WEIRD CHEMIST

P-Block Elements — Solutions

Dimerisation / Polymerisation

DPP – 02

Topic: Dimerisation / Polymerisation **Questions:** 15 Questions **Exam:** JEE / NEET

▶ TYPE 1 : Diborane (B_2H_6) — Structure & Bonding

Key Concepts — Diborane Structure

- B_2H_6 has **4 terminal** B–H bonds (2c–2e) + **2 bridging** B–H–B bonds (3c–2e)
- Total valence electrons in B_2H_6: $2 \times 3 + 6 \times 1 = 12$
- B in B_2H_6: **sp^3** hybridised (4 bonds, tetrahedral geometry)
- 4 terminal H + 2 B lie in **one plane**; 2 bridging H are in a **perpendicular plane**
- Terminal B–H: **shorter** (normal bond); Bridge B–H: **longer** (electron-deficient 3c–2e)
- B_2H_6 acts as **Lewis acid** (electron-deficient B)
- Al_2Cl_6: Al is sp^3; bridging bond = **coordinate bond** (Cl lone pair $\rightarrow$ Al); bridging bond **longer** than terminal

Q1. In which molecule do vacant orbitals not participate in bonding?

Explanation

Checking each option:

- B_2H_6: B uses its empty p orbital to form 3-centre 2-electron (3c–2e) banana bonds with bridging H. Vacant orbital **participates**.
- Al_2Cl_6: Al's empty orbital accepts a lone pair from bridging Cl (coordinate bond). Vacant orbital **participates**.
- $[H_3N \cdot BF_3]$: BF_3's empty p orbital accepts NH_3's lone pair. Vacant orbital **participates**.
- Si_2H_6 (disilane): Si–Si bond is a normal σ bond (2c–2e). All Si–H bonds are also normal 2c–2e bonds. Si uses only its sp^3 hybrid orbitals — no empty orbital involvement in bonding. **Vacant orbitals do NOT participate**.

Approach

Ask: does the molecule need an empty orbital to explain its bonding? B_2H_6, Al_2Cl_6, and adducts — yes, always. Disilane is just a Si–Si chain with sp^3 bonds, like ethane. No deficiency, no need for empty orbitals.

Answer

(4) Si_2H_6

Q2. In diborane

Explanation

B_2H_6 has a total of **6 hydrogen atoms**:

- **4 terminal H**: 2 on each B, lying in the same plane as the two B atoms. Each forms a normal 2c–2e bond.
- **2 bridging H**: These form the two banana-shaped 3c–2e bonds connecting the two B atoms. They lie in a plane *perpendicular* to the terminal plane.

Option (1) is the only correct count.

Approach

Simple count for diborane: 4 terminal + 2 bridging = 6 H total. The bridging H are the "glue" holding the two BH_3 units together. Think of a butterfly: wings = terminal H (flat plane), body = bridging H (perpendicular).

Answer

(1) 2 bridged hydrogen and four terminal hydrogen are present.

Q3. Which statement is correct about diborane (B_2H_6)?

Explanation

Verifying all three statements:

- **(1)** Valence electrons: 2×3 (from B) $+ 6 \times 1$ (from H) $= 12$. **Correct**.
- **(2)** Two of the six H atoms form the two B–H–B bridges. **Correct**.
- **(3)** The two bridging H lie in a plane perpendicular to the plane of the four terminal H and two B atoms. This perpendicular arrangement prevents free rotation about the B–B axis. **Correct**.

All three statements are individually correct $\Rightarrow$ **All of these**.

Approach

When a question has "All of these" and each individual option is a standard textbook fact about diborane — verify each quickly and pick All.

Answer

(4) All of these.

Q4. Which statement is incorrect about the structure of diborane?

Explanation

Checking each option:

- **(1)** All terminal B–H bond lengths are equal. **True** (both terminal B–H bonds on each B are equivalent).
- **(2)** Terminal B–H is a 2-centre 3-electron bond. **False/Incorrect**. Terminal B–H bonds are **2-centre 2-electron** (normal covalent bonds). The 3c–2e bond exists only in the *bridging* B–H–B positions.
- **(3)** Terminal B–H is a 2-centre 2-electron bond. **True**.
- **(4)** Bridge B–H–B is a 3-centre 2-electron bond. **True**.

Option (2) incorrectly assigns the 3-electron count to terminal bonds.

Approach

Key distinction to memorise: **Terminal** B–H = **2c–2e** (normal bond). **Bridging** B–H–B = **3c–2e** (banana/3-centre bond). Never mix these up in an MCQ.

Answer

(2) Terminal B–H described as 2-centre 3-electron bond is **incorrect**; it is 2c–2e.

Q5. The type of hybridisation of boron in diborane is

Explanation

Each B atom in B_2H_6 is bonded to:

- 2 terminal H atoms (2 normal bonds)
- 2 bridging H atoms (participates in 2 three-centre bonds)

Total electron-pair geometry around each B = **4 pairs** $\Rightarrow$ sp^3 **hybridisation** $\Rightarrow$ approximately tetrahedral arrangement.

It is **not** sp^2 (that would give only 3 groups and leave a fully empty p orbital, as in BF_3). In B_2H_6, B uses all four hybrid orbitals for bonding.

Approach

Count the bonds around B: 4 bonds (2 terminal + 2 bridge participations) $\Rightarrow$ 4 orbitals needed $\Rightarrow$ sp^3. Compare: in free BF_3 (no bridge), B has 3 bonds $\Rightarrow$ sp^2.

Answer

(3) sp^3

Q6. Which statement is not correct about diborane? [NTA]

Explanation

Checking each option:

- **(1)** Four terminal B–H bonds are 2c–2e. **True**.
- **(2)** Four terminal H and two B lie in one plane. **True** (the molecular "frame" is planar).
- **(3)** Both B atoms are sp^2 hybridised. **False**. B in B_2H_6 is sp^3, forming 4 bonds. sp^2 would imply only 3 bonds and one empty p orbital — that is the situation in free BF_3, not in diborane.
- **(4)** There are two 3c–2e bonds (the two banana bridges). **True**.

Approach

The trap: students confuse B's hybridisation in BF_3 (sp^2) with B's hybridisation in B_2H_6 (sp^3). In diborane, B uses all four sp^3 orbitals $\Rightarrow$ no empty p orbital remains $\Rightarrow$ not sp^2.

Answer

(3) Both boron atoms are sp^2 hybridised is **incorrect**; they are sp^3.

▶ TYPE 2 : Dimerisation — Comparison, Octet & Applications

Key Concepts — Dimerisation Comparison

- **Lewis acid** = electron pair **acceptor** (needs empty orbital)
- B_2H_6: Lewis acid hydride (electron-deficient B)
- $BeCl_2$(dimer): Be achieves **complete octet** (4 bonds via coordinate bonding from Cl lone pairs)
- BeH_2(dimer) / Ga_2H_6: 3c–2e bonds like diborane $\Rightarrow$ Be/Ga still electron-deficient
- Al_2Br_6: Al empty orbital **involved** in hybridisation ($sp^2 \to sp^3$)
- Cl_2O_6: empty orbital of Cl in ClO_3 **not** involved in hybridisation for dimerisation

Q7. Which molecular hydride acts as a Lewis acid? [AIPMT Pre. 2010]

Explanation

- CH_4: C has complete octet, no empty orbital, no lone pair to donate. **Neither acid nor base**.
- NH_3: N has a lone pair $\Rightarrow$ electron pair **donor** $\Rightarrow$ **Lewis base**.
- H_2O: O has two lone pairs $\Rightarrow$ **Lewis base**.
- B_2H_6: B is electron-deficient (forms 3c–2e bonds because it doesn't have enough electrons). It can accept an electron pair from a donor $\Rightarrow$ **Lewis acid**.

Approach

Lewis acid = "electron hungry." B in B_2H_6 has only 6 electrons per B in the monomer BH_3. Even in the dimer, the 3c–2e bonds leave B deficient. It eagerly accepts lone pairs $\Rightarrow$ Lewis acid.

Answer

(4) B_2H_6

Q8. Which molecule has a complete octet around the central atom?

Explanation

- **$BeCl_2$(dimer)**: Be accepts two lone pairs from the two bridging Cl atoms (coordinate bonds). Total bonds around Be = 2 terminal + 2 coordinate = 4 bonds = **8 electrons** ⇒ **complete octet**.

- **BeH_2(dimer)**: H has no lone pair to donate. Bridging in Be_2H_4 proceeds via 3c–2e bonds (like diborane), giving Be only ∼6 electrons ⇒ **incomplete octet**.
- **BeH_2(s)**: Polymeric chain; Be has 2 bonds = 4 electrons ⇒ **incomplete**.
- **$BeCl_2$(s)**: Infinite chain; Be is bridged but may not achieve full octet depending on polymer structure.

The key difference: Cl has lone pairs to donate; H does not. Only Cl-bridged dimers can complete Be's octet via coordinate bonding.

Approach

Does the bridging atom have a lone pair? Cl: yes ⇒ donates to Be ⇒ complete octet. H: no lone pair ⇒ only 3c–2e bonding possible ⇒ Be stays electron-deficient.

Answer

(1) $BeCl_2$(dimer)

Q9. In which dimer does the empty orbital of the monomer's central atom not involve in hybridisation?

Explanation

- **Ga_2H_6**: Like diborane. Ga in GaH_3 is sp^2 with one empty p orbital. In the dimer, Ga uses this empty orbital for 3c–2e bonding ⇒ empty orbital **involved**.
- **Al_2Br_6**: Al in $AlBr_3$ is sp^2; one empty p orbital. In the dimer, Al accepts Br's lone pair into this orbital, changing to sp^3 ⇒ empty orbital **involved in hybridisation**.
- **Be_2H_4**: Be in BeH_2 is sp with two empty p orbitals. In the dimer, 3c–2e bonding uses these orbitals ⇒ empty orbital **involved**.
- **Cl_2O_6**: The monomer ClO_3 dimerises through O-bridging. Cl in ClO_3 does not use an empty atomic orbital for dimerisation; instead the structure relies on the lone pairs of O and the existing Cl=O bonds. The empty orbital of Cl is **not involved** in hybridisation during dimerisation.

Approach

All Group-13 hydrides/halide dimers (Ga, Al, Be) use the monomer's empty orbital directly. Cl_2O_6 is the odd one out — the Cl centre does not involve its empty orbital in the hybridisation process for dimerisation.

Answer

(4) Cl_2O_6

Q10. In Al_2Cl_6, hybridisation of Al and nature of bridging bond are:

Explanation

Monomer ($AlCl_3$): Al is sp^2 (3 bonds, 1 empty p orbital), trigonal planar.

Dimer (Al_2Cl_6): Each bridging Cl donates a lone pair into Al's empty p orbital. Al now has 4 bonds (2 terminal + 2 bridge) $\Rightarrow$ hybridisation changes to **sp^3** (tetrahedral).

The bridging bond is a **coordinate (dative) bond**: one atom (Cl) provides both electrons. The Al does not contribute electrons to this bond — it only receives them.

Approach

Monomer sp^2 (3 bonds) $\xrightarrow{\text{dimerisation}}$ dimer sp^3 (4 bonds). The change is driven by Cl's lone pair filling Al's empty orbital. That filling = coordinate bond.

Answer

(2) sp^3; coordinate bond.

▶ TYPE 3 : NCERT Based Questions

Key Concepts — Al_2Cl_6 vs BF_3 (NCERT)

- Bridging Al–Cl bond (**221 pm**) > terminal Al–Cl bond (**206 pm**) because bridging Cl's lone pair is shared between **two** Al atoms $\Rightarrow$ bond order per Al < 1
- BF_3 does **not** dimerize: $p\pi$–$p\pi$ back bonding (F $\rightarrow$ B) partially satisfies B's electron deficiency
- Al_2Cl_6 structure: 4-membered ring with $\angle$Al–Cl–Al = 79°, $\angle$Cl–Al–Cl (bridge) = 101°, $\angle$Cl–Al–Cl (terminal) = 118°
- In Al_2Cl_6: Al is sp^3, tetrahedral; bridging bond is **longer** and **coordinate**; terminal bond is **shorter** and **covalent**

Q11. Bridging Al–Cl (221 pm) is longer than terminal Al–Cl (206 pm). Which option best supports this?

Explanation

The bridging Cl uses its lone pair to form a **coordinate bond** with **one** Al. However, because Cl sits between two Al atoms in the ring, the electron density from that lone pair is effectively shared across the Al−Cl−Al unit. This reduces the bond order of each individual Al–Cl interaction below 1 ⇒ weaker bond ⇒ longer bond.

Option (1) is wrong: it says lone pair goes to only one Al — but that would give a normal coordinate bond length, not a longer one.
Options (3) and (4) are factually incorrect generalisations.

Approach

Think of the lone pair as a shared resource. When Cl donates to only one Al (terminal), the bond gets full strength. When it sits between two Al atoms (bridging), each Al gets only "half the attention" ⇒ bond weakens ⇒ longer.

Answer

(2) Bridging Cl shares its lone pair between two Al atoms, reducing bond order per Al ⇒ longer bond.

Q12. Al in Al_2Cl_6 completes its octet by

Explanation

Al in $AlCl_3$ (monomer) has only 6 electrons (3 bonds). The octet requires 8. In Al_2Cl_6, each Al receives a lone pair from a bridging Cl atom via a **coordinate (dative) bond**:

$$\mathrm{Al}\ (6\ \mathrm{e}^-) + \mathrm{Cl\ lone\ pair} \rightarrow \mathrm{Al}\ (8\ \mathrm{e}^-) = \mathrm{complete\ octet}$$

Options (1) and (4) involve electron transfer/ionic bonding — not what happens here. Option (2) describes terminal bonds, which existed in the monomer and don't complete the octet by themselves.

Approach

Al's empty orbital is an open hand. Cl's lone pair fills it. That handshake = coordinate bond. Only that addition takes Al from 6 to 8.

Answer

(3) Accepting a lone pair from bridging Cl atoms.

Q13. BF_3 does not dimerize despite being electron-deficient. Most likely reason:

Explanation

Both BF_3 and $AlCl_3$ are electron-deficient (6 electrons on the central atom). Yet $AlCl_3$ dimerizes while BF_3 does not.

The key difference: F is a **2nd-period element** with filled $2p$ orbitals that perfectly match B's empty $2p$ orbital in size and energy. This enables strong $p\pi$–$p\pi$ **back bonding**: F's lone pair donates sideways into B's empty p orbital, giving B partial electron density. This partially satisfies B's electron deficiency $\Rightarrow$ B has **less need** to dimerize.

Cl in $AlCl_3$ is a 3rd-period element; $3p$–$2p$ overlap with Al is poor $\Rightarrow$ very little back bonding $\Rightarrow$ Al remains strongly electron-deficient $\Rightarrow$ dimerizes readily.

Approach

Back bonding in BF_3 partially fills the empty cup (B's p orbital) from inside the molecule itself. So B has less urgency to find an external lone-pair donor via dimerisation. $AlCl_3$'s cup stays empty $\Rightarrow$ dimerizes.

Answer

(3) F back-donates π electron density into B's empty orbital, partially satisfying B's deficiency $\Rightarrow$ no need to dimerize.

Q14. In Al_2Cl_6: $\angle$Al–Cl–Al = 79°, $\angle$Cl–Al–Cl (bridge) = 101°, $\angle$Cl–Al–Cl (terminal) = 118°. Which conclusion is correct?

Explanation

Given data:

- $\angle$Al–Cl–Al (angle at bridging Cl) $= 79°$
- $\angle$Cl–Al–Cl in the ring (angle at Al, bridge) $= 101°$
- $\angle$Cl–Al–Cl terminal $= 118°$

Clearly: $101° > 79°$. The Cl–Al–Cl bridge angle at Al is larger than the Al–Cl–Al angle at Cl. This asymmetry shows the 4-membered ring is **not** a perfect square (which would require all angles $= 90°$). The ring is non-square/puckered.

Option (1) reverses the comparison — incorrect.
Option (2) claims a perfect square — wrong, angles are 79° and 101°.
Option (4) compares bridge and terminal angles as equal — wrong.

Approach

Read the angles directly: $101°$ at Al $> 79°$ at Cl. Bigger angle at the metal (Al), smaller at the bridging halide (Cl). This is characteristic of the strain in the 4-membered Al_2Cl_2 ring.

Answer

(3) Cl–Al–Cl bridge angle $(101°) >$ Al–Cl–Al angle $(79°)$, showing the ring is puckered/non-square.

Q15. Which set of properties is correct for Al_2Cl_6?

Explanation

Assembling all facts about Al_2Cl_6:

- **Geometry at Al**: 4 bonds (2 terminal + 2 bridge) $\Rightarrow$ **tetrahedral**, sp^3. (*Not* trigonal planar)
- **Bond lengths**: Terminal Al–Cl (206 pm) $<$ Bridging Al–Cl (221 pm) $\Rightarrow$ bridging bond is **longer** than terminal. (*Not* shorter)
- **Nature of bridge bond**: Cl lone pair $\rightarrow$ Al $\Rightarrow$ **coordinate bond**. (*Not* ionic or purely covalent)

Only option (2) correctly states all three: tetrahedral, bridging longer, coordinate bond.

Approach

Three quick checks for Al_2Cl_6: (a) Geometry at Al? $\rightarrow$ tetrahedral (sp^3, 4 bonds). (b) Which bond is longer? $\rightarrow$ bridging (shared lone pair, weaker). (c) Bridge bond type? $\rightarrow$ coordinate (Cl donates to Al). Match all three $\Rightarrow$ option (2).

Answer

(2) Tetrahedral geometry at Al; bridging bond longer than terminal; coordinate bridge bond.

Quick Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	(4)	2	(1)	3	(4)	4	(2)	5	(3)
6	(3)	7	(4)	8	(1)	9	(4)	10	(2)
11	(2)	12	(3)	13	(3)	14	(3)	15	(2)