{-1} (bond dissociation enthalpy).

The H_2 molecule is more stable than two isolated H atoms by 435.8 kJ mol^{-1} (the energy released on bond formation corresponds to the minimum in the potential energy curve).

Answer: As two H atoms approach, new attractive forces (NA-eB and NB-eA) outweigh new repulsive forces, lowering potential energy. At 74 pm (equilibrium bond length), the 1s orbitals overlap and electrons pair (opposite spins) to form a sigma bond. The minimum energy (-435.8 kJ mol^{-1} relative to separated atoms) is the bond enthalpy.

Q34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

SOLUTION

The linear combination of atomic orbitals (LCAO) to form molecular orbitals requires the following conditions:

1. Same or nearly same energy: The combining atomic orbitals must have the same or very similar energy levels. For example, 1s of one atom combines with 1s of another, not with 2s (appreciably different energy).

2. Same symmetry about the molecular axis: The combining atomic orbitals must have the same symmetry with respect to the internuclear (molecular) axis. By convention, the z-axis is the molecular axis. For example, 2pz orbital can combine with another 2pz, but not with 2px or 2py (different symmetry).

3. Maximum overlap: The combining atomic orbitals must overlap to the maximum possible extent. Greater overlap -> greater electron density between nuclei ->

stronger molecular orbital.

Answer: Conditions for LCAO: (1) combining AOs must have same or nearly same energy; (2) they must have same symmetry about the molecular axis; (3) they must overlap to the maximum extent.

Q35 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

SOLUTION

Be has electronic configuration $1s^2\ 2s^2$ (4 electrons per atom). In Be_2 there would be a total of 8 electrons.

Filling molecular orbitals in order of increasing energy:
Be_2: $(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2$

Nb (electrons in bonding MOs) = 2 (σ_{1s}) + 2 (σ_{2s}) = 4
Na (electrons in antibonding MOs) = 2 (σ^*_{1s}) + 2 (σ^*_{2s}) = 4

Bond order = (1/2)(Nb - Na) = (1/2)(4 - 4) = 0

A bond order of zero means that the bonding and antibonding effects exactly cancel each other. There is no net bonding, so Be_2 has no stable existence. The energy of the Be_2 system is no lower than that of two separate Be atoms; hence Be_2 does not form.

Answer: Be_2 has MO configuration $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2$; Nb = 4, Na = 4, bond order = 0. Zero bond order means no net bonding, so Be_2 is unstable and does not exist.

Q36 Compare the relative stability of the following species and indicate their magnetic properties: O_2^+, O_2, O_2^- (superoxide), O_2^{2-} (peroxide)

SOLUTION

Using MO theory (energy order for O_2 and F_2): $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2pz})^2(\pi_{2px})^2(\pi_{2py})^2(\pi^*_{2px})(\pi^*_{2py})(\sigma^*_{2pz})$

O_2^+ (15 electrons): Nb=10, Na=5, Bond order = (10-5)/2 = 2.5. One unpaired electron in π^*_{2px} -> PARAMAGNETIC.

O_2 (16 electrons): Nb=10, Na=6, Bond order = (10-6)/2 = 2.0. Two unpaired electrons (one each in π^*_{2px} and π^*_{2py}) -> PARAMAGNETIC.

O_2^- superoxide (17 electrons): Nb=10, Na=7, Bond order = (10-7)/2 = 1.5. One unpaired electron in pi*2py -> PARAMAGNETIC.

O_2^{2-} peroxide (18 electrons): Nb=10, Na=8, Bond order = (10-8)/2 = 1.0. No unpaired electrons (pi*2px and pi*2py both fully occupied) -> DIAMAGNETIC.

Stability increases with bond order:
Increasing stability: O_2^{2-} (b.o. 1.0) < O_2^- (b.o. 1.5) < O_2 (b.o. 2.0) < O_2^+ (b.o. 2.5)
O_2^+ is the most stable; O_2^{2-} is the least stable.

Answer: Bond orders: O_2^{2-} = 1.0 (diamagnetic) < O_2^- = 1.5 (paramagnetic) < O_2 = 2.0 (paramagnetic) < O_2^+ = 2.5 (paramagnetic). Stability order: O_2^{2-} < O_2^- < O_2 < O_2^+ (higher bond order = more stable).

Q37 Write the significance of a plus and a minus sign shown in representing the orbitals.

SOLUTION

In orbital representations, plus (+) and minus (-) signs indicate the phase (sign) of the wave function (psi) in different regions of space. They are NOT related to electric charge.

Significance:
1. Phase of wave function: The wave function psi can have positive or negative values in different lobes of an orbital. For example, a p orbital has one lobe with psi > 0 (positive phase) and one lobe with psi < 0 (negative phase).

2. Constructive and destructive interference:
When two orbitals with the same phase (both + or both -) overlap, they interfere constructively -> electron density increases between the nuclei -> bonding molecular orbital (lower energy, stable).
When two orbitals with opposite phases (+ with -) overlap, they interfere destructively -> electron density decreases (node) between the nuclei -> antibonding molecular orbital (higher energy, destabilises).

3. Nodal surface: The surface where psi = 0 (change of sign) is a node. Antibonding MOs have a node between the nuclei where electron density is zero.

4. Orbital symmetry: The sign pattern determines which orbitals can combine (same symmetry with respect to bond axis is required for effective overlap).

Answer: The + and - signs indicate the phase (sign) of the wave function, not charge. Same-phase overlap (+ with +) gives constructive interference -> bonding MO (lower energy). Opposite-phase overlap (+ with -) gives destructive interference -> antibonding MO (higher energy, nodal plane between nuclei).

Q38 Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

SOLUTION

Hybridisation in PCl_5:

Ground state electronic configuration of P (Z=15): [Ne] $3s^2$ $3p^3$.

In the excited state, one 3s electron is promoted to an empty 3d orbital: $3s^1$ $3p^3$ $3d^1$.

Five orbitals (1 s + 3 p + 1 d) hybridise to form five sp^3d hybrid orbitals.

These five hybrid orbitals are directed towards the five corners of a trigonal bipyramid.

Each sp^3d hybrid orbital overlaps with a singly occupied 3p orbital of Cl to form P-Cl sigma bonds.

Structure: Trigonal bipyramidal.

Three equatorial P-Cl bonds lie in the equatorial plane, making angles of 120° with each other.

Two axial P-Cl bonds lie above and below the equatorial plane, making 90° with the equatorial plane.

Why axial bonds are longer than equatorial bonds:

The axial bond pairs experience repulsive interactions from three equatorial bond pairs (at 90°, which is a closer angle than 120°). In contrast, each equatorial bond pair experiences repulsion from only two other equatorial bond pairs (at 120°) and repulsion from two axial bond pairs (at 90°).

The greater repulsion suffered by axial bond pairs from three equatorial bond pairs (at 90°) weakens the axial P-Cl bonds slightly, making them slightly longer (hence weaker) compared to the equatorial P-Cl bonds.

Answer: PCl_5: P undergoes sp^3d hybridisation (one 3s + three 3p + one 3d orbital) giving a trigonal bipyramidal shape. Axial bonds are longer because they experience greater repulsion from three equatorial bond pairs (at 90°) than equatorial bonds experience from each other (at 120°), weakening the axial bonds.

Q39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

SOLUTION

Hydrogen bond: An electrostatic attractive force formed between a partially positive hydrogen atom (covalently bonded to a highly electronegative atom X such as F, O, or N) and the lone pair of another electronegative atom (F, O, or N) of the same or different molecule.

Represented as: X-H---Y (where X-H is a covalent bond and ---Y is the hydrogen bond; dotted line represents the H-bond).

Formation: When H is covalently bonded to a very electronegative atom X (F, O, N), the electron pair shifts strongly towards X, leaving H with a large partial positive charge (delta+). This H^(delta+) attracts the lone pair of another electronegative atom Y, forming the hydrogen bond.

Strength comparison with van der Waals forces:
Hydrogen bond strength: typically 10-40 kJ mol^{-1}.
van der Waals forces: typically < 1 to ~10 kJ mol^{-1} (much weaker).

Hydrogen bonds are STRONGER than van der Waals (London dispersion) forces but weaker than covalent bonds (~200-900 kJ mol^{-1}) or ionic bonds.

Answer: Hydrogen bond: electrostatic attraction between X-H^(delta+) and lone pair of electronegative atom Y (X, Y = F, O, N). Strength ~10-40 kJ mol^{-1}. Hydrogen bonds are stronger than van der Waals forces (<~10 kJ mol^{-1}) but weaker than covalent/ionic bonds.

Q40 What is meant by the term bond order? Calculate the bond order of: N_2, O_2, O_2^+ and O_2^-.

SOLUTION

Bond order is defined as one-half the difference between the number of electrons in bonding molecular orbitals (Nb) and the number of electrons in antibonding molecular orbitals (Na):
Bond order = (1/2)(Nb - Na)
Higher bond order -> stronger bond, shorter bond length, higher bond dissociation enthalpy.

N_2 (14 electrons, uses N_2 MO order where $sigma_2pz$ is above pi_2px/pi_2py):

MO config: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2px})^2(\pi_{2py})^2(\sigma_{2pz})^2$
Nb = 2+2+2+2+2 = 10; Na = 2+2 = 4
Bond order = (10-4)/2 = 3 (triple bond)
N_2 is diamagnetic (no unpaired electrons).

O_2 (16 electrons, uses O_2 MO order where σ_{2pz} is below π^*_{2px}/π^*_{2py}):
MO config: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2pz})^2(\pi_{2px})^2(\pi_{2py})^2(\pi^*_{2px})^1(\pi^*_{2py})^1$
Nb = 2+2+2+2 = 10; Na = 2+2+1+1 = 6
Bond order = (10-6)/2 = 2 (double bond)
O_2 is paramagnetic (2 unpaired electrons in π^* orbitals).

O_2^+ (15 electrons, one electron removed from π^*_{2px} of O_2):
Nb = 10; Na = 5
Bond order = (10-5)/2 = 2.5
O_2^+ is paramagnetic (1 unpaired electron).

O_2^- (17 electrons, one electron added to π^*_{2py} of O_2):
Nb = 10; Na = 7
Bond order = (10-7)/2 = 1.5
O_2^- is paramagnetic (1 unpaired electron).

Answer: Bond order = (1/2)(Nb - Na). N_2: bond order = 3 (diamagnetic); O_2: bond order = 2 (paramagnetic); O_2^+: bond order = 2.5 (paramagnetic); O_2^-: bond order = 1.5 (paramagnetic).