WEIRD CHEMIST

Where Chemistry Gets Interesting

DPP-8 Solution Sheet

p-Block Elements — Group 15: The Nitrogen Family

NEET/JEE Revision Series | 50 Questions | Complete Solutions

"Group 15 has ONE big thread running through everything: nitrogen is the odd one out. No d-orbitals, lone pair repulsion, strong triple bond but weak single bond. Master that one idea and 70% of this chapter falls into place."

QUICK ANSWER KEY

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

TOPIC 1 — Introduction

(a) Elements, Nature & Occurrence

SKILL: Analytical Ability

Q.1 Why does nitrogen exist as free gas (N≡N) but phosphorus only as combined phosphate minerals?

[A] Conceptual Approach

Ek simple comparison: N≡N ki triple bond itni strong hai ($\Delta H = 941$ kJ/mol) ki usse todna bahut mushkil hai — isliye N_2 stable gas hai. Phosphorus ki P–P single bond weak hai, O_2 easily react kar leti hai, toh phosphates ban jaate hain.

[S] Step-by-Step Solution

Nitrogen as free gas: The N≡N triple bond has an exceptionally high bond enthalpy (941.4 kJ mol^{-1}), making it **kinetically and thermodynamically very stable**. It is essentially unreactive under normal conditions — the activation energy to break the triple bond is enormous.

Phosphorus never free: Elemental phosphorus is **highly reactive** — the P–P single bond is much weaker, and phosphorus combines readily with atmospheric oxygen over geological time to form stable phosphate minerals (apatite family).

Option (1) is wrong: both elements are non-metals; option (3) uses wrong classification.

[Ans] Final Answer

Option (2): N≡N triple bond is extremely strong (kinetically and thermodynamically stable); phosphorus is highly reactive and forms phosphates

[!] Common Mistake

Option (4) says "phosphorus was never formed as a free element." Wrong! Phosphorus was formed but *reacted away* over time due to its high reactivity. The key distinction is kinetic stability of N_2 vs reactivity of P.

SKILL: Conceptual Clarity

Q.2 Which correctly represents the change in character of Group 15 elements going down the group?

[A] Conceptual Approach

Group mein neeche jaane par metallic character badhta hai. Group 15: N, P = non-metals; As, Sb = metalloids; Bi = metal. Toh trend hai: non-metal → metalloid → metal.

[S] Step-by-Step Solution

Going down Group 15:

N, P: non-metals (no metallic lustre, poor conductors).
As, Sb: metalloids (semiconductor-like, borderline).
Bi: metal (metallic lustre, conductor, low melting point).

Trend: **Non-metal** → **Metalloid** → **Metal**

[Ans] Final Answer

Option (3): Non-metal → Metalloid → Metal

[!] Common Mistake

Option (1) skips metalloid entirely. Both As and Sb are metalloids — they cannot simply be called "metals." The correct 3-step trend is non-metal (N,P) → metalloid (As,Sb) → metal (Bi).

SKILL: Application Skills

Q.3 Sample X = $NaNO_3$, Sample Y = fluorapatite $Ca_9(PO_4)_6{\cdot}CaF_2$, Sample Z = metal sulphides. Which Group 15 elements from X, Y, Z respectively?

[A] Conceptual Approach

X = sodium **nitrate** → N. Y = **phosphate** mineral → P. Z = metal sulphide minerals like realgar, stibnite, bismuthinite → As/Sb/Bi. Simple chemical formula reading.

[S] Step-by-Step Solution

Sample X = $NaNO_3$ (sodium nitrate / Chile saltpetre) → contains **Nitrogen**.

Sample Y = fluorapatite, which is a phosphate mineral → contains **Phosphorus**.

Sample Z = metal sulphide ores (e.g., realgar As_4S_4, stibnite Sb_2S_3, bismuthinite Bi_2S_3) → contains **As/Sb/Bi**.

[Ans] Final Answer

Option (1): X → Nitrogen, Y → Phosphorus, Z → As/Sb/Bi

[!] Common Mistake

Confusing $NaNO_3$ with a phosphorus compound. $NaNO_3$ = sodium *nitrate* = nitrogen compound. $NaNO_3$ is "Chile saltpetre" or "Indian saltpetre" depending on the source. Fluorapatite is clearly a phosphate (note "PO_4" in the formula).

SKILL: Diagram-Based Visual Literacy

Q.4 Student redraws classification chart: moves P to "Metalloids" and Sb to "Non-metals." Which statement about the redrawn chart is correct?

[A] Conceptual Approach

Correct classification: N, P = non-metals; As, Sb = metalloids; Bi = metal. Student moved BOTH P (non-metal) to metalloid AND Sb (metalloid) to non-metal — both are wrong.

[S] Step-by-Step Solution

Original correct classification:
Non-metals: N, P Metalloids: As, Sb Metal: Bi

Student's changes:
- P moved to "Metalloids" — **WRONG**: P is a non-metal.
- Sb moved to "Non-metals" — **WRONG**: Sb is a metalloid.

Both elements are wrongly placed in the redrawn chart.

[Ans] Final Answer

Option (2): Both wrongly placed — P is a non-metal (not metalloid); Sb is a metalloid (not non-metal)

[!] Common Mistake

Options (3) and (4) say "only one is wrong." Both are wrong! P is definitively a non-metal; Sb is definitively a metalloid. Students sometimes confuse P with a metalloid because it has multiple allotropes, but P is always classified as a non-metal in NCERT.

SKILL: Time Management and Strategic Thinking

Q.5 Statements: I. N = 78% of atmosphere. II. P occurs as free element due to high reactivity. III. As, Sb, Bi mainly as sulphide minerals. IV. $NaNO_3$ = Indian saltpetre. Which are true?

[A] Conceptual Approach

I = TRUE. II = FALSE (P is reactive $\Rightarrow$ NOT free element; it occurs ONLY in combined form). III = TRUE. IV = TRUE ($NaNO_3$ = Indian saltpetre; Chile saltpetre is also $NaNO_3$ but from Chile deposits). So I, III, IV correct.

[S] Step-by-Step Solution

Statement I: TRUE — N_2 = 78% by volume of dry air.

Statement II: **FALSE** — Phosphorus is highly reactive, so it does *not* occur as a free element. It occurs only as combined phosphate minerals.

Statement III: TRUE — As (realgar, arsenopyrite), Sb (stibnite Sb_2S_3), Bi (bismuthinite Bi_2S_3) are found mainly as sulphide ores.

Statement IV: TRUE — $NaNO_3$ is known as Indian saltpetre (also Chile saltpetre from a different deposit).

True: I, III, IV.

[Ans] Final Answer

Option (4): I, III and IV only

[!] Common Mistake

Accepting Statement II as true. "High reactivity" means phosphorus CANNOT exist as a free element — it reacts and combines. Statement II reverses the cause-effect: high reactivity ⇒ only in combined form, NOT free.

TOPIC 2 — Atomic Properties

(a)–(d) Electronic Configuration, Atomic Radii, Ionisation Enthalpy & Electronegativity

SKILL: Analytical Ability

Q.6 N→P radius jump is 40 pm; As→Bi increase is only 27 pm over two steps. Why is the heavier-member increase so small?

[A] Conceptual Approach

Yeh wahi concept hai jo Group 13 aur 14 mein tha: d aur f electrons poor shielding dete hain. As ke baad 4d (Sb ke liye) aur 5d + 4f (Bi ke liye) electrons fill hote hain — poor shielding ⇒ high Z_{eff} ⇒ outer electrons contract ⇒ radius increase kam hoti hai.

[S] Step-by-Step Solution

From N to P: No d-block elements in between. Normal increase (40 pm) occurs.

From P to As and beyond: The d-block (10 d-electrons) and for Bi also the f-block (14 f-electrons) are traversed.

d and f electrons provide poor shielding of outer electrons from nuclear charge.
⇒ Z_{eff} is higher than expected ⇒ valence electrons pulled inward ⇒ radius increase is largely counteracted.

Result: only 27 pm increase over two steps (As → Sb → Bi) vs 40 pm in one step (N → P).

[Ans] Final Answer

Option (2): Filled d (and f) orbitals provide poor shielding ⇒ high Z_{eff} pulls valence electrons inward ⇒ expected size increase is largely offset

[!] Common Mistake

Option (1) says "lower nuclear charge." Wrong! As you go down a group, nuclear charge INCREASES at every step. The reason the size doesn't increase much is poor SHIELDING by d/f electrons, not lower nuclear charge.

SKILL: Conceptual Clarity

Q.7 Valence shell config of Group 15 is ns^2np^3. Why is this "extra stable"?

[A] Conceptual Approach

Extra stability of half-filled orbitals. p orbitals = 3 in total. Half-filled = 3 electrons in 3 separate p orbitals (one each, all same spin). s is fully filled (2 electrons). Ye Hund's rule stability hai.

[S] Step-by-Step Solution

Configuration: ns^2np^3

- ns^2: s orbital is **completely filled** (paired electrons, spherically symmetric, extra stable).
- np^3: three p orbitals each with one electron: $p_x^1 p_y^1 p_z^1$ — **half-filled p subshell**.

Half-filled orbitals have extra stability due to: (a) exchange energy maximisation, and (b) symmetrical electron distribution.

This is why Group 15 elements have **higher IE than neighbouring Group 14 and Group 16**.

[Ans] Final Answer

Option (3): s orbital completely filled AND p orbitals half-filled — both contribute to extra stability

[!] Common Mistake

Option (4) says "both s and p are half-filled." Wrong! The s orbital has 2 electrons = COMPLETELY filled. Only the p subshell is half-filled. This is a critical distinction in NEET MCQs.

SKILL: Application Skills

Q.8 $\Delta_i H_1 = 1012$, $\Delta_i H_2 = 1903$, $\Delta_i H_3 = 2910$ kJ/mol for phosphorus. Compare the two successive increases.

[A] Conceptual Approach

Sirf calculate karo: increase 1 ($\Delta_i H_2 - \Delta_i H_1$) vs increase 2 ($\Delta_i H_3 - \Delta_i H_2$). Jo zyada hai woh answer hai.

[S] Step-by-Step Solution

Increase from $\Delta_i H_1$ to $\Delta_i H_2$: $1903 - 1012 = 891$ kJ mol^{-1}

Increase from $\Delta_i H_2$ to $\Delta_i H_3$: $2910 - 1903 = 1007$ kJ mol^{-1}

$1007 > 891$, so the **second increase is larger** (1007 vs 891 kJ mol^{-1}).

This makes sense: each successive ionisation removes an electron from a more positive ion, requiring more energy.

[Ans] Final Answer

Option (2): The increase from $\Delta_i H_2$ to $\Delta_i H_3$ (1007 kJ mol^{-1}) is larger than the increase from $\Delta_i H_1$ to $\Delta_i H_2$ (891 kJ mol^{-1})

[!] Common Mistake

Reading the question as asking which absolute value is larger (they are all different). The question asks about the INCREASE (difference between consecutive values). Always compute $\Delta_i H_{n+1} - \Delta_i H_n$ for each step.

SKILL: Diagram-Based Visual Literacy

Q.9 Table: EN values N=3.0, P=2.1, As=2.0, Sb=1.9, Pb=1.9. Which conclusion is correct?

[A] Conceptual Approach

Data pe dhyan do: N→P drop = 3.0→2.1 = 0.9 (huge!). P→As drop = 0.1. As→Sb = 0.1. Sb→Bi = 0. So big drop at start, then almost constant.

[S] Step-by-Step Solution

Analysis of the data:

- N→P: 3.0 → 2.1 = drop of **0.9** (very large drop)
- P→As: 2.1 → 2.0 = drop of 0.1 (tiny)
- As→Sb: 2.0 → 1.9 = drop of 0.1 (tiny)
- Sb→Bi: 1.9 → 1.9 = no change

Correct interpretation: **large sharp drop from N to P, then nearly constant** from As onward. Covalent radius keeps increasing but EN plateaus.

[Ans] Final Answer

Option (3): Drop from N to P is far sharper than any later drop; EN nearly constant from As onward even as radius keeps increasing

[!] Common Mistake

Option (1) says "decreases steadily and proportionally." The DATA shows it is NOT proportional — the drop from N to P alone is 0.9, while the remaining three steps total only 0.1+0.1+0 = 0.2. "Steady and proportional" is clearly wrong.

SKILL: Time Management and Strategic Thinking

Q.10 Statements: I. IE of Group 15 > Group 14 (same period). II. Covalent & ionic radii DECREASE down Group 15. III. $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. IV. Sb has lower IE than As. Which are true?

[A] Conceptual Approach

I = TRUE (extra stability of half-filled p^3). II = FALSE (radii INCREASE down the group). III = TRUE (successive IEs always increase). IV = TRUE (going down group, IE generally decreases; Sb is below As).

[S] Step-by-Step Solution

Statement I: TRUE — The half-filled p^3 (ns^2np^3) configuration is extra stable, giving Group 15 higher IE than Group 14 (which has np^2) in the same period.

Statement II: **FALSE** — Both covalent and ionic radii **increase** down any group (more electron shells). They do not decrease.

Statement III: TRUE — Successive ionisation enthalpies always increase (removing from more positive ion).

Statement IV: TRUE — Going from As to Sb, IE generally decreases (larger atom, outer electrons farther from nucleus). Sb has lower first IE than As.

True statements: I, III, IV.

[Ans] Final Answer

Option (2): I, III and IV only

[!] Common Mistake

Accepting Statement II as true. Radii always INCREASE going down a group — more electron shells added. "Radii decrease down the group" is one of the most common factual errors in p-block questions.

TOPIC 3 — Physical Properties

(a)–(d) Physical State, Boiling Point, Melting Point & Density

SKILL: Analytical Ability

Q.11 Density increases monotonically N→Bi, but melting point peaks at As then falls. Why do density and melting point NOT follow the same trend?

[A] Conceptual Approach

Density aur melting point ke alag factors hain. Density = atomic mass / volume (packing) — heavier atoms = higher density, simple trend. Melting point depends on bond TYPE and strength — yeh change karta hai jab covalent network solid se metallic bonding mein jaate hain.

[S] Step-by-Step Solution

Density trend (monotonic increase): Density depends on atomic mass and packing efficiency. As atomic mass increases steadily from N to Bi, density increases smoothly.

Melting point trend (non-monotonic): Melting point depends on the **type and strength of interatomic bonding**:

- N: simple diatomic molecule (weak van der Waals) — very low mp
- P, As: covalent network/molecular structures — higher mp
- As: metallic + covalent mix — peaks
- Sb, Bi: increasingly metallic bonding — mp falls back

The bonding CHARACTER changes down the group; density just follows mass.

[Ans] Final Answer

Option (3): Melting point is governed by bonding type/strength (which changes); density depends on atomic mass and packing — the two properties need not follow identical trends

[!] Common Mistake

Option (1) says "density and melting point must always move together." This is a very common misconception. They are governed by DIFFERENT physical factors. Many groups in the periodic table show one property increasing while another peaks and falls.

SKILL: Conceptual Clarity

Q.12 Correct physical state of Group 15 elements at room temperature?

[A] Conceptual Approach

Room temperature = 298 K. N_2 boiling point = 77.2 K (far below 298 K) $\Rightarrow$ gas. P, As, Sb, Bi all have melting points well above 298 K $\Rightarrow$ solids.

[S] Step-by-Step Solution

At room temperature (298 K):

Nitrogen (N_2): bp = 77.2 K. Since 298 K $\gg$ 77.2 K, nitrogen is a **diatomic gas**.

Phosphorus: mp = 317 K. Just above 298 K — technically a **solid** at room temperature.

Arsenic, Antimony, Bismuth: All have mp $\gg$ 298 K — all are **solids**.

Summary: N = diatomic gas; P, As, Sb, Bi = solids.

[Ans] Final Answer

Option (4): Nitrogen is a diatomic gas; phosphorus, arsenic, antimony and bismuth are solids

[!] Common Mistake

Option (2) says "nitrogen and phosphorus are gases." Phosphorus has a melting point of 317 K and boiling point of 554 K — at 298 K it is a SOLID (just barely below its melting point). Only nitrogen is gaseous at room temperature in Group 15.

SKILL: Application Skills

Q.13 Boiling points: N=77.2, P=554, As=888, Sb=1860, Bi=1837 K. Which has highest boiling point?

[A] Conceptual Approach

Direct data reading. Sabse bada value dhundho: 77.2, 554, 888, 1860, 1837. 1860 (Sb) sabse bada hai.

[S] Step-by-Step Solution

From the data:
Sb = 1860 K $>$ Bi = 1837 K $>$ As = 888 K $>$ P = 554 K $>$ N = 77.2 K

Antimony (Sb) has the highest boiling point at 1860 K.

Note: Bi (1837 K) is very close but slightly lower than Sb. This is the notable feature of Group 15 physical data.

[Ans] Final Answer

Option (1): Antimony (Sb) — bp = 1860 K

[!] Common Mistake

Choosing Bismuth because it is at the bottom of the group and students expect "the heaviest = the highest boiling point." Wrong! Bi bp = 1837 K is slightly LESS than Sb bp = 1860 K. Always check the actual data; boiling point does not monotonically increase in Group 15.

SKILL: Diagram-Based Visual Literacy

Q.14 Table: mp (63,317,1089,904,544 K), bp (77.2,554,888,1860,1837 K), density (0.879 to 9.808). Which statement is correct?

[A] Conceptual Approach

Teeno properties ko independently check karo. Density: $0.879<1.823<5.778<6.697<9.808$ = monotonically increasing. MP: $63<317<1089>904>544$ = peaks at As. BP: $77.2<554<888<1860>1837$ = slight dip from Sb to Bi.

[S] Step-by-Step Solution

Checking each option against the data:

(1) "All three increase monotonically" — FALSE (mp peaks at As, bp dips from Sb to Bi).
(2) "Both mp and bp peak at As and decrease" — FALSE (bp keeps rising up to Sb).
(3) "Density shows no clear trend" — FALSE (density increases perfectly monotonically).

(4): Density increases monotonically (correct); mp peaks at As then falls (correct); bp rises overall but dips slightly from Sb to Bi (correct). **All three parts of option (4) match the data.**

[Ans] Final Answer

Option (4): Density increases monotonically; mp peaks at As then falls; bp rises overall with slight dip from Sb to Bi

[!] Common Mistake

Option (2) claims bp also peaks at As. Look at the data: bp As = 888, Sb = 1860 — bp actually INCREASES from As to Sb (not decreases). The peak in bp is at Sb, not As. Melting point peaks at As; boiling point peaks at Sb.

SKILL: Time Management and Strategic Thinking

Q.15 Statements: I. All except N show allotropy. II. Sb bp $>$ Bi bp. III. Metallic character DECREASES down Group 15. IV. As mp $>$ both P and Sb mp. Which are true?

[A] Conceptual Approach

I = TRUE (N doesn't show allotropy; P has white/red/black, As/Sb/Bi have multiple allotropes). II = TRUE (Sb=1860 K $>$ Bi=1837 K). III = FALSE (metallic character INCREASES down the group). IV = TRUE (As mp=1089 K $>$ Sb mp=904 K $>$ P mp=317 K).

[S] Step-by-Step Solution

Statement I: TRUE — Nitrogen does not show allotropy. All others (P = white/red/black; As, Sb, Bi = multiple allotropes) do.

Statement II: TRUE — Sb bp (1860 K) > Bi bp (1837 K). The boiling points are close but Sb is higher.

Statement III: **FALSE** — Metallic character **increases** down any group (increasing atomic size, easier to lose electrons). N, P = non-metals → Bi = metal confirms this.

Statement IV: TRUE — As mp = 1089 K, Sb mp = 904 K, P mp = 317 K. Yes, As has the highest mp.

True: I, II, IV.

[Ans] Final Answer

Option (2): I, II and IV only

[!] Common Mistake

Accepting Statement III. "Metallic character decreases down the group" is exactly backwards. Going from N (non-metal) to Bi (metal) is the clearest possible evidence that metallic character INCREASES. Never confuse this direction.

TOPIC 4 — Chemical Properties

(a) Oxidation States & Disproportionation Trends

SKILL: Analytical Ability

Q.16 BiF_5 is Bi's only +5 compound. Why do Bi(V) compounds act as powerful oxidising agents?

[A] Conceptual Approach

Inert pair effect: Bi ki $6s^2$ electrons reluctant to bond hain. Bi(V) = Bi^{5+} is unstable — it wants to go back to Bi^{3+} by GAINING 2 electrons. Electrons gain karna = oxidising agent banana.

[S] Step-by-Step Solution

Inert pair effect: In Bi (Period 6), the $6s^2$ electrons are held tightly (poor shielding by $5d^{10}$ and $4f^{14}$). The +3 state is far more stable than +5 for Bi.

In Bi(V) compounds: Bi is in a high, unstable oxidation state (+5).
It has a strong tendency to revert to the more stable +3 state by **accepting 2 electrons from a reducing agent**.

Accepting electrons = **oxidising agent**.

This is exactly the same argument as Pb(IV) being an oxidising agent (Group 14).

[Ans] Final Answer

Option (1): Inert pair effect makes +3 more stable; Bi(V) readily accepts 2 electrons to revert to Bi(III) ⇒ acts as oxidising agent

[!] Common Mistake

Option (4): "All metal compounds in highest OS are oxidising agents." While often true, this is an oversimplification and not the correct *reason*. The specific mechanism is the inert pair effect making +3 thermodynamically more stable than +5 for Bi.

SKILL: Conceptual Clarity

Q.17 Which statement about the -3 oxidation state in Group 15 is correct?

[A] Conceptual Approach

-3 oxidation state = gaining 3 electrons = non-metallic behaviour. Going down Group 15, metallic character increases $\Rightarrow$ less tendency to gain electrons $\Rightarrow$ -3 state becomes less common.

[S] Step-by-Step Solution

The tendency to show -3 oxidation state involves **gaining 3 electrons**.

As we go down Group 15:

- Metallic character increases (more electropositive)
- Less tendency to gain electrons
- -3 state becomes *less stable and less common*

Bi: being the most metallic, has the least tendency to form -3 compounds. BiH_3 barely exists; Bi sulphides show Bi in positive states mostly.

The -3 state decreases in stability from N to Bi.

[Ans] Final Answer

Option (4): -3 state decreases in tendency going down the group; Bi hardly forms any -3 compounds

[!] Common Mistake

Option (1) says "tendency to show -3 increases with metallic character." Exact opposite! Metals prefer POSITIVE oxidation states (losing electrons). As metallic character increases, -3 (gaining electrons) becomes LESS favourable.

SKILL: Application Skills

Q.18 $_3HNO_2 \longrightarrow HNO_3 + H_2O + {}_2NO$. Oxidation states of N in HNO_3 and NO respectively?

[A] Conceptual Approach

Oxidation state calculation: HNO_3: H=+1, O=-2, x+1+3(-2)=0, x=+5. NO: N+O=0, O=-2, N=+2.

[S] Step-by-Step Solution

In HNO_3: H = +1, each O = -2 (3 oxygen atoms)

$x + 1 + 3(-2) = 0 \Rightarrow x + 1 - 6 = 0 \Rightarrow x = +5$

In NO: O = -2

$y + (-2) = 0 \Rightarrow y = +2$

Starting N in HNO_2 = $+3$. So N is:

- Oxidised: $+3 \rightarrow +5$ (in HNO_3)
- Reduced: $+3 \rightarrow +2$ (in NO)

This confirms it's a disproportionation (simultaneous oxidation AND reduction of same element).

[Ans] Final Answer

Option (2): HNO_3 = N is $+5$; NO = N is $+2$

[!] Common Mistake

Writing -2 for N in NO (confusing N with S in SO_2 or similar). In NO, oxygen is -2 and nitrogen is $+2$. Remember: in NO, nitrogen is the LESS electronegative atom, so oxygen gets the negative charge.

SKILL: Diagram-Based Visual Literacy

Q.19 Table shows N disproportionates most, P next, As/Sb/Bi least. Increasing stability of +3 state towards disproportionation order?

[A] Conceptual Approach

"Increasing stability towards disproportionation" = starting from the LEAST stable (disproportionates most = N) to MOST stable (disproportionates least = As/Sb/Bi). Order: N < P < As/Sb/Bi.

[S] Step-by-Step Solution

From the table:

- N: +1 to +4 states all disproportionate readily — +3 state is **least stable**
- P: nearly all intermediate states disproportionate — intermediate stability
- As, Sb, Bi: +3 state becomes increasingly stable — **most stable towards disproportionation**

Increasing stability order: N < P < As/Sb/Bi

[Ans] Final Answer

Option (1): N < P < As/Sb/Bi

[!] Common Mistake

Reversing the order. The table says N disproportionates "readily" = LEAST stable of +3. As/Sb/Bi disproportionates least = MOST stable. So going from least to most stable: N < P < As/Sb/Bi. Don't read the question backwards.

SKILL: Time Management and Strategic Thinking

Q.20 Statements: I. BiF_5 is only +5 Bi compound. II. N max covalency = 6 (vacant d-orbitals). III. P can expand covalency beyond 4 (PF_6^-). IV. Stability of +5 INCREASES down Group 15. Which

are true?

[A] Conceptual Approach

I = TRUE. II = FALSE (N has NO d-orbitals; max covalency = 4). III = TRUE. IV = FALSE (+5 DECREASES down the group; inert pair effect makes +3 more stable going down).

[S] Step-by-Step Solution

Statement I: TRUE — BiF_5 is the only well-characterised Bi(V) compound; Bi(V) is otherwise too unstable.

Statement II: **FALSE** — N has **no d-orbitals** in its valence shell (Period 2). Its maximum covalency is **4**, not 6. It's phosphorus and heavier elements that have d-orbitals.

Statement III: TRUE — P (Period 3) has accessible 3d orbitals. PF_6^- has P in 6-coordination (sp^3d^2), demonstrating expanded covalency beyond 4.

Statement IV: **FALSE** — Stability of +5 state *decreases* down Group 15 (inert pair effect increases). It's the +3 state that becomes more stable going down.

True: I and III only.

[Ans] Final Answer

Option (2): I and III only

[!] Common Mistake

Statement IV is the key trap — "stability of +5 increases down Group 15" sounds like the usual "trends increase down a group" but it's WRONG. The inert pair effect means +5 becomes LESS stable going down. N, P show mainly +5; Bi shows mainly +3. Always remember: +5 decreases, +3 increases in stability going down Group 15.

(b) Reactivity with Hydrogen

SKILL: Analytical Ability

Q.21 EH_3 hydrides: thermal stability decreases and reducing power increases from NH_3 to BiH_3. One single explanation for BOTH trends?

[A] Conceptual Approach

Ek hi factor dono explain karta hai: E–H bond ki strength. E–H bond strength decreases down the group (larger atom, longer bond, weaker overlap). Weak bond = breaks easily = less thermal stability AND more reducing power (releases H easily).

[S] Step-by-Step Solution

The common factor: **E–H bond enthalpy decreases** from NH_3 to BiH_3.

Thermal stability: directly proportional to E–H bond strength. Weaker bond ⇒ breaks at lower temperature ⇒ less thermally stable.

Reducing power: ability to donate electrons (here, to lose H). Weaker E–H bond ⇒ H more easily released ⇒ better reducing agent (stronger reductant).

Both trends are explained by the same root cause: decreasing E–H bond strength going down Group 15.

[Ans] Final Answer

Option (2): E–H bond enthalpy decreases down the group; weaker bond ⇒ less stable AND more reducing

[!] Common Mistake

Option (1) cites "increasing atomic size causes greater electron density." While size does increase, the DIRECT link to both trends is specifically E–H bond strength, not just size. Option (2) gives the mechanistic reason.

SKILL: Conceptual Clarity

Q.22 NH_3 has higher boiling point (238.8 K) than PH_3 ($-87.4°C$) despite NH_3 being lighter. Why?

[A] Conceptual Approach

NH_3 boiling point zyada kyun? Because N–H...N hydrogen bonding hai! H-bonding is one of the strongest intermolecular forces. PH_3 mein H-bonding nahi hoti (P is not electronegative enough) — only weak van der Waals.

[S] Step-by-Step Solution

NH_3: N is highly electronegative (3.0), small atom with lone pair ⇒ forms **strong N–H$\cdots$N hydrogen bonds** between molecules.
H-bonding is a strong intermolecular force ⇒ high boiling point (238.8 K).

PH_3: P has lower electronegativity and larger size — cannot form H-bonds.
Only weak van der Waals forces ⇒ low boiling point ($-87.4°C$ = 185.6 K).

Despite NH_3 being lighter, its H-bonding makes its bp anomalously high.

[Ans] Final Answer

Option (3): NH_3 forms intermolecular hydrogen bonds (N–H$\cdots$N); PH_3 cannot (P not electronegative enough) — H-bonding ⇒ higher bp for NH_3

[!] Common Mistake

Option (2) says "NH_3 has more van der Waals forces." Van der Waals forces increase with molecular mass. PH_3 (34 g/mol) > NH_3 (17 g/mol) by van der Waals — so PH_3 should have higher bp by that logic. The ONLY reason NH_3 wins is hydrogen bonding.

SKILL: Application Skills

Q.23 BiH_3 decomposes: $_2BiH_3(g) \longrightarrow {}_2Bi(s) + {}_3H_2(g)$. Which conditions will PREVENT this decomposition?

[A] Conceptual Approach

Le Chatelier's principle: jo conditions reaction ko REVERSE mein push karein woh decomposition prevent karein. Low temperature (exothermic decomposition is favoured by high T? No, bond breaking is endothermic). High H_2 pressure (pushes reaction backward).

[S] Step-by-Step Solution

The reaction $_2BiH_3(g) \longrightarrow {}_2Bi(s) + {}_3H_2(g)$ has $\Delta n_g = 3 - 2 = +1$.

To prevent decomposition = push equilibrium toward BiH_3 (left):

- **Low temperature**: BiH_3 formation from Bi + H_2 is slightly exothermic; decomposition endothermic for Bi–H bond breaking. Low T disfavours bond breaking.
- **High H_2 pressure**: Le Chatelier — adding product (H_2) pushes reaction backward.

Both low temperature AND high H_2 pressure prevent decomposition.

[Ans] Final Answer

Option (4): Low temperature and high H_2 pressure both prevent decomposition of BiH_3

[!] Common Mistake

Option (2) says "high temperature prevents decomposition." For endothermic decomposition (bond breaking requires energy), HIGH temperature PROMOTES decomposition (not prevents it). Low temperature slows it down.

SKILL: Diagram-Based Visual Literacy

Q.24 Bar chart: H-bond enthalpy of EH_3 hydrides decreases from NH_3 to BiH_3. Boiling point anomaly in NH_3. Which statement is correct?

[A] Conceptual Approach

Bar chart shows decreasing E–H bond enthalpy. If purely from size/mass, bp should increase from NH_3 to BiH_3. But NH_3 bp is anomalously HIGH due to H-bonding (anomaly upward). PH_3 bp is LOWER than expected = anomaly downward.

[S] Step-by-Step Solution

From the bar chart: E–H bond enthalpy N–H > P–H > As–H > Sb–H > Bi–H.

Without H-bonding, bp should increase smoothly with molecular mass. But:
• NH_3 bp is **anomalously high** (H-bonding raises it above the expected smooth trend).
• PH_3 shows the "expected" low value without H-bonding.

Statement (3) correctly notes: the bar chart trend (decreasing bond enthalpy) means decreasing thermal stability, and the bp anomaly of NH_3 is due to H-bonding not captured in the bar chart.

[Ans] Final Answer

Option (3): Decreasing E–H bond enthalpy explains decreasing stability; NH_3's anomalously high bp is due to H-bonding

[!] Common Mistake

Option (1) says "higher E–H bond energy means higher bp." Not always! Bp depends on intermolecular forces, not intramolecular bond strength. NH_3 has lower E–H bond energy than... wait, N–H is actually the strongest. But even if it weren't, H-bonding (intermolecular) is what raises bp.

SKILL: Time Management and Strategic Thinking

Q.25 Statements: I. EH_3 hydrides formed by direct combination with H_2. II. NH_3 bp > PH_3 bp (despite lower MW) due to H-bonding. III. Reducing power: NH_3 < BiH_3. IV. All EH_3 are covalent. Which are true?

[A] Conceptual Approach

I = TRUE. II = TRUE (H-bonding in NH_3). III = TRUE (BiH_3 stronger reductant; weaker Bi–H bond). IV = TRUE (all EH_3 hydrides are covalent — no ionic EH_3 in Group 15). All four true.

[S] Step-by-Step Solution

Statement I: TRUE — Group 15 hydrides can be made by direct combination of element with H_2 (though industrial NH_3 uses Haber process).

Statement II: TRUE — NH_3 bp = 238.8 K (anomalously high due to H-bonding); PH_3 bp = 185.6 K. NH_3 is lighter but has higher bp due to H-bonding.

Statement III: TRUE — Reducing power increases from NH_3 to BiH_3. NH_3 is the weakest reductant; BiH_3 is the strongest.

Statement IV: TRUE — All EH_3 (NH_3, PH_3, AsH_3, SbH_3, BiH_3) are covalent compounds (shared electron pairs, not ionic).

All four are correct.

[Ans] Final Answer

Option (1): All of I, II, III and IV are true

[!] Common Mistake

Being tripped by Statement IV — thinking some hydrides might be ionic. In Group 15, all EH_3 hydrides are covalent (like NH_3 = covalent with lone pair). There are no ionic H^- containing Group 15 compounds because N, P, As etc. don't have the correct electrochemistry to form E^{3+} + $3H^-$ ionic salts.

(c) Reactivity with Oxygen

SKILL: Analytical Ability

Q.26 Why does E_2O_5 exist for N and P but Bi_2O_5 is essentially unknown?

[A] Conceptual Approach

+5 OS stability decreases down the group. N and P easily form +5. Bi ki inert pair effect bahut strong hai — Bi^{5+} formation is very unfavourable. So Bi_2O_5 cannot form under normal conditions.

[S] Step-by-Step Solution

The +5 state requires using the ns^2 pair for bonding (both s and p electrons participate).

N, P: Inert pair effect negligible ⇒ +5 state is stable ⇒ N_2O_5, P_2O_5 exist.

Bi: Strong inert pair effect ⇒ $6s^2$ electrons are very reluctant to bond.
Bi^{5+} would be extremely unstable ⇒ Bi_2O_5 is unknown/essentially non-existent.

Only BiF_5 (among +5 Bi compounds) is known, and it is a powerful oxidising agent.

[Ans] Final Answer

Option (1): Inert pair effect increases down Group 15; Bi cannot achieve stable +5 state $\Rightarrow$ Bi_2O_5 unknown

[!] Common Mistake

Option (3) says "oxygen cannot bond with Bi at all." Wrong! Bi_2O_3 (Bi in +3 state) exists and is a well-known basic oxide. It is specifically the +5 state that is inaccessible for Bi due to the inert pair effect.

SKILL: Conceptual Clarity

Q.27 Acidic character of Group 15 trioxides and pentoxides (E_2O_3, E_2O_5). Which trend is correct?

[A] Conceptual Approach

Acidic oxides = non-metal oxides. Going down Group 15, metallic character increases $\Rightarrow$ oxides become more basic (less acidic). For same element: higher OS oxide (E_2O_5) is more acidic than lower OS oxide (E_2O_3).

[S] Step-by-Step Solution

Two trends to know:

(1) Down the group: Both E_2O_3 and E_2O_5 become *less acidic* (more basic) as metallic character increases.

(2) Same element: E_2O_5 is *more acidic* than E_2O_3 for the same element. Higher oxidation state $\Rightarrow$ more covalent $\Rightarrow$ more acidic oxide.

Example: N_2O_5 (acidic) $>$ N_2O_3 (acidic but less so); Bi_2O_3 (basic); Bi_2O_5 (unknown).

[Ans] Final Answer

Option (2): Acidic character DECREASES down the group; within the same element, E_2O_5 is more acidic than E_2O_3

[!] Common Mistake

Option (4) says "acidic character increases down Group 15." Wrong! Acidic oxide character decreases down any group as metallic character increases. As, Sb, Bi oxides are amphoteric or basic. Only N and P oxides are purely acidic.

SKILL: Application Skills

Q.28 Lab test: White P in air gives white smoke (P_4O_{10}) and red P needs heating before it gives P_4O_{10}. Explanation?

[A] Conceptual Approach

White P is highly reactive (strained P_4 tetrahedral structure, weak bonds, reacts at room temperature spontaneously in air). Red P has a more stable polymeric structure $\Rightarrow$ needs heating to react.

[S] Step-by-Step Solution

White phosphorus (P_4): highly strained tetrahedral structure with P–P–P bond angle of 60° (very strained, weakened bonds). Highly reactive.
In air: spontaneously oxidises at room temperature ⇒ white fumes of P_4O_{10} without heating.
P_4 also shows **chemiluminescence** (glows in dark when oxidising slowly).

Red phosphorus: polymeric chain structure, more thermally stable, no strain.
Needs heating ($> 250°C$) before it oxidises appreciably.

[Ans] Final Answer

Option (3): White P (strained P_4 with 60° angles) is highly reactive, burns spontaneously in air; Red P (stable polymer) needs heating

[!] Common Mistake

Option (1) says "red P is more reactive because it's amorphous." Completely wrong! Amorphous materials are not automatically more reactive. White P is more reactive because of the **angular strain** in the P_4 tetrahedron (60° angles are far from the ideal 90–109° for P).

SKILL: Diagram-Based Visual Literacy

Q.29 Pie chart shows Group 15 oxides by acid-base nature: all N and P oxides acidic; As and Sb oxides mostly amphoteric; Bi_2O_3 basic. Which oxide is placed INCORRECTLY in an acidic category?

[A] Conceptual Approach

Chart mein koi oxide acidic category mein wrongly placed hai. As_2O_3 ko amphoteric hona chahiye, acidic nahi. Sb_2O_3 bhi amphoteric hai. N aur P oxides correctly acidic hain.

[S] Step-by-Step Solution

NCERT classification of Group 15 oxides:
Acidic: N_2O_3, N_2O_5, P_4O_6, P_4O_{10}
Amphoteric: As_2O_3, Sb_2O_3 (react with both acid and base)
Basic: Bi_2O_3

If the chart places As_2O_3 in "acidic," that is wrong. As_2O_3 is **amphoteric** (dissolves in NaOH but also in HCl).

[Ans] Final Answer

Option (4): As_2O_3 should be amphoteric, not acidic

[!] Common Mistake

Thinking As_2O_3 is acidic because arsenic is "close to non-metals." While As is adjacent to non-metals, its trioxide is amphoteric (both acid AND base character). Only N and P oxides are purely acidic in Group 15.

SKILL: Time Management and Strategic Thinking

Q.30 Statements: I. P_4O_{10} extremely hygroscopic. II. N_2O_5 is anhydride of HNO_3. III. As_2O_3 is used as a weedkiller (it is amphoteric). IV. Bi_2O_3 reacts with dilute H_2SO_4 (basic oxide). Which are

true?

[A] Conceptual Approach

I = TRUE (P_4O_{10} is one of the best desiccants). II = TRUE ($N_2O_5 + H_2O \rightarrow 2HNO_3$). III = TRUE ($As_2O_3$ is a poison/weedkiller AND it is amphoteric). IV = TRUE ($Bi_2O_3 + H_2SO_4 \rightarrow Bi_2(SO_4)_3 + H_2O$). All four.

[S] Step-by-Step Solution

Statement I: TRUE — P_4O_{10} (phosphorus pentoxide) is an extremely powerful desiccant; it even removes water from concentrated H_2SO_4 and HNO_3.

Statement II: TRUE — N_2O_5 is the acid anhydride of HNO_3: $N_2O_5 + H_2O \rightarrow 2HNO_3$.

Statement III: TRUE — As_2O_3 (arsenious oxide) is a deadly poison historically used as a weed-killer/pesticide. It is also amphoteric.

Statement IV: TRUE — Bi_2O_3 is basic: dissolves in dilute H_2SO_4 to give $Bi_2(SO_4)_3$.

All four are correct.

[Ans] Final Answer

Option (2): All four statements — I, II, III and IV — are correct

[!] Common Mistake

Doubting Statement III (mixing up As_2O_3 as "only a poison, not a chemical"). As_2O_3 is indeed both a poison AND an amphoteric oxide that was historically used as a weedkiller/rodenticide (arsenious oxide = rat poison).

(d)–(e) Reactivity with Halogens & Anomalous Behaviour of Nitrogen

SKILL: Analytical Ability

Q.31 EX_3 trihalides: order of reactivity in hydrolysis $BiCl_3 > SbCl_3 > AsCl_3 > PCl_3$. Why does NF_3 NOT hydrolyse?

[A] Conceptual Approach

Hydrolysis mechanism: water's O donates lone pair into the central atom's empty d-orbital (first step). N mein d-orbitals nahi hain! Isliye NF_3 hydrolyse nahi hoti. Yeh wohi concept hai jo CCl_4 ke saath tha.

[S] Step-by-Step Solution

Hydrolysis mechanism of EX_3:
Step 1: O of H_2O donates lone pair into **vacant d-orbital** of E.
Step 2: F/Cl leaves as HF/HCl. Repeat until $E(OH)_3$ formed.

NF_3 exception: N is a Period 2 element with **no d-orbitals**. The first step (lone pair donation into d-orbital) cannot occur. The hydrolysis mechanism is blocked.

Same principle as CCl_4 not hydrolysing (C also has no d-orbitals).

[Ans] Final Answer

Option (3): N lacks d-orbitals; the hydrolysis mechanism (lone pair donation into empty d-orbital) cannot proceed for NF_3

[!] Common Mistake

Option (1) says "N–F bond is too strong to break." N–F is actually not a particularly strong bond. C–F is the strongest carbon-halogen bond, but the reason NF_3 doesn't hydrolyse is the *mechanistic* impossibility — no d-orbitals for the nucleophilic attack step.

SKILL: Conceptual Clarity

Q.32 PF_5 exists but NF_5 does not. Why?

[A] Conceptual Approach

PF_5 mein P ki +5 valency hai = 5 bonds. P (Period 3) ke paas 3d orbitals hain ⇒ expand kar sakta hai to 5 bonds (sp^3d hybridisation). N (Period 2) mein NO d-orbitals ⇒ max 4 bonds only. Toh NF_5 possible hi nahi hai.

[S] Step-by-Step Solution

PF_5: P (Period 3) has accessible 3d orbitals. Using sp^3d hybridisation:
1s + 3p + 1d = 5 orbitals ⇒ 5 P–F bonds possible ⇒ PF_5 exists (trigonal bipyramidal).

NF_5: N (Period 2) has ONLY 2s and 2p orbitals in valence shell. No d-orbitals available.
Maximum bonds N can form = 4 (using sp^3, including the N^+ as in NH_4^+).

Cannot form 5 bonds ⇒ NF_5 **does not and cannot exist**.

[Ans] Final Answer

Option (2): N lacks d-orbitals (Period 2) — cannot expand covalence beyond 4; P has 3d orbitals allowing sp^3d hybridisation for PF_5

[!] Common Mistake

Option (1) says "N is too electronegative to bond with F." While N is electronegative, it does bond with F (NF_3 exists!). The reason NF_5 is impossible is not electronegativity but the *structural impossibility* of forming 5 bonds without d-orbitals.

SKILL: Application Skills

Q.33 N_2 triple bond (941 kJ/mol) makes it unreactive but P_4 with only single P–P bonds is highly reactive. Correct comparison?

[A] Conceptual Approach

N_2: triple bond = 941 kJ/mol to break. P_4: P–P single bond = 200 kJ/mol + **angular strain** (60° angles in tetrahedron). Strained single bonds are much easier to break. Toh N is kinetically inert; P is kinetically reactive.

[S] Step-by-Step Solution

N_2: Has a very strong N≡N triple bond (941 kJ mol^{-1}). Enormous activation energy needed to break this bond. ⇒ **Kinetically inert**.

P_4 (white phosphorus): Has only P–P *single* bonds, but:

- P_4 has a strained tetrahedral structure (P–P–P angle = 60°, much less than ideal)
- Angular strain weakens the bonds
- Low activation energy for reaction ⇒ **highly reactive**

P cannot form a P≡P triple bond effectively (large 3p orbitals, poor pπ–pπ overlap).

[Ans] Final Answer

Option (3): N_2 triple bond (941 kJ/mol) = kinetically inert; P_4 single bonds with angular strain = highly reactive

[!] Common Mistake

Option (2) says "N_2 is thermodynamically more stable." While N_2 is very stable, the key point here is **kinetic** stability (high activation energy). P_4 bonds are thermodynamically weaker AND kinetically easier to break due to angular strain.

SKILL: Diagram-Based Visual Literacy

Q.34 Diagram: N_2 sp-hybridised with σ + 2π bonds, lone pair on each N. Why is the lone pair behaviour of N_2 different from NH_3?

[A] Conceptual Approach

N_2 mein lone pair sp orbital mein hai (more s-character, held close to nucleus, less available for donation). NH_3 mein lone pair sp^3 orbital mein hai (more p-character, more directional, easily donates to Lewis acids). Isliye NH_3 zyada basic hai.

[S] Step-by-Step Solution

N_2 lone pairs: Each N is sp-hybridised. The lone pair occupies an **sp orbital** (50% s-character). High s-character ⇒ electrons held tightly close to nucleus ⇒ **less available for donation** ⇒ poor Lewis base.

NH_3 lone pair: N is sp^3-hybridised. Lone pair in an **sp^3 orbital** (25% s-character, 75% p-character). More directional, more available ⇒ **good Lewis base / nucleophile**.

This explains why NH_3 is strongly basic but N_2 is essentially non-basic.

[Ans] Final Answer

Option (1): N_2 lone pair in sp orbital (high s-character, tightly held) ⇒ not available for donation; NH_3 lone pair in sp^3 orbital (high p-character) ⇒ readily donates

[!] Common Mistake

Option (3) says "N_2 lone pair is in a π bond." No! The lone pairs are in σ-type sp-hybridised orbitals on each N atom (directed away from the triple bond). The two π bonds in N_2 are the *bonding* pairs, not lone pairs.

SKILL: Time Management and Strategic Thinking

Q.35 Statements: I. N cannot form pentahalides (no d-orbitals). II. NF_3 is a stronger Lewis base than PF_3. III. N_2 is kinetically inert due to strong triple bond. IV. All EX_5 pentahalides formed by E reacting with excess halogen. Which are true?

[A] Conceptual Approach

I = TRUE. II = FALSE (NF_3 is a WEAKER Lewis base than PF_3; F is more electronegative than N, pulls electron density away from N, reducing its lone pair availability). III = TRUE. IV = TRUE (EX_5 by direct combination: P + $5Cl_2 \rightarrow PCl_5$).

[S] Step-by-Step Solution

Statement I: TRUE — N (Period 2) has no d-orbitals; max 4 bonds; NF_5 impossible.

Statement II: **FALSE** — NF_3 is a **weaker** Lewis base than PF_3.
In NF_3: F is highly electronegative, withdraws electron density from N $\Rightarrow$ N lone pair less available.
In PF_3: despite F present, P's lone pair is in a larger orbital and more available. Also P can use d-orbitals for back-bonding differently. NF_3 is actually a **poorer** Lewis base than NH_3 and than PF_3.

Statement III: TRUE — N≡N bond enthalpy = 941 kJ mol^{-1}; very high activation energy.

Statement IV: TRUE — For example, P + excess $Cl_2 \rightarrow PCl_5$ (direct combination).

True: I, III and IV.

[Ans] Final Answer

Option (3): I, III and IV only

[!] Common Mistake

Statement II: many students accept NF_3 as a stronger Lewis base because "N is smaller and more electronegative." But the 3 highly electronegative F atoms in NF_3 pull electron density strongly *away from N*. This makes the N lone pair LESS available than in PF_3 where back-bonding is different. NF_3 is actually a weak Lewis base.

(d) Reactivity with Halogens

SKILL: Analytical Ability

Q.36 N forms no pentahalide (no d-orbitals); P readily forms PCl_5. Same underlying reason as N's max covalency restriction. Correct identification?

[A] Conceptual Approach

Ek hi root cause: N ke paas d-orbitals nahi hain (Period 2 element). Isi wajah se: (a) max covalency = 4, (b) no pentahalide possible, (c) no sp^3d hybridisation, (d) no expanded octet. P ke paas 3d hain $\Rightarrow$ sab possible.

[S] Step-by-Step Solution

Root cause for both restrictions: N's valence shell ($n = 2$) contains only 2s and 2p orbitals. **No d-orbitals** are present or accessible.

This single fact explains:

- Max covalency of N = 4 (can only use sp^3)
- N cannot form NX_5 (would need sp^3d, requires d-orbital)
- N cannot form $[NF_6]^-$-type expanded species
- N cannot use $d\pi$–$p\pi$ bonding

Phosphorus ($n = 3$): has 3d orbitals ⇒ can form PCl_5 (sp^3d), $[PF_6]^-$ (sp^3d^2).

[Ans] Final Answer

Option (4): Both restrictions share the same root cause — absence of accessible d-orbitals in N's valence shell ($n = 2$)

[!] Common Mistake

Option (1) says "N is too electronegative." N does bond with 5 atoms... wait, no it doesn't. The point is it CANNOT form 5 bonds not because of electronegativity but because of orbital availability. NF_3 exists (3 N–F bonds), so N can bond with F — it just can't form a fifth bond.

SKILL: Conceptual Clarity

Q.37 Which statement about stability of Group 15 trihalides is correct?

[A] Conceptual Approach

Most Group 15 elements form stable EX_3 trihalides. Nitrogen is special: among its trihalides, only NF_3 is stable. NCl_3, NBr_3, NI_3 are unstable/explosive. P, As, Sb form all stable trihalides.

[S] Step-by-Step Solution

P, As, Sb: All form stable trihalides EX_3 (PF_3, PCl_3, PBr_3, PI_3, etc.).

Nitrogen trihalides:

- NF_3: **stable** (F is small, bond strong, thermodynamically favoured)
- NCl_3: unstable/explosive
- NBr_3: unstable, decomposes readily
- NI_3: extremely explosive even when dry

Bi: Forms BiX_3 trihalides (stable, predominantly ionic for BiF_3).

So: among nitrogen's trihalides, **only NF_3 is stable**.

[Ans] Final Answer

Option (2): All trihalides except nitrogen's are stable; among nitrogen's, only NF_3 is known to be stable

[!] Common Mistake

Option (1) says "all trihalides are equally stable." NCl_3 is notoriously explosive (used in early chlorine chemistry, caused accidents). NI_3 is so sensitive it explodes with a touch of a feather. Only NF_3 is stable

among nitrogen trihalides.

SKILL: Application Skills

Q.38 BiF_3 is predominantly ionic trihalide. Pentahalides are more covalent than trihalides. How does BiF_5 compare to BiF_3 in bonding character?

[A] Conceptual Approach

Two separate facts: (1) BiF_3 = ionic. (2) pentahalides always more covalent than trihalides. Combining: BiF_5 must be more covalent than BiF_3, even though BiF_3 itself is ionic. Pentahalide logic overrides.

[S] Step-by-Step Solution

Fact 1: BiF_3 is predominantly ionic (Bi^{3+} and 3 F^-; Bi is the most metallic Group 15 element).

Fact 2: Pentahalides are more covalent than trihalides for the same element. Reason: Bi^{5+} has higher charge density (smaller, higher charge) $\Rightarrow$ more polarising $\Rightarrow$ more covalent character (Fajans' rules).

Conclusion: BiF_5 should be **more covalent** than BiF_3, consistent with the pentahalide-vs-trihalide trend applying to all Group 15 elements, including bismuth.

[Ans] Final Answer

Option (4): BiF_5 would be more covalent than BiF_3 — pentahalide-vs-trihalide covalency trend applies even to Bi

[!] Common Mistake

Option (2) says "BiF_5 would be more ionic since Bi is the most metallic." Being metallic only explains why BiF_3 is ionic (Bi as metal). But comparing trihalide vs pentahalide: the +5 state has higher charge density on the central atom, making the bond MORE covalent regardless of how metallic the element is.

SKILL: Diagram-Based Visual Literacy

Q.39 Table of halide facts for Group 15. N = no pentahalide + only NF_3 stable; P/As/Sb = stable EX_3 and EX_5; Bi = stable BiX_3, BiF_3 ionic. Which statement follows from the table?

[A] Conceptual Approach

Direct table reading. Option (3) says N is the only element whose trihalides are mostly unstable (only NF_3 stable) AND Bi is the only one whose trihalide with F is predominantly ionic. Both facts are directly in the table.

[S] Step-by-Step Solution

From the table:

(1) FALSE: "N is the only element capable of forming a stable pentahalide" — Table says N forms **NO** pentahalide!
(2) FALSE: "All equally stable trihalides and pentahalides" — N has no pentahalide; N's trihalides mostly unstable.
(3) **TRUE**: "N is the only element whose trihalides are mostly unstable" (only NF_3 is stable), **AND** "Bi is the only element whose trihalide with F is predominantly ionic" (BiF_3 is ionic, unlike covalent PF_3, AsF_3,

SbF_3).
(4) FALSE: Bi forms stable BiX_3 halides (the table explicitly lists this).

[Ans] Final Answer

Option (3): N's trihalides mostly unstable (only NF_3 stable); BiF_3 is the only predominantly ionic trihalide among Group 15

[!] Common Mistake

Option (1) says N forms pentahalide — directly contradicts the table! Always read the table before answering. The table explicitly states N "forms no pentahalide" as its distinguishing fact.

SKILL: Time Management and Strategic Thinking

Q.40 Statements: I. N no pentahalide (no d-orbitals). II. Pentahalides more covalent than trihalides. III. NCl_3 stable like NF_3. IV. BiF_3 is the only predominantly ionic trihalide among Group 15. True ones?

[A] Conceptual Approach

I = TRUE. II = TRUE (Fajans' rules, higher charge density in +5). III = FALSE (NCl_3 is unstable/explosive; ONLY NF_3 is stable among N trihalides). IV = TRUE. So I, II, IV correct.

[S] Step-by-Step Solution

Statement I: TRUE — N (Period 2, no d-orbitals) cannot form pentahalides.

Statement II: TRUE — In +5 state, central E^{5+} has higher charge density (smaller ionic size, higher charge) $\Rightarrow$ polarises halide more strongly $\Rightarrow$ more covalent character (Fajans' rules).

Statement III: **FALSE** — NCl_3 is **NOT stable** like NF_3. NCl_3 is explosive and unstable. Only NF_3 is a stable nitrogen trihalide.

Statement IV: TRUE — BiF_3 is the only trihalide among all Group 15 elements that is predominantly ionic rather than covalent.

True: I, II, IV.

[Ans] Final Answer

Option (3): I, II and IV only

[!] Common Mistake

Statement III is the critical trap. Students assume "if NF_3 is stable, NCl_3 (another nitrogen trihalide) should also be stable." WRONG! Nitrogen trihalide stability is unique to NF_3. F is uniquely small and electronegative, making N–F bonds strong. NCl_3 is actually explosive — historically caused many industrial accidents.

TOPIC 4e & 5 — Reactivity with Metals & Anomalous Behaviour of Nitrogen

(e) Reactivity with Metals

Q.41 Al^{3+} (aluminium) + P (-3): what is the correct formula for the binary compound?

[A] Conceptual Approach

Simple charge balancing: Al = +3, P = -3. Combine to get neutral compound. Total positive charge must equal total negative charge. Al^{3+} and P^{3-} are equal in magnitude $\Rightarrow$ 1:1 ratio = AlP.

[S] Step-by-Step Solution

Al^{3+} and P^{3-} (phosphide ion):

Charge balance: $1 \times (+3) + 1 \times (-3) = 0 \Rightarrow$ formula = **AlP**

Similar examples from NCERT: Ca_3N_2 (Ca^{2+} and N^{3-}: 3 Ca balanced by 2 N); Ca_3P_2; Zn_3Sb_2 (Zn^{2+} and Sb^{3-}: 3 Zn balanced by 2 Sb).

[Ans] Final Answer

Option (3): AlP (1:1 ratio since Al^{3+} and P^{3-} have equal and opposite charges)

[!] Common Mistake

Writing Al_3P_2 (confusing with Zn_3Sb_2 where Zn is +2 not +3). Al is +3, P is -3; they match exactly, so 1 Al : 1 P. Only when the charges DON'T match do you need to cross-multiply (e.g., Al_2S_3 where Al=+3 and S=-2).

Q.42 Group 15 elements react with metals and show which oxidation state, and why?

[A] Conceptual Approach

Metals = electropositive (want to lose electrons). Group 15 elements = more electronegative than metals $\Rightarrow$ they gain electrons from metals $\Rightarrow$ -3 state. This is the opposite of what happens when Group 15 bonds with electronegative halogens (+3 or +5 states).

[S] Step-by-Step Solution

When Group 15 elements react with metals:

Metals are more electropositive (lower EN) than Group 15 elements.
$\Rightarrow$ Electrons flow **from metal to Group 15 element**.
$\Rightarrow$ Group 15 element **gains 3 electrons** to complete its octet.
$\Rightarrow$ Shows -3 **oxidation state** (nitride N^{3-}, phosphide P^{3-}, arsenide As^{3-}, etc.)

Contrast: with halogens (more electronegative than Group 15), the Group 15 element LOSES electrons $\Rightarrow$ +3 or +5.

[Ans] Final Answer

Option (4): They show -3 because metals are more electropositive; Group 15 element gains 3 electrons (instead of losing them when bonding with electronegative halogens)

[!] Common Mistake

Option (1) says OS is fixed and doesn't depend on reaction partner. Completely wrong! OS of an element in a compound is determined by the relative electronegativities of the bonded atoms. Group 15 with metals =

−3; with halogens = +3 or +5. Completely opposite!

Topic 5: Anomalous Behaviour of Nitrogen

SKILL: Analytical Ability

Q.43 N≡N bond enthalpy = 941 kJ/mol (very strong), yet N–N single bond is WEAKER than P–P. Apparent contradiction — correct resolution?

[A] Conceptual Approach

Contradiction kyun hai? Triple bond strong hai ⇒ expect karo ki single bond bhi strong hoga. But N–N single bond weak hai. Explanation: N atoms are very small. When two N atoms form a single bond (with lone pairs on each), those lone pairs are very close together ⇒ lone pair repulsion (interelectronic repulsion) weakens the single bond.

[S] Step-by-Step Solution

Why N≡N is so strong: N's small, compact 2p orbitals overlap extremely effectively to form two strong pπ–pπ bonds (in addition to the σ bond). Small size = better overlap = strong triple bond.

Why N–N single bond is weak: A single N–N bond brings two small N atoms (each with a lone pair) very close together. The lone pairs on adjacent N atoms repel each other strongly (interelectronic repulsion), which **weakens the single bond**.

These are **two separate effects of the same small size**:

- Small size ⇒ good p-orbital overlap ⇒ strong triple bond
- Small size ⇒ lone pairs too close ⇒ weak single bond

[Ans] Final Answer

Option (2): Same small size causes TWO opposite effects — good pπ overlap (strong triple bond) but lone pair repulsion at short N–N distance (weak single bond)

[!] Common Mistake

Option (3) says "phosphorus is stronger in every context." Wrong! The triple bond of N≡N (941 kJ/mol) is FAR stronger than any P–P bond. It is specifically the N–N *single* bond that is weaker (due to lone pair repulsion). P–P single bond is stronger because P atoms are larger (lone pairs farther apart, less repulsion).

SKILL: Conceptual Clarity

Q.44 Why can N form pπ–pπ multiple bonds with itself and with C, O, but heavier Group 15 elements cannot?

[A] Conceptual Approach

pπ–pπ bond = sideways overlap of p-orbitals. N (Period 2): compact 2p orbitals ⇒ good sideways overlap. Heavier elements (Si, P, As, Sb): large, diffuse 3p, 4p, 5p orbitals ⇒ poor sideways overlap ⇒ no effective pπ–pπ bonds. Same as Group 14 concept.

[S] Step-by-Step Solution

Condition for pπ–pπ bonding: both atoms need small, compact p-orbitals that can come close enough for effective sideways overlap.

N (Period 2): 2p orbitals are small and compact. Excellent sideways overlap with other 2p orbitals (of C, O, or another N) $\Rightarrow$ forms N=N, N$\equiv$N, N=O, C=N, C$\equiv$N, etc.

P, As, Sb, Bi: Have 3p, 4p, 5p, 6p orbitals respectively. These orbitals are **large and diffuse** $\Rightarrow$ cannot come close enough for effective sideways overlap $\Rightarrow$ no pπ–pπ bonding.

[Ans] Final Answer

Option (4): Heavier elements have large, diffuse orbitals — poor pπ–pπ sideways overlap; nitrogen's compact 2p orbitals overlap effectively

[!] Common Mistake

Option (3) says "pπ–pπ bonding requires d-orbitals which only N has." Completely wrong on two counts: (a) N does NOT have d-orbitals, and (b) pπ–pπ bonding has nothing to do with d-orbitals. d-orbitals are needed for dπ–pπ bonding (which P uses), not pπ–pπ.

SKILL: Application Skills

Q.45 P can form $R_3P{=}O$ and $R_3P{=}CH_2$ using dπ–pπ bonding. Can N form analogous $R_3N{=}O$?

[A] Conceptual Approach

dπ–pπ bond = N's or P's d-orbital overlaps with O's p-orbital. P has 3d orbitals (available). N has NO d-orbitals (Period 2). So N cannot form dπ–pπ bonds. $R_3N{=}O$ type structure is impossible for N in this bonding mode.

[S] Step-by-Step Solution

dπ–pπ bonding mechanism: Central atom's d-orbital overlaps sideways with a ligand's p-orbital. Requires d-orbital on the central atom.

P (Period 3): Has 3d orbitals $\Rightarrow$ can form $R_3P{=}O$ (dπ–pπ: P 3d + O 2p).

N (Period 2): **NO d-orbitals** in valence shell $\Rightarrow$ cannot form dπ–pπ bonds.

$\therefore$ $R_3N{=}O$ **cannot form** via dπ–pπ bonding.

(N_2O is known but has a different electronic structure: $N{\equiv}N^+{-}O^- \leftrightarrow {}^-N{=}N^+{=}O$, involving p$\pi$–p$\pi$ bonds, not dπ–pπ.)

[Ans] Final Answer

Option (3): No, N cannot form $R_3N{=}O$ via dπ–pπ bonding — N has no d-orbitals in its valence shell

[!] Common Mistake

Option (4) says "N never bonds with oxygen." Completely wrong! N bonds with O in many compounds: NO, NO_2, N_2O_3, N_2O_5, HNO_3 etc. The specific restriction is on the *type* of bonding (dπ–pπ is impossible for N), not bonding with O altogether.

SKILL: Diagram-Based Visual Literacy

Q.46 Table: N uses pπ–pπ triple bond (941 kJ/mol); P/As/Sb use single E–E bonds (P–P stronger than N–N single bond); Bi = metallic. Despite highest bond enthalpy in N≡N, which element has strongest catenation?

[A] Conceptual Approach

Catenation = ability to form chains of same element. Depends on SINGLE bond strength (chains = sigma bonds). N–N single bond = weak (lone pair repulsion). P–P single bond = stronger. So P catenates more than N despite N≡N being very strong.

[S] Step-by-Step Solution

From the table:

- N's triple bond (941 kJ/mol) is strong, but this is a **triple** bond
- For catenation, we need stable **single** E–E bonds (chains)
- Single N–N bond is **weaker** than single P–P bond
- $\therefore$ N has LESS tendency to catenate than P

Strongest catenation in Group 15: **P** (strongest single E–E bond among the group).
Order: P $>$ As $>$ Sb $\approx$ N; Bi essentially no catenation.

[Ans] Final Answer

Option (2): Despite having the highest bond enthalpy (triple bond), N has weaker catenation than P — catenation depends on single bond strength, and N–N single bond is weaker than P–P

[!] Common Mistake

Option (2) says N has the strongest catenation because it has the highest bond enthalpy. This is the exact misconception the question tests! The 941 kJ/mol value is for the N≡N TRIPLE bond. For catenation (chains = single bonds), N–N single bond is actually WEAK ($<$ P–P). Bismuth has the weakest catenation (metallic bonding, essentially no covalent chains).

SKILL: Time Management and Strategic Thinking

Q.47 Statements: I. N small + high EN $\Rightarrow$ pπ–pπ bonds with itself, C, O. II. N–N single bond STRONGER than P–P. III. P, As form dπ–dπ bonds with transition metals. IV. N max covalency = 4 (same root cause as inability to form dπ–pπ). True ones?

[A] Conceptual Approach

I = TRUE. II = FALSE (N–N single bond is WEAKER than P–P due to lone pair repulsion). III = TRUE (P as ligand in complexes uses d-orbital back-bonding). IV = TRUE (both due to absence of d-orbitals in N). So I, III, IV correct.

[S] Step-by-Step Solution

Statement I: TRUE — N's small size and high EN make its 2p orbitals compact, enabling excellent pπ–pπ overlap. Forms N=O, N≡N, C=N, C≡N etc.

Statement II: **FALSE** — N–N single bond is **weaker** than P–P single bond. Lone pair repulsion at close N–N distance weakens it. This is the key anomaly.

Statement III: TRUE — $P(C_2H_5)_3$ and similar P-ligands use P's 3d orbitals to form $d\pi$–$d\pi$ or $d\pi$–$p\pi$ back-bonding with transition metals (important in organometallic chemistry).

Statement IV: TRUE — Both limitations (max covalency 4 AND no $d\pi$–$p\pi$ bonding) have the *same root cause*: absence of d-orbitals in N's Period 2 valence shell.

True: I, III and IV.

[Ans] Final Answer

Option (3): I, III and IV only

[!] Common Mistake

Statement II: "N–N stronger than P–P because N is smaller and bonds shorter = stronger." This reasoning fails for *single* bonds between atoms that carry lone pairs. Lone pair repulsion in the very short N–N single bond actually WEAKENS it compared to P–P (longer, less repulsion). Shorter $\neq$ always stronger when lone pairs are involved.

NCERT In-Text Examples & Questions

SKILL: Analytical Ability

Q.48 N restricted to EX_3 only (no pentahalide); pentahalides more covalent than trihalides. What do these two facts together imply about N's halogen chemistry vs P?

[A] Conceptual Approach

Combine both facts: N stays in EX_3 only $\Rightarrow$ never accesses the more-covalent EX_5 level. P can access both EX_3 AND more-covalent EX_5. So N's halide range is more limited AND stuck at the less-covalent level.

[S] Step-by-Step Solution

Fact 1: N can only form EX_3 (no d-orbitals $\Rightarrow$ max 4 bonds total, 3 with halogen and 1 lone pair remaining).

Fact 2: EX_5 pentahalides are more covalent than EX_3 trihalides.

Combined implication: Nitrogen is permanently restricted to EX_3 — it can *never* access the additional covalent character of EX_5. P, however, accesses both EX_3 and more-covalent EX_5.

$\Rightarrow$ N's halogen chemistry is: **(a) more limited in scope** (only EX_3), and **(b) unable to reach the higher covalency** level that P can.

[Ans] Final Answer

Option (3): N restricted to EX_3 only — never accesses the more-covalent EX_5 character; P can access both

[!] Common Mistake

Option (1) says N's halides are "always more ionic than P's." Not necessarily! NF_3 can be quite covalent (N–F bonds). The point is N is LIMITED in scope (only EX_3) compared to P which can form both EX_3 and the more covalent EX_5.

SKILL: Conceptual Clarity

Q.49 Why does PH_3 have a lower boiling point than NH_3?

[A] Conceptual Approach

Same concept as Q22 but in NCERT in-text format. PH_3 mein H-bonding nahi hai (P not electronegative enough). NH_3 mein N–H...N H-bonding strong hai. H-bonding raises bp significantly. Despite PH_3 being heavier, NH_3 has higher bp.

[S] Step-by-Step Solution

NH_3 bp = 238.8 K: N is small, highly electronegative (EN = 3.0), and has lone pair $\Rightarrow$ forms strong **N–H$\cdots$N hydrogen bonds** between molecules $\Rightarrow$ high bp.

PH_3 bp = 185.6 K: P is larger, less electronegative (EN = 2.1) — too low to participate in H-bonding $\Rightarrow$ only weak van der Waals forces hold molecules together $\Rightarrow$ low bp.

H-bonding in NH_3 is an **intermolecular** force much stronger than the van der Waals forces in PH_3.

[Ans] Final Answer

Option (2): PH_3 molecules are not associated by hydrogen bonds (P not electronegative enough); NH_3 has strong N–H$\cdots$N H-bonds

[!] Common Mistake

Option (1) says "PH_3 has smaller molar mass than NH_3." PH_3 (M = 34 g/mol) has a LARGER molar mass than NH_3 (M = 17 g/mol). The question even says "heavier element." If pure van der Waals were operating, PH_3 would have the higher bp. It is lower ONLY because NH_3 has H-bonding.

SKILL: Application Skills

Q.50 Pentahalides more covalent than trihalides. Which correctly explains this? (NCERT)

[A] Conceptual Approach

Yeh Fajans' rules wala concept hai. +5 state mein central atom smaller hai aur 5+ charge hai $\Rightarrow$ very high charge density $\Rightarrow$ strongly polarises the halide anion $\Rightarrow$ more covalent character. +3 state mein polarising power less.

[S] Step-by-Step Solution

Compare EX_3 (+3 state) vs EX_5 (+5 state) for the same element:

EX_5 has E in +5 state: Higher effective charge, smaller ionic size (more electrons removed $\Rightarrow$ contraction) $\Rightarrow$ very high charge density.

By **Fajans' rules**: higher charge density of E^{5+} compared to E^{3+} polarises the surrounding halide ions more strongly $\Rightarrow$ electron cloud of halide distorted toward E $\Rightarrow$ **more covalent character**.

$\therefore$ EX_5 is always more covalent than EX_3 for any Group 15 element (where both exist).

[Ans] Final Answer

Option (4): E^{5+} has higher charge density than E^{3+} $\Rightarrow$ polarises halide more strongly $\Rightarrow$ more covalent character (Fajans' rules)

[!] Common Mistake

Option (1) says "more halogen atoms = more covalent." Wrong reasoning! The number of atoms is not the direct cause. It is the oxidation state of the central atom (E^{5+} vs E^{3+}) and its resulting charge density that determines covalent character.

DPP-8 Complete!

"Group 15 was never 50 random facts.

It was always ONE story: nitrogen is anomalous because of no d-orbitals, and that single fact explains the triple bond strength, the weak single bond, no pentahalide, no $p\pi$–$p\pi$ in heavier members, and NF_3 not hydrolysing. You now see the thread. That is chemistry thinking."

— Your Weird Chemist