



WEIRD CHEMIST

Group 15 Elements — The Nitrogen Family

DPP-8

Chapter: p-Block Elements

TOPIC 1 Introduction

(a) Elements, Nature & Occurrence

SKILL: Analytical Ability

Q1. Nitrogen exists in nature as a free diatomic gas making up about 78% of the atmosphere, while phosphorus is never found in the elemental state and occurs only as combined phosphate minerals such as those of the apatite family. Which of the following best explains this difference in occurrence? [JEE]

- (1) Nitrogen is lighter than air and therefore escapes upward into the atmosphere, while phosphorus being denser sinks into the earth's crust
- (2) The N_2 molecule is held by an extremely strong $N \equiv N$ triple bond, making it kinetically and thermodynamically very stable and unreactive, whereas elemental phosphorus is highly reactive and combines readily with oxygen to form stable phosphates over geological time
- (3) Nitrogen is a non-metal and must therefore exist as a gas, while phosphorus is a metalloid and must therefore exist only as a mineral
- (4) Phosphorus was never formed as a free element during the origin of the solar system, unlike nitrogen

SKILL: Conceptual Clarity

Q2. Which of the following correctly represents the change in character of Group 15 elements on moving down the group? [NEET]

- | | |
|---|---|
| (1) Non-metal $\rightarrow$ Metal $\rightarrow$ Metalloid | (3) Non-metal $\rightarrow$ Metalloid $\rightarrow$ Metal |
| (2) Metal $\rightarrow$ Metalloid $\rightarrow$ Non-metal | (4) Metalloid $\rightarrow$ Non-metal $\rightarrow$ Metal |

SKILL: Application Skills

Q3. A geology student collects three samples for analysis: Sample X is largely $NaNO_3$, Sample Y is fluorapatite $Ca_9(PO_4)_6 \cdot CaF_2$, and Sample Z is a mixture of metal sulphides. Which Group 15 elements would the student most likely extract from X, Y and Z respectively? [NEET]

- | | |
|------------------------------------|------------------------------------|
| (1) Nitrogen, Phosphorus, As/Sb/Bi | (3) Nitrogen, As/Sb/Bi, Phosphorus |
| (2) Phosphorus, Nitrogen, As/Sb/Bi | (4) As/Sb/Bi, Phosphorus, Nitrogen |

SKILL: Diagram-Based Visual Literacy

Q4. A classification chart correctly sorts Group 15 elements as: **Non-metals** – N, P; **Metalloids** – As, Sb; **Metal** – Bi. A student redraws this chart but moves phosphorus into the “Metalloids” box and antimony into the “Non-metals” box, leaving everything else unchanged. Which statement about the redrawn chart is correct? [JEE]

- (1) The redrawn chart is correct, since phosphorus and antimony are borderline elements
- (2) The redrawn chart is incorrect; phosphorus is a non-metal and antimony is a metalloid, so both elements are now wrongly placed
- (3) The redrawn chart is partially correct; only the placement of antimony is wrong
- (4) The redrawn chart is partially correct; only the placement of phosphorus is wrong

SKILL: Time Management and Strategic Thinking

Q5. Consider the following statements about Group 15 elements and select the option with the correct combination of true statements: [JEE]

- I. Nitrogen constitutes about 78% by volume of the atmosphere.
- II. Phosphorus occurs abundantly in nature as the free element on account of its high reactivity.
- III. Arsenic, antimony and bismuth are found mainly as sulphide minerals.
- IV. Sodium nitrate, NaNO_3 , is known as Indian saltpetre.

- (1) I and III only (2) I, II and III only (3) II and IV only (4) I, III and IV only

TOPIC 2 Atomic Properties

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

SKILL: Analytical Ability

Q6. The covalent radii of Group 15 elements are N = 70, P = 110, As = 121, Sb = 141 and Bi = 148 pm. The increase from N to P (40 pm) is far larger than the combined increase from As to Bi (27 pm over two steps). Which of the following best explains this much smaller increase across the heavier members? [JEE]

- (1) Heavier elements have lower nuclear charge, so their electrons are held more loosely, which partly cancels the expected size increase
- (2) From As onward, completely filled intervening d (and, for Bi, f) orbitals shield the increasing nuclear charge poorly, pulling the valence electrons inward and largely offsetting the size increase expected from added shells
- (3) As, Sb and Bi are metalloids or metals rather than non-metals, and metals always show a smaller radius increase than non-metals

- (4) Covalent radius values for heavier elements are measured less precisely, which makes the increase appear artificially small

SKILL: Conceptual Clarity

Q7. The valence shell configuration of Group 15 elements is ns^2np^3 . Why is this configuration described as “extra stable”? [NEET]

- (1) The s orbital is empty and the p orbitals are completely filled
(2) Both the s and p orbitals are completely filled
(3) The s orbital is completely filled and the p orbitals are half-filled
(4) Both the s and p orbitals are half-filled

SKILL: Application Skills

Q8. For phosphorus, the three successive ionisation enthalpies are $\Delta_i H_1 = 1012$, $\Delta_i H_2 = 1903$ and $\Delta_i H_3 = 2910 \text{ kJ mol}^{-1}$. Comparing the two successive increases, which statement is correct? [NEET]

- (1) Both increases are exactly equal
(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})
(3) The increase from $\Delta_i H_1$ to $\Delta_i H_2$ is larger than the increase from $\Delta_i H_2$ to $\Delta_i H_3$
(4) Both increases are negative, since ionisation enthalpy decreases down the group

SKILL: Diagram-Based Visual Literacy

Q9. The table below lists the electronegativity and covalent radius of Group 15 elements. Based on this data, which statement is correct? [JEE]

Element	N	P	As	Sb	Bi
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius (pm)	70	110	121	141	148

- (1) Electronegativity decreases steadily and proportionally with increasing covalent radius across all five elements
(2) The drop in electronegativity from N to P is far sharper than any later drop, and electronegativity becomes nearly constant from As onward even as covalent radius keeps increasing
(3) Covalent radius and electronegativity both increase together down the group
(4) Bismuth has the highest electronegativity because it has the largest covalent radius

SKILL: Time Management and Strategic Thinking

Q10. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. The ionisation enthalpy of Group 15 elements is greater than that of the corresponding Group 14 elements due to the extra stability of the half-filled p^3 configuration.
- II. Covalent and ionic radii decrease down Group 15.
- III. For any Group 15 element, $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$.
- IV. Antimony (Sb) has a lower first ionisation enthalpy than arsenic (As).

- (1) I, III and IV only (2) I and II only (3) II, III and IV only (4) I, II, III and IV

TOPIC 3 Physical Properties

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

SKILL: Analytical Ability

Q11. The data show that density increases monotonically all the way from nitrogen to bismuth ($0.879 \rightarrow 1.823 \rightarrow 5.778 \rightarrow 6.697 \rightarrow 9.808 \text{ g cm}^{-3}$), while melting point does *not* increase monotonically – it rises from N to As and then falls back down to Bi ($63 \rightarrow 317 \rightarrow 1089 \rightarrow 904 \rightarrow 544 \text{ K}$). Which of the following is the most reasonable interpretation of this contrast? [JEE]

- (1) Density and melting point must always move in the same direction for any group of elements; this data is anomalous and likely contains a measurement error
- (2) Since metallic character increases steadily down the group, melting point should also increase steadily; the data for As, Sb and Bi must be listed out of order
- (3) Melting point is governed mainly by the type and strength of bonding holding atoms together, which can change in character (e.g. covalent vs. increasingly metallic) down a group, whereas density depends more directly on atomic mass and packing efficiency – so the two properties need not follow identical trends even within the same group
- (4) Both properties are entirely random and cannot be explained by any underlying chemical principle

SKILL: Conceptual Clarity

Q12. Which of the following correctly describes the physical state of Group 15 elements at room temperature? [NEET]

- (1) All five elements are diatomic gases
- (2) Nitrogen and phosphorus are gases; arsenic, antimony and bismuth are solids
- (3) All five elements are solids, including nitrogen
- (4) Nitrogen is a diatomic gas; phosphorus, arsenic, antimony and bismuth are solids

SKILL: Application Skills

Q13. Based on the boiling point data (N = 77.2, P = 554, As = 888, Sb = 1860, Bi = 1837 K), which Group 15 element has the **highest** boiling point? [NEET]

(1) Antimony

(2) Bismuth

(3) Nitrogen

(4) Arsenic

SKILL: Diagram-Based Visual Literacy

Q14. The table below lists melting point, boiling point and density for Group 15 elements. Based on this, which statement is correct? [JEE]

Property	N	P	As	Sb	Bi
Melting point/K	63	317	1089	904	544
Boiling point/K	77.2	554	888	1860	1837
Density/g cm ⁻³	0.879	1.823	5.778	6.697	9.808

- (1) All three properties (melting point, boiling point, density) increase monotonically from N to Bi
(2) Melting point and boiling point both peak at arsenic and then decrease all the way to bismuth
(3) Density is the only property that does not show a clear trend down the group
(4) Density increases monotonically from N to Bi, melting point peaks at arsenic before falling, and boiling point rises overall but dips very slightly from Sb to Bi

SKILL: Time Management and Strategic Thinking

Q15. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Except nitrogen, all Group 15 elements show allotropy.
II. Antimony has a higher boiling point than bismuth.
III. Metallic character decreases down the group due to increasing ionisation enthalpy.
IV. The melting point of arsenic is higher than that of both phosphorus and antimony.

- (1) I, II and III only (2) I, II and IV only (3) II, III and IV only (4) I, II, III and IV

TOPIC 4 Chemical Properties

(a) Oxidation States & Disproportionation Trends

SKILL: Analytical Ability

Q16. Going down Group 15, the stability of the +5 oxidation state decreases while that of +3 increases, to the point that bismuth's only well-characterised +5 compound is BiF₅. Which of the following best explains why Bi(V) compounds, where they do exist, tend to act as powerful oxidising agents? [JEE]

- (1) Because Bi(V) compounds have a smaller ionic radius than Bi(III) compounds, making them more reactive
- (2) Because the inert pair effect makes the +3 state more stable than +5 for bismuth, so Bi(V) species readily gain two electrons to revert to the more stable +3 state, acting as oxidising agents in the process
- (3) Because fluorine in BiF₅ is more electronegative than bismuth, which automatically makes any fluoride compound a strong oxidiser
- (4) Because bismuth is a metal, and all compounds of metals in their highest oxidation state are oxidising agents

SKILL: Conceptual Clarity

Q17. Which of the following statements about the -3 oxidation state in Group 15 is correct? [NEET]

- (1) The tendency to show -3 oxidation state increases down the group due to increasing metallic character
- (2) The tendency to show -3 oxidation state decreases down the group; bismuth hardly forms any -3 compounds
- (3) Only nitrogen and bismuth show a -3 oxidation state
- (4) The -3 oxidation state is equally common for all Group 15 elements

SKILL: Application Skills

Q18. In the disproportionation reaction $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$, nitrogen in HNO₂ (oxidation state +3) is simultaneously oxidised and reduced. What are the oxidation states of nitrogen in the two products HNO₃ and NO respectively? [NEET]

- (1) +5 and +2 (2) +5 and -2 (3) +2 and +5 (4) +4 and +1

SKILL: Diagram-Based Visual Literacy

Q19. The table below summarises how intermediate oxidation states behave in solution for nitrogen, phosphorus, and the As/Sb/Bi trio. Based on this, which sequence correctly arranges them in order of *increasing* stability of the +3 state towards disproportionation? [JEE]

Element(s)	Behaviour of intermediate states
N	All states +1 to +4 disproportionate readily in acid solution
P	Nearly all intermediate states disproportionate into +5 and -3 (acid and alkali)
As, Sb, Bi	+3 state becomes increasingly stable towards disproportionation

- (1) $N < P < As/Sb/Bi$ (2) $As/Sb/Bi < P < N$ (3) $P < N < As/Sb/Bi$ (4) $N < As/Sb/Bi < P$

SKILL: Time Management and Strategic Thinking

Q20. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. The only well-characterised +5 oxidation state compound of bismuth is BiF_5 .
- II. Nitrogen can show a maximum covalency of 6 because it has vacant d orbitals.
- III. Phosphorus can expand its covalency beyond 4 because it has vacant d orbitals in its outermost shell, as seen in PF_6^- .
- IV. The stability of the +5 oxidation state increases down Group 15 while that of +3 decreases.

- (1) I and III only (2) I, II and III only (3) II and IV only (4) I, II, III and IV

(b) Reactivity towards Hydrogen — Hydrides

SKILL: Analytical Ability

Q21. The E–H bond dissociation enthalpy, $\Delta_{diss}H^\circ(E-H)$, falls steadily from 389 kJ mol^{-1} in NH_3 to 255 kJ mol^{-1} in SbH_3 , and ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Which of the following best explains the connection between these two trends? [JEE]

- (1) A weaker E–H bond means the hydride breaks down more easily and is oxidised more readily, releasing hydrogen – so weaker bonds correspond to greater reducing power
- (2) A weaker E–H bond raises the boiling point of the hydride, and higher-boiling compounds are always stronger reducing agents
- (3) A weaker E–H bond increases the H–E–H bond angle, and it is this angle that determines reducing strength
- (4) Bond dissociation enthalpy and reducing character are unrelated; the increase in reducing power comes entirely from increasing atomic size, independent of bond strength

SKILL: Conceptual Clarity

Q22. Which of the following correctly represents the order of decreasing basicity of Group 15 hydrides? [NEET]

- (1) $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$ (3) $PH_3 > NH_3 > AsH_3 > SbH_3 > BiH_3$
(2) $BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$ (4) $NH_3 > AsH_3 > PH_3 > BiH_3 > SbH_3$

SKILL: Application Skills

Q23. The E–H bond dissociation enthalpies are $\text{NH}_3 = 389$, $\text{PH}_3 = 322$, $\text{AsH}_3 = 297$ and $\text{SbH}_3 = 255$ kJ mol^{-1} . Which consecutive pair shows the *smallest* drop in bond dissociation enthalpy? [NEET]

- (1) NH_3 to PH_3 (2) PH_3 to AsH_3 (3) AsH_3 to SbH_3 (4) NH_3 to SbH_3

SKILL: Diagram-Based Visual Literacy

Q24. The table below gives the E–H bond length and bond dissociation enthalpy for four Group 15 hydrides. Based on this data, which statement is correctly supported? [JEE]

Property	NH_3	PH_3	AsH_3	SbH_3
(E–H) distance / pm	101.7	141.9	151.9	170.7
$\Delta_{\text{diss}}H^\circ(\text{E–H}) / \text{kJ mol}^{-1}$	389	322	297	255

- (1) As the E–H bond length increases down the group, the bond dissociation enthalpy also increases, showing that longer bonds are stronger
 (2) As the E–H bond length increases down the group, the bond dissociation enthalpy decreases, consistent with longer bonds generally being weaker
 (3) Bond length and bond dissociation enthalpy show no relationship in this data
 (4) The E–H bond is strongest in SbH_3 because it has the longest bond length

SKILL: Time Management and Strategic Thinking

Q25. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. The reducing character of Group 15 hydrides increases from NH_3 to BiH_3 .
 II. NH_3 is the strongest reducing agent among all the Group 15 hydrides.
 III. The boiling point of PH_3 (185.5 K) is lower than that of NH_3 (238.5 K), even though phosphorus is the heavier element.
 IV. The standard enthalpy of formation, $\Delta_f H^\circ$, of NH_3 is negative while that of all the other Group 15 hydrides is positive.

- (1) I, III and IV only (2) I, II and III only (3) II, III and IV only (4) I, II, III and IV

(c) Reactivity towards Oxygen — Oxides

SKILL: Analytical Ability

Q26. For Group 15 oxides, the oxide in the higher oxidation state (E_2O_5) is more acidic than the corresponding E_2O_3 oxide of the same element, and acidic character of the oxides also decreases down the group. Based on both trends together, which is the most reasonable prediction for the relative acidity of N_2O_5 and Bi_2O_3 ? [JEE]

- (1) Bi_2O_3 will be more acidic than N_2O_5 , since bismuth being a metal automatically forms more acidic oxides than non-metals
- (2) N_2O_5 and Bi_2O_3 will have similar acidity, since the two trends (oxidation state and group position) cancel each other out
- (3) Acidity cannot be predicted from oxidation state or group position; it depends only on the physical state of the oxide
- (4) N_2O_5 will be far more acidic than Bi_2O_3 , since N_2O_5 benefits from being both a higher-oxidation-state oxide and an oxide of the lightest element in the group, while Bi_2O_3 suffers on both counts

SKILL: Conceptual Clarity

Q27. Which of the following correctly classifies the acid-base character of the $E_2\text{O}_3$ oxides of Group 15 elements? [NEET]

- (1) N_2O_3 and P_2O_3 are amphoteric; As_2O_3 and Sb_2O_3 are acidic; Bi_2O_3 is basic
- (2) All $E_2\text{O}_3$ oxides of Group 15 are amphoteric, with no clear trend down the group
- (3) N_2O_3 and P_2O_3 are purely acidic; As_2O_3 and Sb_2O_3 are amphoteric; Bi_2O_3 is predominantly basic
- (4) N_2O_3 and P_2O_3 are basic; As_2O_3 and Sb_2O_3 are amphoteric; Bi_2O_3 is acidic

SKILL: Application Skills

Q28. Since As_2O_3 and Sb_2O_3 are amphoteric oxides, which of the following reagents would be expected to react with As_2O_3 ? [NEET]

- (1) Only acids such as HCl
- (2) Only bases such as NaOH
- (3) Neither acids nor bases
- (4) Both acids (HCl) and bases (NaOH)

SKILL: Diagram-Based Visual Literacy

Q29. The table below lists the elemental character and the acid-base nature of the $E_2\text{O}_3$ oxide for each Group 15 element. Based on this, which statement is correct? [JEE]

Element	N	P	As	Sb	Bi
Character of element	Non-metal	Non-metal	Metalloid	Metalloid	Metal
Nature of $E_2\text{O}_3$	Acidic	Acidic	Amphoteric	Amphoteric	Basic

- (1) The acid-base trend in the table is opposite to the established non-metal-to-metal trend for these elements
- (2) There is no relationship between an element's classification (non-metal/metalloid/metal) and the acid-base character of its oxide
- (3) The acid-base trend in the table mirrors the established non-metal-to-metal character trend for these elements
- (4) Only nitrogen's oxide is acidic; all the others are basic

SKILL: Time Management and Strategic Thinking

Q30. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. All Group 15 elements form two types of oxides, E_2O_3 and E_2O_5 .
- II. For a given element, the E_2O_3 oxide is more acidic than the E_2O_5 oxide.
- III. Acidic character of the oxides decreases down the group.
- IV. Bi_2O_5 is more acidic than Bi_2O_3 .

- (1) I, II and III only (2) I, III and IV only (3) II and IV only (4) I, II, III and IV

(d) Reactivity towards Halogens**SKILL: Analytical Ability**

Q31. Nitrogen cannot form a pentahalide (NX_5), whereas phosphorus readily forms PCl_5 and PF_5 . This directly parallels a fact established earlier about nitrogen's bonding capacity. Which of the following correctly identifies the shared underlying reason? [JEE]

- (1) Nitrogen is too electronegative to bond with five halogen atoms simultaneously, regardless of orbital availability
- (2) Nitrogen's valence shell ($n = 2$) has no accessible d orbitals, so it cannot expand its covalency beyond 4 – the same reason it is restricted to a maximum covalency of 4 and cannot form PF_6^- -type expanded species, whereas phosphorus's valence shell does have accessible d orbitals
- (3) Nitrogen forms only ionic bonds, while phosphorus forms only covalent bonds, and pentahalides require covalent bonding
- (4) Pentahalides require the central atom to be a metal, and nitrogen is a non-metal while phosphorus is a metalloid

SKILL: Conceptual Clarity

Q32. Which of the following statements about the stability of Group 15 trihalides is correct? [NEET]

- (1) All trihalides of Group 15 elements, including those of nitrogen, are equally stable
- (2) None of the nitrogen trihalides are stable, not even NF_3
- (3) Trihalide stability has no connection to which element is involved
- (4) All trihalides except those of nitrogen are stable; among nitrogen's trihalides, only NF_3 is known to be stable

SKILL: Application Skills

Q33. BiF_3 is the one trihalide described as predominantly ionic, while pentahalides in general are described as more covalent than the corresponding trihalide. Based on these two facts together, how would BiF_5 most reasonably be expected to compare to BiF_3 in terms of bonding character? [NEET]

- (1) BiF_5 would be expected to be more covalent than BiF_3 , consistent with the general pentahalide-vs-trihalide trend applying even to bismuth
- (2) BiF_5 would be expected to be more ionic than BiF_3 , since bismuth is the most metallic element in the group
- (3) BiF_5 and BiF_3 would have identical bonding character, since both contain the same two elements
- (4) The comparison cannot be made since BiF_5 does not exist for any Group 15 element

SKILL: Diagram-Based Visual Literacy

Q34. The table below summarises distinguishing facts about the halides of each Group 15 element (or group of elements). Based on this, which statement correctly follows from the table? [JEE]

Element(s)	Distinguishing halide fact
N	Forms no pentahalide (d orbitals unavailable); only NF_3 is a stable trihalide
P, As, Sb	Form stable EX_3 and EX_5 halides; trihalides predominantly covalent
Bi	Forms stable BiX_3 halides; BiF_3 alone is predominantly ionic rather than covalent

- (1) Nitrogen is the only element in the group capable of forming a stable pentahalide
- (2) All Group 15 elements form equally stable trihalides and pentahalides with no exceptions
- (3) Nitrogen is the only element whose trihalides are mostly unstable, and bismuth is the only element whose trihalide with fluorine is predominantly ionic rather than covalent
- (4) Bismuth cannot form any stable halide at all

SKILL: Time Management and Strategic Thinking

Q35. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- Nitrogen does not form a pentahalide because d orbitals are unavailable in its valence shell.
- Pentahalides are more covalent than the corresponding trihalides.
- NCl_3 is known to be a stable compound, just like NF_3 .
- BiF_3 is the one trihalide among all Group 15 trihalides that is predominantly ionic rather than covalent.

- (1) I, II and III only
- (2) II, III and IV only
- (3) I, III and IV only
- (4) I, II and IV only

(e) Reactivity towards Metals

Q36. Group 15 elements exhibit a -3 oxidation state when forming binary compounds with metals, as seen in Ca_3N_2 , Ca_3P_2 , Zn_3Sb_2 and Mg_3Bi_2 . Based on this pattern, what would be the correctly bal-

anced formula for the binary compound formed between aluminium (Al^{3+}) and phosphorus (showing its -3 oxidation state)? [JEE]

- (1) Al_3P_2 (2) Al_3P (3) AlP (4) Al_2P_3

Q37. Earlier, we saw that Group 15 elements form halides showing $+3$ and $+5$ oxidation states. When these same elements react with metals instead of halogens, what oxidation state do they exhibit, and why? [NEET]

- (1) They still show $+3$ and $+5$, since oxidation state is a fixed property of an element and does not depend on the reaction partner
(2) They show 0 , since reactions with metals always produce elemental products rather than compounds
(3) They show $+1$, since metals always force a $+1$ oxidation state regardless of the other element involved
(4) They show -3 , because metals are more electropositive than the Group 15 elements, so the Group 15 element gains electrons (instead of losing them, as it does when bonding with more electronegative halogens)

TOPIC 5 Anomalous Behaviour of Nitrogen

Bonding, Catenation & Covalency Limitations

SKILL: Analytical Ability

Q38. Nitrogen's triple bond ($N \equiv N$) has an exceptionally high bond enthalpy of $941.4 \text{ kJ mol}^{-1}$, yet the single N–N bond is actually weaker than the single P–P bond, and nitrogen's tendency to catenate is correspondingly weaker than phosphorus's. Which of the following correctly resolves this apparent contradiction? [JEE]

- (1) Nitrogen cannot form any bonds to itself at all; the 941.4 kJ/mol value must refer to a different molecule entirely
(2) The triple bond is strong because nitrogen's small, compact p orbitals overlap effectively to form strong $p\pi-p\pi$ bonds, but a single N–N bond brings the small, electron-dense nitrogen atoms (with their lone pairs) very close together, and the resulting interelectronic repulsion between the non-bonding lone pairs weakens that single bond – two separate effects of the same small size pulling in opposite directions
(3) Phosphorus is simply a stronger element than nitrogen in every bonding context, so all phosphorus bonds are stronger than all nitrogen bonds
(4) Bond enthalpy values are unrelated to catenation tendency, so the two facts are coincidental and not connected to each other

SKILL: Conceptual Clarity

Q39. Why can nitrogen form $p\pi-p\pi$ multiple bonds with itself and with elements like C and O, while heavier Group 15 elements cannot? [NEET]

- (1) Nitrogen has more valence electrons available for π bonding than the heavier elements
- (2) Heavier elements are metals or metalloids and therefore cannot form covalent π bonds under any circumstances
- (3) $p\pi-p\pi$ bonding requires the presence of d orbitals, which only nitrogen possesses
- (4) The atomic orbitals of heavier elements are too large and diffuse to achieve effective $p\pi-p\pi$ overlap, whereas nitrogen's compact $2p$ orbitals overlap effectively

SKILL: Application Skills

Q40. Phosphorus can form compounds such as $R_3P=O$ and $R_3P=CH_2$ using $d\pi-p\pi$ bonding. Which of the following correctly predicts whether nitrogen can form an analogous $R_3N=O$ compound using the same type of bonding, and why? [NEET]

- (1) Yes, nitrogen can form $R_3N=O$ via $d\pi-p\pi$ bonding, since nitrogen is smaller and forms stronger bonds than phosphorus
- (2) Yes, nitrogen can form $R_3N=O$ via $d\pi-p\pi$ bonding, because all Group 15 elements have identical bonding capability
- (3) No, nitrogen cannot form $R_3N=O$ via $d\pi-p\pi$ bonding, because nitrogen's valence shell has no d orbitals available to participate in this type of bonding, unlike phosphorus
- (4) No, nitrogen cannot form $R_3N=O$ via $d\pi-p\pi$ bonding, because nitrogen never bonds with oxygen under any circumstances

SKILL: Diagram-Based Visual Literacy

Q41. The table below summarises the type of bonding shown by Group 15 elements in their elemental forms. Based on this table and the passage, which statement is correct? [JEE]

Element(s)	Bonding in elemental form
N	$N \equiv N$ triple bond ($p\pi-p\pi$), bond enthalpy $941.4 \text{ kJ mol}^{-1}$ (very high)
P, As, Sb	Single E–E bonds; single P–P bond is stronger than single N–N bond
Bi	Metallic bonding

- (1) Despite having the highest bond enthalpy (from its $N \equiv N$ triple bond), nitrogen has weaker catenation tendency than phosphorus, because catenation depends on single E–E bond strength, and the single N–N bond is weaker than the single P–P bond
- (2) Nitrogen has the strongest catenation tendency in the group, since it has the highest bond enthalpy of all listed bonds
- (3) Bismuth has the strongest catenation tendency, since metallic bonding is always stronger than covalent bonding

(4) All Group 15 elements show identical catenation tendency, since they all belong to the same group

SKILL: Time Management and Strategic Thinking

Q42. Consider the following statements and select the option with the correct combination of true statements: [JEE]

- I. Nitrogen's small size and high electronegativity allow it to form effective $p\pi-p\pi$ bonds with itself and with carbon and oxygen.
- II. The N–N single bond is stronger than the P–P single bond due to nitrogen's smaller size.
- III. Phosphorus and arsenic can form $d\pi-d\pi$ bonds with transition metals when compounds like $P(C_2H_5)_3$ act as ligands.
- IV. Nitrogen's restriction to a maximum covalency of four is due to the same lack of d orbitals that also prevents it from forming $d\pi-p\pi$ bonds.

- (1) I, II and III only (2) II, III and IV only (3) I, III and IV only (4) I, II, III and IV

NCERT In-Text Examples & Questions

SKILL: Analytical Ability

Q43. Nitrogen does not form a pentahalide at all (it lacks the d orbitals needed to expand its covalency beyond four), and separately, pentahalides are known to be more covalent than the corresponding trihalides. Taken together, what do these two facts imply about nitrogen's halogen chemistry compared to phosphorus's? [NCERT]

- (1) Nitrogen's halides are always more ionic than phosphorus's, since ionic character and covalent character are unrelated to pentahalide formation
- (2) Both facts are unrelated; pentahalide covalency has nothing to do with which oxidation states an element can access
- (3) Since nitrogen is permanently restricted to the trihalide oxidation state, it can never access the additional covalent character that the pentahalide state would provide – so nitrogen's halogen chemistry is both more limited in scope (only EX_3) and, in a sense, "stuck" at the relatively less-covalent end of the halide spectrum, while phosphorus can access both the EX_3 and the more-covalent EX_5 forms
- (4) Nitrogen actually forms more covalent halides than phosphorus overall, because trihalides are listed first in the passage and are therefore the "default" more important state

SKILL: Conceptual Clarity

Q44. Why does PH_3 have a lower boiling point than NH_3 , even though phosphorus is the heavier element? [NCERT]

- (1) PH_3 has a smaller molar mass than NH_3 , and lighter molecules always boil at lower temperatures

- (2) PH_3 molecules are not associated through hydrogen bonding in the liquid state, unlike NH_3 , which has strong intermolecular hydrogen bonds
- (3) Phosphorus is a metalloid while nitrogen is a non-metal, and metalloid hydrides always have lower boiling points
- (4) PH_3 has weaker van der Waals forces than NH_3 because phosphorus is larger, and larger atoms always have weaker intermolecular forces

SKILL: Application Skills

Q45. Pentahalides (EX_5) are more covalent than the corresponding trihalides (EX_3) of the same Group 15 element. Which of the following correctly explains this observation? [NCERT]

- (1) Pentahalides contain more halogen atoms, and compounds with more atoms are always more covalent regardless of charge or size
- (2) Trihalides are always solids while pentahalides are always gases, and gaseous compounds are inherently more covalent
- (3) The +5 oxidation state involves more d -orbital participation than the +3 state for every Group 15 element, which directly increases covalent character
- (4) In the +5 oxidation state, the central atom carries a higher effective positive charge and a smaller size than in the +3 state, giving it greater charge density; by Fajans' rules, this higher charge density polarises the halide ions more strongly, increasing covalent character

SKILL: Diagram-Based Visual Literacy

Q46. The table below pairs four facts (from NCERT's worked Examples and In-text Questions) with their underlying root cause. Based on this, which single fact shares its root cause with nitrogen's restriction to a maximum covalency of four? [NCERT]

Source	Core fact	Root cause
Example 7.1	N forms no penta-halide	Absence of d orbitals in N's valence shell
Example 7.2	PH_3 has lower b.p. than NH_3	Absence of hydrogen bonding in PH_3
Intext 7.1	Pentahalides more covalent than tri-halides	Higher charge density of E^{5+} vs. E^{3+}
Intext 7.2	BiH_3 is the strongest reducing agent	Weakest, most easily broken Bi–H bond

- (1) Intext 7.2 (2) Example 7.2 (3) Intext 7.1 (4) Example 7.1

SKILL: Time Management and Strategic Thinking

Q47. Consider the following statements and select the option with the correct combination of true statements: [NCERT]

- I. Nitrogen does not form a pentahalide because it has no accessible d orbitals to expand its covalency beyond four.
- II. NH_3 has a lower boiling point than PH_3 because NH_3 lacks hydrogen bonding.
- III. Pentahalides are more covalent than trihalides because the central atom carries a higher charge density in the +5 state.
- IV. BiH_3 is the strongest reducing agent among Group 15 hydrides.

(1) I, III and IV only (2) I, II and III only (3) II, III and IV only (4) I, II, III and IV