WEIRD CHEMIST

Where Chemistry Gets Interesting

DPP-6 Solution Sheet

p-Block Elements — Group 13: The Boron Family

NEET Revision Series | 50 Questions | Complete Solutions

"Understanding WHY each answer is correct is the difference between guessing and knowing."

QUICK ANSWER KEY

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	(2)	11	(2)	21	(2)	31	(2)	41	(2)
2	(2)	12	(1)	22	(2)	32	(2)	42	(2)
3	(2)	13	(3)	23	(2)	33	(1)	43	(2)
4	(2)	14	(3)	24	(2)	34	(2)	44	(2)
5	(2)	15	(1)	25	(2)	35	(2)	45	(2)
6	(4)	16	(2)	26	(3)	36	(2)	46	(1)
7	(2)	17	(2)	27	(2)	37	(2)	47	(2)
8	(2)	18	(3)	28	(1)	38	(2)	48	(2)
9	(2)	19	(2)	29	(2)	39	(3)	49	(2)
10	(2)	20	(2)	30	(2)	40	(2)	50	(2)

TOPIC 1 — Introduction

(a) Elements of Group 13

Q.1 Which is the correct list of all elements belonging to Group 13?

[A] Conceptual Approach

Group 13 is the Boron Family. Remember the mnemonic: **B Al Ga In Tl** (Boron, Aluminium, Gallium, Indium, Thallium). These are the 5 elements with outer config ns^2np^1.

[S] Step-by-Step Solution

Group 13 = **B, Al, Ga, In, Tl** — the p-block elements with 3 valence electrons.

Option (1): B, C, N, O, F = Period 2 elements, not Group 13.
Option (3): Be, Mg, Ca, Sr, Ba = Group 2 (alkaline earth metals).
Option (4): Na, K, Rb, Cs, Fr = Group 1 (alkali metals).

[Ans] Final Answer

Option (2): B, Al, Ga, In, Tl

[!] Common Mistake

Confusing Group 13 with Period 2. B is in Period 2, but Group 13 goes DOWN the group (B, Al, Ga, In, Tl), not across the period.

(b) Nature — Metal or Non-Metal

Q.2 Which correctly describes the variation in metallic character across Group 13?

[A] Conceptual Approach

In any group, metallic character increases going DOWN. In Group 13: B (non-metal, semiconductor/metalloid) → Al, Ga, In, Tl (all metals). Note: B is a metalloid/non-metal; Al is the first metal.

[S] Step-by-Step Solution

Boron: non-metal (NCERT calls it a "typical non-metal"; hard, does not conduct electricity).
Aluminium, Gallium, Indium, Thallium: all are metals (conduct electricity, metallic lustre, ductile).

Going down Group 13: non-metallic → metallic character increases.

[Ans] Final Answer

Option (2): Boron is a non-metal; Al, Ga, In, Tl are metals

[!] Common Mistake

Option (3) says Al is also a non-metal. Wrong! Aluminium is definitely a metal — highly conducting, ductile, forms Al^{3+} ions. Only boron is non-metallic in Group 13.

Q.3 Boron is a "typical non-metal" in NCERT. Which property best justifies this?

[A] Conceptual Approach

Non-metals are typically: hard (if solid), poor electrical conductors, high melting point (if crystalline lattice). Boron is a black, extremely hard crystalline solid — none of the usual "soft, low melting" non-metal images apply, but it doesn't conduct electricity.

[S] Step-by-Step Solution

Boron is:

- Extremely hard (hardest element after diamond)
- Black coloured crystalline solid with very strong covalent lattice
- Does **NOT** conduct electricity (not a metal)
- Very high melting point (2453 K)

These properties together justify it being called a typical non-metal despite being a solid.

[Ans] Final Answer

Option (2): Extremely hard, black solid with strong crystalline lattice; does not conduct electricity

[!] Common Mistake

Option (1) says "low melting point and soft texture." That is WRONG — boron has one of the highest melting points in Group 13 (2453 K) and is extremely hard, not soft.

(c) Occurrence

Q.4 Correct abundance of boron in earth's crust and its important ores?

[A] Conceptual Approach

NCERT facts: Boron is a rare element ($< 0.0001\%$ by mass in earth's crust). Its important minerals are: orthoboric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot {}_{10}H_2O$), kernite ($Na_2B_4O_7 \cdot {}_4H_2O$), and colemanite ($Ca_2B_6O_{11} \cdot {}_5H_2O$).

[S] Step-by-Step Solution

Boron abundance: very small $< 0.0001\%$ by mass (fairly rare).

Important ores/minerals of boron:

- Orthoboric acid: H_3BO_3
- Borax: $Na_2B_4O_7 \cdot {}_{10}H_2O$
- Kernite: $Na_2B_4O_7 \cdot {}_4H_2O$
- Colemanite: $Ca_2B_6O_{11} \cdot {}_5H_2O$

Option (3) gives 27.7% which is aluminium's abundance, not boron's.

[Ans] Final Answer

Option (2): Abundance $< 0.0001\%$; ores: orthoboric acid, borax, kernite, colemanite

[!] Common Mistake

Mixing boron and aluminium data. 27.7% = silicon abundance; 8.3% = aluminium abundance. Boron is a RARE element with abundance $< 0.0001\%$.

Q.5 Percentage abundance of aluminium and its important minerals?

[A] Conceptual Approach

NCERT: Aluminium is the most abundant metal in earth's crust at 8.3% by mass. Its important minerals are bauxite ($Al_2O_3 \cdot {}_2H_2O$) and cryolite (Na_3AlF_6).

[S] Step-by-Step Solution

Aluminium abundance: 8.3% by mass (most abundant metal).

Important minerals:

- Bauxite: $Al_2O_3 \cdot {}_2H_2O$
- Cryolite: Na_3AlF_6

Option (1) says 45.5% — that is oxygen's abundance. Option (3) says 27.7% — that is silicon's abundance.

[Ans] Final Answer

Option (2): 8.3% by mass; bauxite ($Al_2O_3 \cdot {}_2H_2O$) and cryolite (Na_3AlF_6)

[!] Common Mistake

Remembering 8.3% as boron's abundance. Boron is RARE ($< 0.0001\%$); ALUMINIUM is 8.3%. Three numbers to remember: O = 45.5%, Si = 27.7%, Al = 8.3%.

TOPIC 2 — Atomic Properties

(a) Electronic Configuration

Q.6 Which element has noble gas core + 10 d-electrons + 14 f-electrons + 10 d-electron cores, making its structure the most complex?

[A] Conceptual Approach

Build up the configurations down Group 13. After indium (noble gas core + 10d), thallium has BOTH d and f electrons in its inner core: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$. This f-block contribution makes it the most complex.

[S] Step-by-Step Solution

Electronic configurations of Group 13:

- B: [He] $2s^2\ 2p^1$ — simple
- Al: [Ne] $3s^2\ 3p^1$ — noble gas core only
- Ga: [Ar] $3d^{10}\ 4s^2\ 4p^1$ — noble gas + 10d
- In: [Kr] $4d^{10}\ 5s^2\ 5p^1$ — noble gas + 10d
- **Tl**: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$ — noble gas + 14f + 10d = **most complex!**

[Ans] Final Answer

Option (4): Thallium (Tl)

[!] Common Mistake

Confusing Tl with In. Indium has [Kr]$4d^{10}5s^25p^1$ (d-electrons only). Thallium has BOTH $4f^{14}$ and $5d^{10}$ in addition to the xenon core, making it the most complex configuration.

Q.7 Why is the electronic structure of gallium more complex than aluminium?

[A] Conceptual Approach

Al = [Ne] $3s^2\ 3p^1$ (simple noble gas core, no d electrons). Ga = [Ar] $3d^{10}\ 4s^2\ 4p^1$ (noble gas core PLUS 10 d-electrons). The filled d-subshell makes Ga's structure more complex.

[S] Step-by-Step Solution

Aluminium: [Ne] $3s^2\ 3p^1$ — only noble gas (neon) core.

Gallium: [Ar] $3d^{10}\ 4s^2\ 4p^1$ — noble gas (argon) core PLUS 10 filled d-electrons.

The presence of 10 d-electrons in Ga's inner core (that Al lacks) makes its structure more complex.

[Ans] Final Answer

Option (2): Gallium has noble gas core + 10 d-electrons; aluminium has only a simple noble gas core

[!] Common Mistake

Thinking the difference is just more protons (option 3). All Period 4 elements have more protons than Period 3, but the KEY difference is the d-subshell that gets filled in Period 4 ($3d^{10}$ in Ga).

(b) Atomic Radii

Q.8 Atomic radius of Ga (135 pm) is LESS than Al (143 pm) — best reason?

[A] Conceptual Approach

Going from Al to Ga: we cross the first row of d-block ($3d^{10}$ fills). d-electrons shield poorly (they are in the same shell level and diffuse). So despite more electrons in Ga, the effective nuclear charge felt by outer electrons is HIGHER than expected.

[S] Step-by-Step Solution

Between Al (Period 3) and Ga (Period 4), 10 d-electrons are added ($3d^{10}$).

d-electrons provide **poor shielding** of outer electrons from nuclear charge because:
- d-orbitals are diffuse and don't effectively screen the nucleus

$\therefore$ Effective nuclear charge (Z_{eff}) on the 4p electron in Ga is **higher than expected**.
Higher $Z_{eff} \Rightarrow$ outer electrons pulled closer $\Rightarrow$ **smaller radius than Al**.

[Ans] Final Answer

Option (2): 10 d-electrons in Ga provide poor shielding $\Rightarrow$ unexpectedly high Z_{eff} on outer electrons

[!] Common Mistake

Option (1) says "higher nuclear charge pulls electrons closer." While true, it's incomplete. The KEY concept is POOR SHIELDING by d-electrons making Z_{eff} unexpectedly high — just having higher Z doesn't explain why Ga is SMALLER than Al.

Q.9 Correct order of atomic radii for Group 13 elements?

[A] Conceptual Approach

General trend: radius increases down group. BUT Ga $<$ Al (due to poor d-electron shielding). Order: B $<$ Ga $<$ Al $<$ In $<$ Tl.

[S] Step-by-Step Solution

Element	Atomic Radius	Note
B	85 pm	smallest
Al	143 pm	increases normally
Ga	135 pm	**anomalously smaller than Al** (d-electron shielding)
In	167 pm	increases
Tl	170 pm	largest

Correct order: $r_B < r_{Ga} < r_{Al} < r_{In} < r_{Tl}$

[Ans] Final Answer

Option (2): $r_B < r_{Ga} < r_{Al} < r_{In} < r_{Tl}$

[!] Common Mistake

Assuming radius always increases smoothly (option 1). The Ga anomaly (Ga $<$ Al due to poor d-shielding) is a critical NEET fact. Option (1) would be correct only if there were no d-block between Al and Ga.

(c) Ionisation Enthalpy

Q.10 Discontinuity in ionisation enthalpy between In and Tl — correct explanation?

[A] Conceptual Approach

Between In (Period 5) and Tl (Period 6): 14 f-electrons (lanthanide series) AND 10 d-electrons are added. f-electrons shield EVEN WORSE than d-electrons. This is called lanthanide contraction — it raises Z_{eff} on Tl's outer electrons significantly, making IE higher than expected.

[S] Step-by-Step Solution

Between In and Tl, the entire lanthanide series (14 f-electrons, $4f^{14}$) is added.

f-electrons shield extremely poorly (even worse than d-electrons).

$\therefore$ The 10 d-electrons AND 14 f-electrons in Tl's core provide poor shielding.
Z_{eff} on Tl's outer ($6s^2 6p^1$) electrons is much higher than expected.

This makes Tl's ionisation enthalpy higher than simple size argument would predict.

[Ans] Final Answer

Option (2): 10 d-electrons AND 14 f-electrons in Tl provide poor shielding $\Rightarrow$ higher Z_{eff} than expected

[!] Common Mistake

Option (4) mentions the inert pair effect. While inert pair effect is real for Tl, it does NOT explain why ionisation enthalpy is higher than expected. The poor shielding by d and f electrons is the correct explanation for the IE discontinuity.

Q.11 Order of first three successive ionisation enthalpies for Group 13 elements?

[A] Conceptual Approach

Group 13 has config ns^2np^1. Removing 3 electrons: first removes the p electron (relatively easy), then two s electrons (harder). Each successive IE is higher because you're removing from a more positively charged ion.

[S] Step-by-Step Solution

$\Delta_i H_1$: Remove 1 electron from neutral atom (ns^2np^1) — remove p electron (easiest).
$\Delta_i H_2$: Remove from M^+ (ns^2) — remove s electron, higher charge, harder.
$\Delta_i H_3$: Remove from M^{2+} (ns^1) — remove last s electron, even harder.

$\therefore \Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$

[Ans] Final Answer

Option (2): $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$

[!] Common Mistake

Picking option (1) — decreasing order. Successive ionisation enthalpies ALWAYS increase. Each removal is from a progressively more positive species with fewer electrons, so it always takes MORE energy.

Q.12 From Al to Ga, IE does not decrease as expected. Correct reason?

[A] Conceptual Approach

Same logic as Q8 and Q10: $3d^{10}$ fills between Al and Ga. Poor d-electron shielding raises Z_{eff} on Ga's outer electrons. Higher $Z_{eff} \Rightarrow$ harder to remove electrons $\Rightarrow$ IE doesn't decrease as expected.

[S] Step-by-Step Solution

Between Al and Ga, 10 d-electrons ($3d^{10}$) are introduced.

Poor screening by d-electrons $\Rightarrow$ Z_{eff} on Ga's 4p electron is unexpectedly high.
Harder to remove $\Rightarrow$ Ga's IE is NOT lower than Al's as simple size argument would predict.

[Ans] Final Answer

Option (1): Poor screening by 10 d-electrons increases Z_{eff}, preventing expected decrease in IE

[!] Common Mistake

Option (3) says "inert pair effect in Ga stabilises 4s electrons." Inert pair effect is significant only in heavier elements (In, Tl), NOT in Ga. The correct reason for Ga's anomalously high IE is poor d-electron shielding.

(d) Electronegativity

Q.13 Correct description of electronegativity trend in Group 13?

[A] Conceptual Approach

Electronegativity (EN) generally decreases down a group as atomic size increases. In Group 13, the trend is irregular: B > Al (big drop), then Al ≈ Ga ≈ In ≈ Tl (slight increase or irregular). The NCERT description: decreases from B to Al then increases slightly or shows discrepancy.

[S] Step-by-Step Solution

EN values (Pauling scale): B (2.0) > Al (1.5) ≈ Ga (1.6) ≈ In (1.7) ≈ Tl (1.8).

Trend: EN **first decreases** from B to Al (large drop), then **increases marginally** or becomes irregular from Al to Tl due to discrepancies in atomic size (d/f orbital effects).

This matches option (3).

[Ans] Final Answer

Option (3): EN first decreases from B to Al, then increases marginally due to discrepancies in atomic size

[!] Common Mistake

Option (1) says EN increases steadily. Completely wrong. B is much more electronegative than Al (B=2.0, Al=1.5). Going down, EN generally decreases (more metallic character).

TOPIC 3 — Physical Properties

(a) Physical State at Room Temperature

Q.14 Correct physical state of all Group 13 elements at 298 K?

[A] Conceptual Approach

All Group 13 elements are SOLIDS at 298 K — but gallium is special: its melting point is 303 K, so it melts just above room temperature (in your hand or in summer). At 298 K it is technically solid but very close to its melting point.

[S] Step-by-Step Solution

At 298 K:

- B (mp = 2453 K): solid
- Al (mp = 933 K): solid
- Ga (mp = 303 K): **solid**, but just barely! Melts at 303 K (very close to RT)
- In (mp = 430 K): solid
- Tl (mp = 577 K): solid

All are solids at 298 K, but gallium's unusually low melting point (303 K) means it melts just above room temperature.

[Ans] Final Answer

Option (3): All solids except gallium, which has unusually low mp (303 K) and melts just above RT

[!] Common Mistake

Option (2) says gallium is liquid at RT. At exactly 298 K, Ga is still solid (mp = 303 K > 298 K). But it melts very easily — even body heat (310 K) can melt it. Option (3) correctly says it melts "just above room temperature."

(b) Boiling Point Order

Q.15 Correct decreasing order of boiling points: B=3923 K, Al=2740 K, Ga=2676 K, In=2353 K, Tl=1730 K?

[A] Conceptual Approach

Simply arrange the given values in decreasing order. Boron has the highest boiling point (covalent lattice). The order decreases down the group.

[S] Step-by-Step Solution

Given values: B = 3923 K, Al = 2740 K, Ga = 2676 K, In = 2353 K, Tl = 1730 K

Decreasing order: **B > Al > Ga > In > Tl**

Note: Boron has such a high boiling point due to its giant covalent lattice structure.
Also notable: Ga has a very high boiling point (2676 K) despite its very low melting point (303 K) — huge liquid range, useful for high-temperature thermometry.

[Ans] Final Answer

Option (1): B > Al > Ga > In > Tl

[!] Common Mistake

Confusing boiling and melting point order. The boiling point order (B highest) is different from what you might expect if you only remember Ga's low MELTING point. Ga melts at 303 K but boils at 2676 K — a huge difference!

(c) Melting Point Order

Q.16 Why does boron have unusually high melting point? Which has the lowest melting point?

[A] Conceptual Approach

Boron: giant covalent lattice (like diamond) = requires enormous energy to break = very high mp. Gallium: mp = 303 K = lowest in group. The variation: B (very high) then drops irregularly.

[S] Step-by-Step Solution

Boron's high melting point (2453 K): Due to its extremely strong covalent crystalline lattice (icosahedral B_{12} units linked by covalent bonds). Very high energy needed to break these strong bonds.

Lowest melting point: Gallium at only 303 K (melts in warm hands!). This is anomalously low due to weak metallic bonding in Ga's crystal structure.

[Ans] Final Answer

Option (2): B has highest mp due to strong crystalline lattice; Ga (303 K) has the lowest mp

[!] Common Mistake

Option (1) says Al has the lowest mp. Wrong! Gallium (303 K) has the lowest melting point in Group 13. Al melts at 933 K, which is much higher than Ga.

Q.17 Which of the statements I–IV about melting/boiling points of Group 13 are correct?

[A] Conceptual Approach

Check each statement against NCERT data:
I. B high mp due to crystalline lattice — TRUE.
II. Ga mp = 303 K, melts in summer — TRUE.
III. Ga bp = 2676 K, useful for high-T thermometry — TRUE.
IV. All mp increase smoothly going down — FALSE (Ga anomaly!).

[S] Step-by-Step Solution

Statement I: TRUE — B's crystalline lattice gives very high mp (2453 K).
Statement II: TRUE — Ga mp = 303 K; summer ambient can exceed this.
Statement III: TRUE — Ga has huge liquid range (303 to 2676 K); ideal for high-T measurement.
Statement IV: FALSE — melting points do NOT increase smoothly; Ga (303 K) is anomalously low compared to Al (933 K) and In (430 K).

Correct statements: I, II, and III only.

[Ans] Final Answer

Option (2): I, II and III only

[!] Common Mistake

Including Statement IV as correct. The melting point order is NOT smooth: B (2453) $\gg$ Al (933) $>$ In (430) $>$ Tl (577) $>$ Ga (303). Gallium's unexpectedly low mp breaks any smooth trend.

(d) Density

Q.18 Correct order of increasing density for Group 13 elements?

[A] Conceptual Approach

Density generally increases down a group. NCERT values: B (2.35) $<$ Al (2.70) $<$ Ga (5.91) $<$ In (7.31) $<$ Tl (11.85) g/cm^3. Increasing order: B $<$ Al $<$ Ga $<$ In $<$ Tl.

[S] Step-by-Step Solution

Density (g/cm^3): B = 2.35, Al = 2.70, Ga = 5.91, In = 7.31, Tl = 11.85

Increasing order: **B $<$ Al $<$ Ga $<$ In $<$ Tl**

As atomic mass increases rapidly down the group while volume doesn't increase proportionally, density increases.

[Ans] Final Answer

Option (3): B $<$ Al $<$ Ga $<$ In $<$ Tl

[!] Common Mistake

Option (2) puts In before Ga. Wrong! Ga (5.91) $<$ In (7.31). The density increases smoothly from B to Tl — no anomaly here unlike radius or IE.

Q.19 Correct description of density trend and electrical conductivity for Group 13 (excluding B)?

[A] Conceptual Approach

Density increases from Al to Tl (heavier atoms). Al, Ga, In, Tl are all metals $\Rightarrow$ all good conductors of electricity. Boron (non-metal) is a semiconductor, not a good conductor.

[S] Step-by-Step Solution

Density: Increases from B to Tl (Al $<$ Ga $<$ In $<$ Tl).

Electrical conductivity: Al, Ga, In, Tl are all **soft metals with high electrical conductivity** (typical metallic behaviour).

The question says "excluding boron," so we focus on the 4 metals: all good conductors.

[Ans] Final Answer

Option (2): Density increases; Al, Ga, In, Tl are soft metals with high electrical conductivity

[!] Common Mistake

Option (3) says only Al is a good conductor. Wrong! All four metals (Al, Ga, In, Tl) conduct electricity well — they are all typical metals.

TOPIC 4 — Chemical Properties

(a) Oxidation States

Q.20 Boron forms only covalent compounds and cannot form B^{3+} ions. Best explanation?

[A] Conceptual Approach

For ionic bond to form, the energy released by lattice formation must compensate the ionisation energy. For B^{3+}, you must remove all 3 electrons from a very small atom. The sum of first three IEs of B is enormous — this energy can never be recovered by lattice formation.

[S] Step-by-Step Solution

Sum of IEs for B: $\Delta_i H_1 + \Delta_i H_2 + \Delta_i H_3 = 6.886$ MJ/mol (very large).

Boron is very small (r = 85 pm) and very electronegative (2.0).
For B^{3+} to form, this enormous energy must be recovered by lattice/solvation enthalpy — which is **energetically unfavourable**.

$\therefore$ Boron only forms **covalent compounds** (shares electrons rather than completely losing them).

[Ans] Final Answer

Option (2): Sum of first three IEs of boron is very high due to small size $\Rightarrow$ B^{3+} formation is energetically unfavourable

[!] Common Mistake

Option (4) says Al is a non-metal and more likely to form ionic compounds. Completely wrong! Al IS a metal and DOES form Al^{3+} in ionic compounds. Boron (non-metal, small, high IE) cannot form B^{3+}.

Q.21 Which correctly explains the inert pair effect?

[A] Conceptual Approach

Inert pair effect = heavier elements retain their ns^2 electrons and don't participate in bonding. REASON: poor shielding by intervening d and f electrons increases Z_{eff} on the ns electrons, making them "contract" closer to nucleus and harder to ionise.

[S] Step-by-Step Solution

In heavier Group 13 elements (In, Tl): many d and f electrons are present in inner shells.

d and f electrons shield poorly $\Rightarrow$ nuclear charge is felt more strongly by the ns electrons.
ns electrons are pulled closer to nucleus (contracted) $\Rightarrow$ they become **reluctant to participate in bonding**.

This tendency of ns^2 electrons to remain non-bonding = **Inert Pair Effect**.

Result: Tl prefers +1 (loses only p electron) over +3 (would need to lose ns^2 as well).

[Ans] Final Answer

Option (2): Poor shielding by d and f orbitals increases Z_{eff} on ns electrons, making them reluctant to bond

[!] Common Mistake

Option (1) says ns electrons are lost FIRST. Wrong! In the inert pair effect, ns electrons are RETAINED (not lost), and only the np electron is removed (giving +1 state). The ns^2 pair is the "inert pair."

Q.22 Correct trend in relative stability of +1 oxidation state down Group 13?

[A] Conceptual Approach

Inert pair effect becomes MORE pronounced going DOWN the group (more d and f electrons to shield poorly). So stability of +1 state INCREASES from Al to Tl.

[S] Step-by-Step Solution

The inert pair effect strengthens going down the group:

Al: inert pair effect minimal $\Rightarrow$ Al^{3+} very stable, Al^{+} rare.
Ga: slight inert pair effect.
In: moderate; both +1 and +3 exist.
Tl: strong inert pair effect $\Rightarrow$ Tl^{+} predominates; Tl^{3+} is highly oxidising.

Stability of +1 state: Al $<$ Ga $<$ In $<$ Tl.

[Ans] Final Answer

Option (2): Tl $>$ In $>$ Ga $>$ Al

[!] Common Mistake

Option (1) gives the reverse order (Al $>$ Ga $>$ In $>$ Tl). This would mean Al has the most stable +1 state, which is completely wrong. Al almost exclusively shows +3. It is THALLIUM that predominantly shows +1.

Q.23 In Tl, +1 state is predominant and +3 is highly oxidising. Explanation?

[A] Conceptual Approach

Direct application of inert pair effect for Tl. The $6s^2$ electrons in Tl are contracted and held tightly by the high effective nuclear charge (due to poor d and f shielding). They form the "inert pair."

[S] Step-by-Step Solution

Thallium (Z = 81): [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^1$

Due to **inert pair effect**: the $6s^2$ electrons are contracted (held tightly by high Z_{eff}) and reluctant to be removed.

$\therefore$ Only the $6p^1$ electron is removed easily $\Rightarrow$ **Tl^+** (+1 state) predominates.

Removing all 3 electrons to give Tl^{3+} requires enormous energy $\Rightarrow$ Tl^{3+} is a **strong oxidising agent** (eager to get electrons back).

[Ans] Final Answer

Option (2): Inert pair effect makes $6s^2$ electrons of Tl reluctant to bond $\Rightarrow$ Tl^+ more stable than Tl^{3+}

[!] Common Mistake

Option (1) says large atomic radius makes +3 state more stable. Wrong! Large size should actually make +3 LESS stable (harder to form M^{3+} and have it exist in solution). The inert pair effect is the correct explanation.

Q.24 Which combination of statements I–IV about oxidation states is correct?

I. Tl: +1 predominant, +3 highly oxidising.
II. +1 compounds more ionic than +3 compounds.
III. In BF_3, boron has 8 electrons (not Lewis acid).
IV. Stability of +1 state increases: Al < Ga < In < Tl.

[A] Conceptual Approach

Check each statement:
I: TRUE (Tl inert pair effect).
II: TRUE (+1 = larger ion, lower charge density = more ionic; +3 = small, high charge = covalent).
III: FALSE! BF_3 has only 6 electrons around B (electron deficient = strong Lewis acid).
IV: TRUE (inert pair effect increases down group).

[S] Step-by-Step Solution

Statement I: TRUE — Tl^+ predominates; Tl^{3+} is a powerful oxidant.
Statement II: TRUE — M^+ has lower charge, larger size $\Rightarrow$ ionic. M^{3+} has high polarising power $\Rightarrow$ covalent.
Statement III: **FALSE** — BF_3 has only 6 electrons around B (3 bond pairs). Electron deficient $\Rightarrow$ it IS a Lewis acid!
Statement IV: TRUE — Tl shows highest stability in +1 state (inert pair effect).

Correct statements: I, II, and IV.

[Ans] Final Answer

Option (2): I, II and IV only

[!] Common Mistake

Accepting Statement III. BF_3 is THE classic example of a Lewis acid (electron deficient, only 6 electrons around B, accepts lone pair). Never say BF_3 is not a Lewis acid — that is a fundamental NEET concept!

Q.25 $E°(Al^{3+}/Al) = -1.66$ V and $E°(Tl^{3+}/Tl) = +1.26$ V. Correct conclusion?

[A] Conceptual Approach

More negative E° = stronger reducing agent = more electropositive. Al ($E^\circ = -1.66$ V) much more electropositive than Tl. Positive E° for Tl^{3+}/Tl means Tl^{3+} wants to accept electrons back (is a good oxidising agent); Tl^+ is the stable ion.

[S] Step-by-Step Solution

$E^\circ(Al^{3+}/Al) = -1.66$ V: Very negative $\Rightarrow$ Al is a strong reducing agent, highly electropositive, readily forms Al^{3+}.

$E^\circ(Tl^{3+}/Tl) = +1.26$ V: Positive $\Rightarrow$ Tl^{3+} is a powerful **oxidising agent** (pulls electrons from other species). Tl^+ (not Tl^{3+}) is the stable ion in solution.

$\therefore$ Al is more electropositive; Tl^{3+} is unstable and oxidising; Tl^+ predominates.

[Ans] Final Answer

Option (2): Al is more electropositive; Tl^{3+} is unstable and a powerful oxidising agent; Tl^+ is more stable

[!] Common Mistake

Option (1) says Tl is more electropositive because E° is positive. Wrong! Positive E° means the ion tends to GAIN electrons (be reduced), meaning the metal is LESS electropositive, not more. Al's highly negative E° makes it the more electropositive metal.

Q.26 Why are +1 state compounds more ionic than +3 state compounds?

[A] Conceptual Approach

Two reasons work together: (1) M^+ is larger (less charge removed) $\Rightarrow$ lower charge density $\Rightarrow$ less polarising power $\Rightarrow$ more ionic. (2) M^{3+} is tiny and triply charged $\Rightarrow$ very high charge density $\Rightarrow$ polarises anion $\Rightarrow$ covalent character.

[S] Step-by-Step Solution

+1 state (M^+): Only the np^1 electron lost. M^+ has larger size (less contraction), lower charge (1+), low polarising power $\Rightarrow$ forms **ionic bonds**.

+3 state (M^{3+}): All 3 valence electrons lost. M^{3+} is tiny (highly contracted) with 3+ charge = very high charge density and polarising power $\Rightarrow$ polarises anion $\Rightarrow$ **covalent character**.

Both (1) and (2) together explain the observation.

[Ans] Final Answer

Option (3): Both (1) and (2) correctly explain why +1 state compounds are more ionic

[!] Common Mistake

Choosing only option (1) or only option (2). Both reasons are complementary and valid. The contrast is complete: M^+ (large, low charge $\Rightarrow$ ionic) vs M^{3+} (small, high charge $\Rightarrow$ covalent).

(b) Reactivity Towards Air

Q.27 Aluminium reacts with air to form Al_2O_3 but does not corrode further. Correct explanation?

[A] Conceptual Approach

Al reacts with O_2 to form Al_2O_3. This oxide layer is very thin, dense, and adheres tightly to the surface. It acts as a physical barrier, preventing O_2 from reaching the metal below (unlike iron rust which is porous and flakes off).

[S] Step-by-Step Solution

When Al is exposed to air: $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

The **Al_2O_3 layer** formed is:

- Very thin but extremely tough and dense
- Strongly adherent to the Al surface
- Impermeable to oxygen and moisture

This passive oxide layer prevents further oxidation of the underlying metal.

[Ans] Final Answer

Option (2): Al forms a thin, tough Al_2O_3 layer that acts as a protective barrier against further reaction

[!] Common Mistake

Option (1) says Al reacts with N_2 to form a nitride layer. Wrong! The protective layer is Al_2O_3 (oxide), not a nitride. Al does react with N_2 at high temperatures, but the passivation in air is due to the oxide layer.

Q.28 Correct pair of equations for Group 13 element E reacting with O_2 and N_2?

[A] Conceptual Approach

Group 13 oxides: E_2O_3 (E is trivalent). Nitrides: EN (E is trivalent, N is -3: EN formula). Check balancing in each option.

[S] Step-by-Step Solution

Oxide formation: $4E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$ — gives E_2O_3 (Group 13 oxide).

Nitride formation: $2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$ — gives EN (E^{3+}, N^{3-}: electroneutrality requires EN).

Option (1) matches: $2E + 3O_2 \rightarrow 2E_2O_3$ (correct stoichiometry) and $2E + N_2 \rightarrow 2EN$ (correct formula).

[Ans] Final Answer

Option (1): $2E(s) + 3O_2(g) \rightarrow 2E_2O_3(s)$ and $2E(s) + N_2(g) \rightarrow 2EN(s)$

[!] Common Mistake

Option (2) writes $4E + 3O_2 \rightarrow 2E_2O_3$ — this is ALSO balanced correctly for the oxide! But it then writes EN_2 for the nitride, which is wrong (E is +3, N is -3, so formula must be EN, not EN_2).

Q.29 How does the nature of Group 13 oxides vary down the group?

[A] Conceptual Approach

NCERT: B_2O_3 = acidic (non-metal oxide). Al_2O_3, Ga_2O_3 = amphoteric (borderline metal). In and Tl oxides = basic (typical metals). The trend: acidic → amphoteric → basic, which is the standard group trend from non-metal to metal character.

[S] Step-by-Step Solution

Oxide	Nature
B_2O_3	**Acidic** (non-metallic oxide; reacts with bases)
Al_2O_3	**Amphoteric** (reacts with both acids and bases)
Ga_2O_3	**Amphoteric**
In_2O_3	**Basic**
Tl_2O	**Basic**

Trend: Acidic (B) → Amphoteric (Al, Ga) → Basic (In, Tl).

[Ans] Final Answer

Option (2): B_2O_3 acidic; Al_2O_3 and Ga_2O_3 amphoteric; oxides of In and Tl basic

[!] Common Mistake

Option (1) says B_2O_3 is basic. Completely wrong! B_2O_3 is the classic acidic non-metallic oxide. It reacts with bases (NaOH) to form borates, and is used in glass industry.

Q.30 How does B_2O_3 (acidic) react with basic metallic oxide?

[A] Conceptual Approach

General rule: Acidic oxide + Basic oxide → Salt. B_2O_3 (acidic) + CaO (basic) → $Ca(BO_2)_2$ (calcium metaborate). This is similar to CO_2 + CaO → $CaCO_3$.

[S] Step-by-Step Solution

Acidic oxide B_2O_3 + Basic oxide CaO → Salt (metal borate):

$$B_2O_3 + CaO \rightarrow Ca(BO_2)_2 \quad \text{(calcium metaborate)}$$

This is a standard acid-base reaction between oxides, forming a salt.

[Ans] Final Answer

Option (2): B_2O_3 reacts with basic metallic oxides (e.g., CaO) to form metal borates (e.g., $Ca(BO_2)_2$)

[!] Common Mistake

Option (3) says B_2O_3 doesn't react because it's a non-metallic oxide and non-metallic oxides are inert. Wrong! Non-metallic oxides are ACIDIC and react readily with basic oxides. This is a fundamental acid-base concept.

Q.31 Which combination of statements I–IV about reactivity towards air is correct?

I. B_2O_3 is acidic, reacts with basic metallic oxides to form metal borates.

II. Oxides of In and Tl are amphoteric.

III. Al and Ga oxides are amphoteric.
IV. At high T, Group 13 elements react with N_2 to form nitrides of formula EN.

[A] Conceptual Approach

I: TRUE. II: FALSE (In/Tl oxides are BASIC, not amphoteric). III: TRUE. IV: TRUE.
Check statement II carefully — it's the trap!

[S] Step-by-Step Solution

Statement I: TRUE — $B_2O_3 + CaO \rightarrow Ca(BO_2)_2$ (correct).
Statement II: **FALSE** — Oxides of In and Tl are **basic**, NOT amphoteric.
Statement III: TRUE — Al_2O_3 and Ga_2O_3 are amphoteric.
Statement IV: TRUE — At high T: $2E + N_2 \rightarrow 2EN$.

Correct statements: I, III, and IV.

[Ans] Final Answer

Option (2): I, III and IV only

[!] Common Mistake

Accepting Statement II as correct. In and Tl are typical METALS $\Rightarrow$ their oxides are BASIC (not amphoteric).
Amphoteric oxides = Al_2O_3 and Ga_2O_3 (the borderline metals).

(c) Reactivity Towards Acids and Alkalies

Q.32 Concentrated HNO_3 renders Al passive. Correct explanation?

[A] Conceptual Approach

Passivation by conc. HNO_3 = same mechanism as with air. The strongly oxidising conc. HNO_3 rapidly oxidises the Al surface forming a dense, adherent Al_2O_3 layer that prevents further reaction.

[S] Step-by-Step Solution

Concentrated HNO_3 is a powerful oxidising agent.

It rapidly oxidises the surface of aluminium to form a thin, dense **Al_2O_3 passive layer**.

This oxide layer:

- Is impermeable to the acid
- Prevents further reaction between Al and HNO_3
- Makes Al appear "passive" (unreactive)

That's why Al containers can store conc. HNO_3 safely (used in the chemical industry).

[Ans] Final Answer

Option (2): Conc. HNO_3 forms a thin, tough protective oxide layer on Al surface, preventing further reaction

[!] Common Mistake

Option (3) says HNO_3 converts Al to $Al(NO_3)_3$ which coats the surface. Wrong! The protective layer is Al_2O_3 (oxide), not a nitrate salt. Same as the air passivation mechanism.

Q.33 Which pair of reactions correctly demonstrates Al's amphoteric character?

[A] Conceptual Approach

Amphoteric = reacts with BOTH acids AND bases. With acid (HCl): forms $AlCl_3$ + H_2. With base (NaOH): forms $Na[Al(OH)_4]$ (sodium tetrahydroxoaluminate) + H_2. Both release H_2.

[S] Step-by-Step Solution

With dilute HCl (acid):

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

With NaOH (base):

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$$

In both cases: $AlCl_3$ or $Na[Al(OH)_4]$ formed; H_2 gas liberated.

[Ans] Final Answer

Option (1): Reacts with HCl to give $AlCl_3$ and with NaOH to give $Na[Al(OH)_4]$, liberating H_2 in both cases

[!] Common Mistake

Option (2) says Al doesn't react with NaOH. Very wrong! Al readily dissolves in NaOH solution (this is why you should never clean Al pans with caustic soda). The NaOH reaction liberates H_2 and forms the aluminate complex.

Q.34 Student adds excess NaOH to Al metal. Products formed and IUPAC name?

[A] Conceptual Approach

Al + excess NaOH solution: the product is $Na[Al(OH)_4]$ (tetrahydroxoaluminate) + H_2. IUPAC name: sodium tetrahydroxoaluminate(III). The "(III)" because Al is in +3 oxidation state.

[S] Step-by-Step Solution

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) + 3H_2(g) \uparrow$$

Products: **$Na[Al(OH)_4]$** and **H_2 gas**.

IUPAC name of $Na[Al(OH)_4]$: **Sodium tetrahydroxoaluminate(III)**.
("Tetrahydroxo" = 4 OH^- ligands; "aluminate" = complex with Al as central atom; "(III)" = Al oxidation state).

[Ans] Final Answer

Option (2): $Na[Al(OH)_4]$ and H_2; sodium tetrahydroxoaluminate(III)

[!] Common Mistake

Choosing option (4) $NaAlO_2$ (sodium meta-aluminate). $NaAlO_2$ is the anhydrous form; the product in AQUEOUS NaOH is $Na[Al(OH)_4]$ (tetrahydroxoaluminate). NCERT specifically gives this formula for the aqueous reaction.

Q.35 Correct balanced equation for Al with dilute HCl?

[A] Conceptual Approach

Al is +3 in $AlCl_3$. Balance: $2Al \rightarrow 2Al^{3+}$ (lose $6e^-$); $6HCl \rightarrow 6H^+ + 6Cl^-$; $6H^+ + 6e^- \rightarrow 3H_2$.

[S] Step-by-Step Solution

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

In ionic form: $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

Check: 2 Al atoms balanced; 6 Cl^- balanced; 6 H balanced ($3H_2$); charge balanced.

[Ans] Final Answer

Option (2): $\mathbf{2Al}(s) + 6\mathbf{HCl}(aq) \rightarrow \mathbf{2Al^{3+}}(aq) + 6\mathbf{Cl^-}(aq) + 3\mathbf{H_2}(g)$

[!] Common Mistake

Option (3) writes $H_3(g)$ as product. H_3 does not exist! The gas liberated is H_2 (dihydrogen). Each H^+ gains one electron; two H^+ combine to give one H_2 molecule.

Q.36 Which combination of statements I–IV about reactivity towards acids/alkalies is correct?

I. Boron does not react with acids and alkalies even at moderate temperature.
II. Al dissolves in dilute HCl liberating H_2.
III. Conc. HNO_3 reacts vigorously with Al and dissolves it completely.
IV. Product when Al reacts with NaOH = sodium tetrahydroxoaluminate(III).

[A] Conceptual Approach

I: TRUE (B is very unreactive at moderate T). II: TRUE. III: FALSE (conc. HNO_3 PASSIVATES Al, does NOT dissolve it). IV: TRUE. Answer: I, II, IV.

[S] Step-by-Step Solution

Statement I: TRUE — Boron is highly resistant to acids and alkalies at moderate temperatures.
Statement II: TRUE — $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$.
Statement III: **FALSE** — Conc. HNO_3 passivates Al (forms protective oxide layer); it does NOT dissolve Al vigorously.
Statement IV: TRUE — $Na[Al(OH)_4]$ = sodium tetrahydroxoaluminate(III).

Correct statements: I, II, and IV.

[Ans] Final Answer

Option (2): I, II and IV only

[!] Common Mistake

Accepting Statement III. This is the classic trap! Conc. HNO_3 does NOT dissolve Al — it PASSIVATES it. Dilute HNO_3 would react; concentrated HNO_3 makes Al passive (same with Fe and Cr).

(d) Reactivity Towards Halogens

Q.37 Group 13 elements form trihalides (EX_3). What does thallium form and why?

[A] Conceptual Approach

Thallium: strong inert pair effect ⇒ +1 state predominant. With halogens: Tl forms TlX (monohalide, +1 state) rather than TlX_3 (+3 state). Exception to the group trend.

[S] Step-by-Step Solution

All Group 13 elements react with halogens to form **EX_3** (trihalide)...
EXCEPT Thallium: due to the strong inert pair effect in Tl, the $6s^2$ electrons are retained.

$\therefore$ Thallium forms **TlX** (monohalide, +1 oxidation state) rather than TlX_3.

The +1 state of Tl is more stable than +3 due to contraction and high Z_{eff} on 6s electrons.

[Ans] Final Answer

Option (2): Tl forms TlX (monohalide) because the inert pair effect makes +1 the predominant oxidation state

[!] Common Mistake

Option (1) says "inert pair effect not strong enough with halogens." Wrong! Halogens are very electronegative and still can't overcome Tl's inert pair effect. Tl remains predominantly +1 even with the most electronegative halogen (F).

Q.38 White fumes around open bottle of anhydrous $AlCl_3$. Why?

[A] Conceptual Approach

Anhydrous $AlCl_3$ is a strong Lewis acid. It reacts with the water vapour in air (atmospheric moisture) to hydrolyse partially, producing HCl gas. HCl gas in moist air appears as white fumes.

[S] Step-by-Step Solution

Anhydrous $AlCl_3$ is highly hygroscopic (absorbs moisture from air).

When it encounters atmospheric moisture (H_2O vapour):

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl(g)$$

The **HCl gas** produced reacts with atmospheric moisture to form tiny droplets of hydrochloric acid mist, which appears as **white fumes**.

[Ans] Final Answer

Option (2): Anhydrous $AlCl_3$ partially hydrolysed by atmospheric moisture ⇒ HCl gas ⇒ white fumes

[!] Common Mistake

Option (1) says $AlCl_3$ sublimes to give white vapours. While $AlCl_3$ does sublime (forms Al_2Cl_6 dimers), the WHITE FUMES specifically come from HCl produced by hydrolysis with atmospheric moisture. Sublimation vapours alone would not be white.

Q.39 Correct product when aluminium reacts with chlorine gas?

[A] Conceptual Approach

Al is in Group 13: +3 is the common oxidation state. Cl is -1 in chlorides. $Al^{3+} + 3Cl^- \rightarrow AlCl_3$. Balanced: $2Al + 3Cl_2 \rightarrow 2AlCl_3$.

[S] Step-by-Step Solution

Al shows +3 oxidation state with halogens.

$2Al(s) + 3Cl_2(g) \xrightarrow{\Delta} 2AlCl_3(s)$

Product: **$AlCl_3$** (aluminium trichloride).

Note: $AlCl_3$ exists as dimer **Al_2Cl_6** in vapour phase and in non-polar solvents.

[Ans] Final Answer

Option (3): $AlCl_3$

[!] Common Mistake

Writing AlCl (option 1). AlCl would mean Al is +1, which is not the standard state for Al. Only thallium prefers +1 in halides. Aluminium ALWAYS forms AlX_3 with halogens.

TOPIC 5 — Anomalous Behaviour of Boron

Q.40 Trihalides of Group 13 (except B) hydrolyse in water to give $[M(H_2O)_6]^{3+}$ and $[M(OH)_4]^-$. Which species form during hydrolysis of $AlCl_3$ in water?

[A] Conceptual Approach

$AlCl_3$ hydrolyses in water. Al can expand its coordination number beyond 4 (has d-orbitals available). In water: Al forms the octahedral hexaaqua complex $[Al(H_2O)_6]^{3+}$. In the presence of OH^-, it forms $[Al(OH)_4]^-$. The question asks which pair — answer: octahedral hexaaqua complex + HCl.

[S] Step-by-Step Solution

When $AlCl_3$ dissolves in water:

$$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

The complex ion formed: **Octahedral $[Al(H_2O)_6]^{3+}$** (Al coordinates with 6 water molecules).
Also HCl is produced (the solution becomes acidic).

(With excess NaOH: $[Al(H_2O)_6]^{3+} + 4OH^- \rightarrow [Al(OH)_4]^- + 6H_2O$)

[Ans] Final Answer

Option (2): Octahedral $[Al(H_2O)_6]^{3+}$ and HCl

[!] Common Mistake

Option (1) says tetrahedral $[Al(OH)_4]^-$ and HCl. While $[Al(OH)_4]^-$ does form with excess base, the direct hydrolysis product in neutral water gives $[Al(H_2O)_6]^{3+}$ first. In basic conditions, you get the tetrahedral hydroxo complex.

Q.41 Trihalides of Group 13 hydrolyse to give $[M(OH)_4]^-$ and $[M(H_2O)_6]^{3+}$, but boron is an exception. Best explanation?

[A] Conceptual Approach

$[M(OH)_4]^-$ = tetrahedral (4-coordinate). $[M(H_2O)_6]^{3+}$ = octahedral (6-coordinate). Both require coordination numbers of 4 or 6. Boron's maximum covalence is 4, so $[B(OH)_4]^-$ could theoretically form... BUT boron cannot form 6-coordinate species. More importantly, boron lacks d-orbitals so it can only go up to 4 coordination. It forms $B(OH)_3$, not $[B(H_2O)_6]^{3+}$.

[S] Step-by-Step Solution

Heavier Group 13 elements (Al, Ga, In, Tl) have **d-orbitals available** $\Rightarrow$ can expand coordination number to 6 $\Rightarrow$ form octahedral $[M(H_2O)_6]^{3+}$.

Boron lacks d-orbitals $\Rightarrow$ maximum covalence = 4.
Boron cannot form octahedral $[B(H_2O)_6]^{3+}$ (needs CN=6).

Instead, BCl_3 hydrolyses to give **$B(OH)_3$** (boric acid) or **$[B(OH)_4]^-$** (tetrahedral, CN=4, possible) but NOT the octahedral aqua complex seen for Al.

No d-orbitals $\Rightarrow$ cannot achieve the coordination numbers typical of heavier analogues.

[Ans] Final Answer

Option (2): Boron lacks d-orbitals; max covalence = 4; cannot form $[B(H_2O)_6]^{3+}$ (needs CN=6) like other Group 13 elements

[!] Common Mistake

Option (3) says B–Cl bond is very strong and resists hydrolysis. Wrong! BCl_3 is actually hydrolysed more readily than $AlCl_3$. The reason B doesn't form the same products is its limited coordination number due to no d-orbitals.

Q.42 Maximum covalence of B is 4; for Al and heavier elements it can exceed 4. Why?

[A] Conceptual Approach

Covalence > 4 requires expanding the octet, which needs participation of d-orbitals. Boron (Period 2) has no d-orbitals in its valence shell (2s, 2p only). Al (Period 3) has 3d orbitals that are energetically accessible.

[S] Step-by-Step Solution

Boron (Period 2): Valence shell = 2s, 2p only. **No d-orbitals** available.
Maximum covalence = 4 (can accommodate at most 4 bond pairs: use sp^3 hybridisation).

Aluminium (Period 3): Valence shell = 3s, 3p, **3d** (accessible).

Can use d-orbitals for bonding ⇒ can expand octet ⇒ coordination number > 4.
Example: AlF_6^{3-} has Al with coordination number 6 (octahedral sp^3d^2).

[Ans] Final Answer

Option (2): Boron has no d-orbitals (max covalence = 4); Al and heavier elements have accessible d-orbitals allowing expansion beyond 4

[!] Common Mistake

Option (4) says Al has smaller atomic radius than B. Completely false! Al (143 pm) is much larger than B (85 pm). Size is not the reason — the presence of d-orbitals is the key difference.

Q.43 B cannot form BF_6^{3-} but Al readily forms AlF_6^{3-}. Correct reason for boron's inability?

[A] Conceptual Approach

BF_6^{3-} would require B to form 6 bonds = coordination number 6 = needs d-orbitals for sp^3d^2 hybridisation. Boron has no d-orbitals (Period 2). Maximum covalence of B = 4. Hence BF_4^- exists (sp^3) but BF_6^{3-} cannot.

[S] Step-by-Step Solution

BF_6^{3-} requires B to bond with 6 F atoms (coordination number = 6).

This needs sp^3d^2 hybridisation involving d-orbitals.

Boron (Period 2) has **no d-orbitals** ⇒ cannot expand octet beyond 8 electrons (max 4 bonds).

Therefore maximum complex from B with F is $\mathbf{[BF_4]^-}$ (4-coordinate, sp^3).

Al (Period 3) has 3d orbitals ⇒ forms $[AlF_6]^{3-}$ (6-coordinate, sp^3d^2).

[Ans] Final Answer

Option (2): Boron has no d-orbitals ⇒ cannot expand its octet; maximum covalence cannot exceed 4

[!] Common Mistake

Option (1) says B has high electronegativity and repels fluoride. Wrong! B (EN=2.0) is not so electronegative that it repels F^-. In fact, B DOES form $[BF_4]^-$. The limitation is purely the availability of d-orbitals.

Q.44 BF_3 reacts with NH_3. Correct description of change in geometry of boron?

[A] Conceptual Approach

BF_3: B is sp^2 hybridised (planar, trigonal), only 6 electrons. When NH_3 donates its lone pair to B's empty orbital: B becomes sp^3 (tetrahedral). Boron changes from trigonal planar to tetrahedral as it completes its octet.

[S] Step-by-Step Solution

Before reaction — BF_3:
B: sp^2 hybridised, **trigonal planar** geometry, only 6 electrons (electron deficient).

Reaction: NH_3 donates lone pair to empty p-orbital of B:

$$BF_3 + NH_3 \rightarrow F_3B \leftarrow NH_3$$

After reaction — $BF_3 \cdot NH_3$ adduct:
B: now has 4 bonds (3 to F, 1 coordinate to N), **sp^3 hybridised, tetrahedral geometry**.
Boron changes: **planar (sp^2) → tetrahedral (sp^3)**.

[Ans] Final Answer

Option (2): Boron changes from planar (sp^2) to tetrahedral (sp^3); BF_3 accepts lone pair from NH_3 (Lewis acid-base)

[!] Common Mistake

Option (1) says BF_3 is electron-rich and donates electrons. Completely wrong! BF_3 is electron DEFICIENT (Lewis acid). It has an empty orbital and ACCEPTS the lone pair from NH_3. NH_3 is the Lewis base (donor).

Q.45 Number of electrons around central atom in BCl_3 and $AlCl_3$; are they Lewis acids?

[A] Conceptual Approach

BCl_3: B has 3 bond pairs = 6 electrons (electron deficient, NOT an octet). $AlCl_3$: Al has 3 bond pairs = 6 electrons too. Both are electron deficient ⇒ both are Lewis acids (accept lone pairs).

[S] Step-by-Step Solution

BCl_3: B forms 3 bonds with Cl (3 bond pairs = **6 electrons** around B). Incomplete octet ⇒ electron deficient.

$AlCl_3$: Al forms 3 bonds with Cl (3 bond pairs = **6 electrons** around Al). Electron deficient.

Both are **electron deficient** (only 6 electrons, need 8 for octet).
∴ Both act as **Lewis acids** by accepting lone pairs from donors.

[Ans] Final Answer

Option (2): 6 electrons in both; electron deficient ⇒ both act as Lewis acids

[!] Common Mistake

Option (1) says 8 electrons in both (they are Lewis bases). Wrong! In EX_3 compounds of Group 13, the central atom has only 6 electrons (3 bond pairs). This is why they are called "electron deficient" and are strong Lewis acids.

Q.46 In Al_2Cl_6 dimer, bridging Al–Cl (221 pm) is longer than terminal Al–Cl (206 pm). Why is bridging bond weaker?

[A] Conceptual Approach

In the dimer, each bridging Cl donates its lone pair to TWO Al atoms simultaneously. The lone pair is shared between two Al centres, so the bond order per Al is less than 1. Less electron density per bond = weaker, longer bond.

[S] Step-by-Step Solution

Structure of Al_2Cl_6: two Al centres bridged by two Cl atoms (each Cl bridges between both Al).

Terminal Al–Cl bond: Cl donates to ONE Al only ⇒ full bond, shorter (206 pm), stronger.

Bridging Al–Cl bond: Bridging Cl donates its lone pair to **TWO Al atoms simultaneously**. Electron density is shared between two bonds ⇒ **lower bond order per Al** ⇒ bond is longer (221 pm) and weaker.

[Ans] Final Answer

Option (1): Bridging Cl donates to two Al atoms simultaneously ⇒ reduced bond order per Al ⇒ longer and weaker bridging bond

[!] Common Mistake

Option (3) says both bonds are coordinate bonds of equal strength. Wrong! The bridging bond IS a coordinate bond, but because the lone pair is shared between TWO Al atoms, each bond is weaker than the terminal (single Al) coordinate bond.

Q.47 $AlCl_3$ dimerises to Al_2Cl_6, but BF_3 does NOT dimerize through halogen bridging. Why?

[A] Conceptual Approach

Two reasons together explain why BF_3 doesn't dimerize: (1) Boron's small size and maximum covalence of 4 — but dimerization would only give CN=4 for B, which IS within limit. (2) BF_3 has significant B–F back-bonding (ppi-ppi): F's lone pairs partially back-donate into B's empty p-orbital, reducing B's electron deficiency. So B doesn't need to dimerize to achieve octet; it accepts external lone pairs instead. Option (2) captures the key: boron prefers to act as Lewis acid with external donors rather than bridge.

[S] Step-by-Step Solution

$AlCl_3$ dimerises: Al is electron deficient; Cl acts as bridging donor; Al can accommodate 4 bonds (tetrahedron in dimer). No back-bonding (3p−3d back donation from Cl to Al is weak).

BF_3 does NOT dimerize:

- Boron's small size means it prefers to complete its octet by accepting a lone pair from **one external donor** (like NH_3), acting as a Lewis acid, rather than bridging with F.
- B–F back-bonding (F lone pair → B empty p-orbital) partially satisfies boron, reducing the drive to dimerize.
- Boron's maximum covalence is 4 — it could technically bridge, but prefers the Lewis acid route.

[Ans] Final Answer

Option (2): Boron's small size and absence of d-orbitals limit max covalence to 4; prefers Lewis acid behaviour with external donors over bridging

[!] Common Mistake

Option (4) says fluorine is too small to act as a bridging atom. While F is smaller than Cl, fluorine DOES bridge in some fluorine-containing compounds. The real reason is boron's preference for Lewis acid behaviour and B–F back-bonding that reduces electron deficiency.

Q.48 Product when BF_3 reacts with NH_3 is $F_3B{\leftarrow}NH_3$. What type of bond forms between B and

N?

[A] Conceptual Approach

In the BF_3–NH_3 adduct: NH_3 donates its lone pair to boron's empty orbital. The B–N bond is formed by BOTH electrons coming from nitrogen. This is a coordinate bond (dative bond) or Lewis acid-base interaction.

[S] Step-by-Step Solution

BF_3: Lewis acid (empty orbital on B, only 6 electrons).
NH_3: Lewis base (lone pair on N).

Nitrogen's lone pair is donated into B's empty p-orbital:
N $:\rightarrow$ B (both electrons come from N)

This bond is: **Coordinate bond** (also called dative bond or Lewis acid-base interaction).
Once formed, it is identical to a regular covalent bond, but was formed by donation from one atom.

[Ans] Final Answer

Option (2): Coordinate bond (dative bond) — lone pair from N donated to empty orbital of B; Lewis acid-base interaction

[!] Common Mistake

Option (1) says normal covalent bond with one electron from each. Wrong! In B–N bond of this adduct, BOTH electrons come from N (nitrogen's lone pair). This is the definition of a coordinate/dative bond, not a normal covalent bond.

Q.49 In acidified aqueous solution, $AlCl_3$ forms $[Al(H_2O)_6]^{3+}$. Hybridisation of Al in this complex?

[A] Conceptual Approach

$[Al(H_2O)_6]^{3+}$: Al is the central atom, bonded to 6 water molecules (6-coordinate). 6 bonds arranged octahedrally $\Rightarrow$ sp^3d^2 hybridisation.

[S] Step-by-Step Solution

In $[Al(H_2O)_6]^{3+}$:

- Al is coordinated to 6 H_2O molecules
- Coordination number = 6
- Geometry: **octahedral**
- Hybridisation: **sp^3d^2**

Al uses 1s + 3p + 2d = 6 orbitals for bonding.

[Ans] Final Answer

Option (2): sp^3d^2

[!] Common Mistake

Option (1) writes sp^3 (tetrahedral, CN=4). Wrong for a 6-coordinate complex. Tetrahedral Al would be $[AlCl_4]^-$ (CN=4, sp^3). For 6-coordinate octahedral complex $[Al(H_2O)_6]^{3+}$: sp^3d^2.

Q.50 Which combination of statements I–IV about anomalous properties of boron and Group 13 trends is correct?

I. Trihalides of all Group 13 are covalent and hydrolysed in water.

II. $[M(OH)_4]^-$ and $[M(H_2O)_6]^{3+}$ exist for all Group 13 elements including boron.

III. BF_3 acts as a Lewis acid and reacts with NH_3 to complete boron's octet.

IV. Most metal halides of Group 13 dimerise through halogen bridging where metal accepts electrons from halogen.

[A] Conceptual Approach

I: Mostly TRUE (all trihalides are covalent; all do hydrolyse, though B gives different products). II: FALSE — boron is the EXCEPTION and does NOT form these species. III: TRUE. IV: TRUE (in Al_2Cl_6, bridging Cl donates to Al).

[S] Step-by-Step Solution

Statement I: TRUE — Trihalides of all Group 13 are covalent and do hydrolyse (B gives $B(OH)_3$ or H_3BO_3; others give $[M(H_2O)_6]^{3+}$).

Statement II: **FALSE** — Boron is the EXCEPTION. It does NOT form $[B(OH)_4]^-$ or $[B(H_2O)_6]^{3+}$ in the same way as heavier elements (no d-orbitals for 6-coordination).

Statement III: TRUE — $BF_3 + NH_3 \rightarrow F_3B{\leftarrow}NH_3$; B completes its octet.

Statement IV: TRUE — In Al_2Cl_6 dimer: bridging Cl donates lone pair to Al (coordinate bond); metal accepts.

Correct statements: I, III, and IV.

[Ans] Final Answer

Option (2): I, III and IV only

[!] Common Mistake

Accepting Statement II. This is the MAIN anomaly of boron in this chapter — it does NOT form $[M(OH)_4]^-$ or $[M(H_2O)_6]^{3+}$ because it lacks d-orbitals and cannot expand coordination number to 6. Boron is the exception, not the rule.

"The Boron Family is all about TWO big ideas:
the inert pair effect taking over from Tl,
and boron being the odd one out because of no d-orbitals.
Nail those two, and Group 13 becomes easy."

— Your Weird Chemist