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INORGANIC

CH 07

p-Block Elements II — Nitrogen & Oxygen Families (Groups 15–16)

07

Trends in groups 15 and 16, anomalous nitrogen and oxygen, hydrides, N_2, NH_3, oxides of nitrogen, nitric acid, phosphorus allotropes, phosphine, halides and oxoacids of P, O_2 and ozone, sulphur allotropes, SO_2, the contact process and oxoacids of S — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Explain trends in groups 15 and 16 and the anomalous behaviour of N and O
- Compare hydrides of groups 15 and 16: bond angle, stability, basicity, acidity and reducing character
- Write preparation and key reactions of N_2, NH_3, HNO_3, PH_3, PCl_3, PCl_5, O_3, SO_2 and H_2SO_4
- Describe oxides of nitrogen and oxoacids of phosphorus and sulphur, including their structures and basicity
- Predict products of metals with dilute and concentrated nitric and sulphuric acids

INSIDE

A The big picture
B Group 15: trends

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Small first members, weaker bonds below.

IN ONE LINE

N and O are small and electronegative, form pπ–pπ multiple bonds and hydrogen bonds, and cannot expand beyond four bonds; down each group hydrides become less stable and more acidic or reducing, and the lower oxidation state (+3 for Bi, +4 for Te) becomes favoured.

Property	Group 15 (N → Bi)	Group 16 (O → Po)
Valence configuration	$ns^2\ np^3$	$ns^2\ np^4$
Oxidation states	−3 to +5; +3 grows down (Bi^{3+})	−2, +2, +4, +6; +4 grows down
Character	N, P non-metals; As, Sb metalloids; Bi metal	O, S non-metals; Se, Te metalloids; Po metal
First member	N_2 gas, N≡N; max covalency 4	O_2 gas, O=O; mostly −2; H-bonding

THINK OF IT LIKE THIS

The first member of each group is like the youngest, smallest sibling who can only hold four friends' hands at once — but holds two hands with the same friend (multiple bonds). The bigger siblings have more hands (d orbitals) and hold up to five or six partners, but each grip is weaker.

SECTION B

Group 15: trends

B

Data first.

Property	N	P	As	Sb	Bi
Covalent radius / pm	70	110	121	141	148
ΔiH_1 / kJ mol^{-1}	1402	1012	947	834	703

Property	N	P	As	Sb	Bi
Electronegativity	3.0	2.1	2.0	1.9	1.9

- **Ionisation enthalpy is higher than in group 14** — the half-filled p^3 subshell is stable.
- **Nitrogen is anomalous:** small, highly electronegative, forms pπ–pπ multiple bonds (N≡N, N=O), has no d orbitals (max covalency 4), and its N–N single bond is weak (lone-pair repulsion).
- **Inert pair effect:** +5 stability falls down the group; Bi(V) is a strong oxidant ($NaBiO_3$) and BiF_5 is the only well-characterised Bi(V) compound.
- Nitrogen forms NCl_3 but no NCl_5; P forms both PCl_3 and PCl_5.

Hydrides EH_3

Hydride	Bond angle	Thermal stability	Basicity	Reducing power
NH_3	107.8°	Highest	Highest	Lowest
PH_3	93.6°	↓	↓	↑
AsH_3	91.8°	↓	↓	↑
SbH_3	91.3°	↓	↓	↑
BiH_3	90°	Lowest	Lowest	Highest

- Bond angle falls because the central atom grows and bonding pairs move away from it, so they repel each other less (and the larger atoms use almost pure p orbitals).
- **Boiling points:** $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$ — NH_3 is high because of hydrogen bonding.

SECTION C

C

Dinitrogen and ammonia

The two nitrogen compounds asked most.

Dinitrogen

- **Lab:** $NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2 + 2H_2O + NaCl$ (warm).
- From ammonium dichromate: $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$ (green Cr_2O_3 — the "volcano" experiment).
- **Very pure N_2:** heat sodium or barium azide: $Ba(N_3)_2 \rightarrow Ba + 3N_2$.
- Inert at room temperature (N≡N bond enthalpy 941.4 kJ mol^{-1}); reacts with Li at room temperature and with Mg, Ca at high temperature to give nitrides; with O_2 only at about 2000 K (lightning) → NO.

Ammonia

- **Haber process:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H = -46.1$ kJ per mole of NH_3; about 200 atm, 700 K, iron oxide catalyst with K_2O and Al_2O_3 promoters.
- Trigonal pyramidal (sp^3, one lone pair); highly soluble in water; weak base: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.
- **Lewis base:** with Cu^{2+} it gives deep blue $[Cu(NH_3)_4]^{2+}$; it dissolves AgCl as $[Ag(NH_3)_2]^+$.
- Precipitates metal hydroxides: $FeCl_3 + NH_4OH \rightarrow Fe(OH)_3$ (brown); $ZnSO_4 + NH_4OH \rightarrow Zn(OH)_2$ (white).

SECTION D

D

Oxides of nitrogen and nitric acid

Five oxides, one important acid.

Oxide	Oxidation state of N	Nature	Appearance	Structure / note
N_2O	+1	Neutral	Colourless gas (laughing gas)	Linear N–N–O; from heating NH_4NO_3
NO	+2	Neutral	Colourless gas	Odd electron, paramagnetic; Cu + dil. HNO_3
N_2O_3	+3	Acidic	Blue solid	Anhydride of HNO_2
NO_2	+4	Acidic	Brown gas	Odd electron, paramagnetic; dimerises to colourless N_2O_4
N_2O_5	+5	Acidic	Colourless solid	Anhydride of HNO_3

Nitric acid — Ostwald process

1. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (Pt/Rh gauze, about 500 K, 9 bar)
2. $2NO + O_2 \rightleftharpoons 2NO_2$
3. $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (NO is recycled); concentrated to about 68% by distillation, 98% with conc. H_2SO_4

Metal + HNO_3	Main products
Cu + dilute ($8HNO_3$)	$3Cu(NO_3)_2 + 2NO + 4H_2O$
Cu + concentrated ($4HNO_3$)	$Cu(NO_3)_2 + 2NO_2 + 2H_2O$
Zn + dilute ($10HNO_3$)	$4Zn(NO_3)_2 + N_2O + 5H_2O$
Zn + concentrated ($4HNO_3$)	$Zn(NO_3)_2 + 2NO_2 + 2H_2O$

Metal + HNO_3	Main products
Cr, Al, Fe + concentrated	Passive (oxide film)

- Non-metals are oxidised to their oxoacids: $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$; $C \rightarrow CO_2$; $S_8 \rightarrow H_2SO_4$; $P_4 \rightarrow H_3PO_4$.
- **Brown ring test for NO_3^-:** add $FeSO_4$ and run conc. H_2SO_4 down the side; NO_3^- is reduced to NO, which forms brown $[Fe(H_2O)_5(NO)]^{2+}$ at the junction.
- In HNO_3 the N is planar (sp^2); one N–O is an ordinary single bond to OH and the other two share a double bond by resonance.

SOLVED EXAMPLE 01 — PREDICTING HNO_3 PRODUCTS

Write equations for copper with (a) dilute and (b) concentrated nitric acid, and name the gases.

SOLUTION

1. (a) $3Cu + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$.
2. (b) $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$.

ANSWER Dilute gives colourless NO (which turns brown in air); concentrated gives brown NO_2.

CHECK YOURSELF

C1 Which oxides of nitrogen are paramagnetic?

C2 Why does NO_2 dimerise?

Answers at the end of the chapter.

SECTION E

Phosphorus and its compounds

E

Allotropes, phosphine, halides and oxoacids.

Allotrope	Structure	Properties
White	Discrete P_4 tetrahedra (angle 60°, strained)	Waxy, poisonous, glows in the dark (chemiluminescence), catches fire in air (stored under water), soluble in CS_2
Red	Polymeric chains of P_4 units	Made by heating white P at 573 K in an inert atmosphere; less reactive, does not glow, insoluble in CS_2
Black	Layered (α and β forms)	Made by heating red P at high temperature or under pressure; least reactive

Phosphine, PH_3

- From calcium phosphide: $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$.
- From white P: $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (inert atmosphere) — a disproportionation.
- Pure PH_3 does not catch fire; impure PH_3 (with P_2H_4 or P_4 vapour) does — used in Holme's signals with acetylene.
- Weakly basic: $PH_3 + HI \rightarrow PH_4I$. Forms black Cu_3P_2 with $CuSO_4$ solution.

Phosphorus halides

	PCl_3	PCl_5
Preparation	$P_4 + 6Cl_2 \rightarrow 4PCl_3$; or $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$P_4 + 10Cl_2 \rightarrow 4PCl_5$; or $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
Shape	Pyramidal (sp^3)	Trigonal bipyramidal (sp^3d); axial bonds (240 pm) longer than equatorial (202 pm)
Hydrolysis	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$	$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$; then $POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$
With alcohols / acids	$3ROH \rightarrow 3RCl + H_3PO_3$	$ROH \rightarrow RCl + POCl_3 + HCl$
Solid state	Molecular	Ionic: $[PCl_4]^+[PCl_6]^-$

Oxoacids of phosphorus

Acid	Formula	Oxidation state of P	P-OH groups (basicity)	P-H bonds	Note
Hypophosphorous	H_3PO_2	+1	1 (monobasic)	2	Strong reducing agent
Phosphorous	H_3PO_3	+3	2 (dibasic)	1	Reducing; $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$ on heating
Orthophosphoric	H_3PO_4	+5	3 (tribasic)	0	Not reducing
Pyrophosphoric	$H_4P_2O_7$	+5	4	0	P–O–P bridge
Metaphosphoric	$(HPO_3)_n$	+5	1 per P	0	Cyclic or chain

KEY IDEA

Basicity = number of ionisable P–OH groups, not the number of H atoms. H atoms bonded directly to P are not acidic but give reducing power: acids with P–H bonds (H_3PO_2, H_3PO_3) reduce $AgNO_3$ to Ag.

SOLVED EXAMPLE 02 — **BASICITY OF H_3PO_3**

Why is H_3PO_3 dibasic although it has three hydrogen atoms?

SOLUTION

1. Structure: one P=O, two P–OH and one P–H bond around a tetrahedral P.
2. Only H attached to O can ionise; the P–H hydrogen is not acidic.

ANSWER Two ionisable P–OH groups → dibasic; it forms NaH_2PO_3 and Na_2HPO_3 only.

CHECK YOURSELF

C3 Why is white phosphorus more reactive than red?

C4 How many P–H bonds are there in hypophosphorous acid?

Answers at the end of the chapter.

SECTION F

Group 16: trends

F

Oxygen stands apart again.

Property	O	S	Se	Te	Po
ΔiH_1 / kJ mol^{-1}	1314	1000	941	869	813
Electron gain enthalpy / kJ mol^{-1}	-141	-200	-195	-190	-174
Electronegativity	3.50	2.44	2.48	2.01	1.76

- **Electron gain enthalpy of O is less negative than S** — the small O atom repels the incoming electron (compare F and Cl).
- **Ionisation enthalpy of group 16 is lower than group 15** — removing an electron from p^4 relieves pairing (N > O, P > S).
- **Oxygen is anomalous:** small, highly electronegative, H-bonding (water is liquid, H_2S a gas), max covalency 2 to 4, shows -2 almost always (+2 only in OF_2, +1 in O_2F_2).
- Down the group, +4 becomes more stable than +6 (inert pair). Polonium is radioactive.

Hydrides H_2E

Hydride	Bond angle	b.p. / K	Thermal stability	Acid strength
H_2O	104.5°	373	Highest	Lowest
H_2S	92°	213	↓	↑
H_2Se	91°	232	↓	↑

Hydride	Bond angle	b.p. / K	Thermal stability	Acid strength
H_2Te	90°	269	Lowest	Highest

Acid strength rises down the group because the H–E bond gets longer and weaker; reducing power rises for the same reason (H_2Te is the strongest reducing agent).

SECTION G

Dioxygen and ozone

O_2 and its reactive allotrope.

- **Lab O_2:** $2KClO_3 \rightarrow 2KCl + 3O_2$ (MnO_2 catalyst, heat); also $2H_2O_2 \rightarrow 2H_2O + O_2$ and $2HgO \rightarrow 2Hg + O_2$.
- O_2 is **paramagnetic** (two unpaired $\pi*$ electrons). It combines with most elements, often only on heating.
- **Oxides:** acidic (SO_2, CO_2, Cl_2O_7, Mn_2O_7), basic (Na_2O, CaO), amphoteric (Al_2O_3, ZnO), neutral (CO, NO, N_2O).

Ozone, O_3

- Made by **silent electric discharge** through dry O_2: $3O_2 \rightleftharpoons 2O_3$, $\Delta H = +142$ kJ mol^{-1} (endothermic, so the discharge avoids heat that would decompose it).
- **Structure:** bent (about 117°), both O–O bonds equal (128 pm) by resonance; diamagnetic.
- **Strong oxidant** (it gives nascent O): $PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$; $2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2$ — the liberated I_2 is titrated to estimate ozone.
- The stratospheric ozone layer absorbs UV. NO from supersonic jets and Cl atoms from CFCs destroy it: $NO + O_3 \rightarrow NO_2 + O_2$.

SECTION H

Sulphur, SO_2 and sulphuric acid

The industrial heart of group 16.

Allotrope	Form	Stable	Note
Rhombic (α)	Yellow crystals; S_8 crown rings	Below 369 K	Insoluble in water, soluble in CS_2
Monoclinic (β)	Needle-shaped; S_8 rings	Above 369 K	Made by melting and cooling rhombic S
S_2 vapour	Diatomic	At high temperature	Paramagnetic, like O_2

The **transition temperature** between rhombic and monoclinic sulphur is 369 K.

Sulphur dioxide

- From burning sulphur, or $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$; industrially by roasting sulphide ores.
- Acidic: $SO_2 + H_2O \rightarrow H_2SO_3$; with NaOH → Na_2SO_3.
- **Reducing agent** (in the presence of water): turns acidified $K_2Cr_2O_7$ from orange to green and decolourises acidified $KMnO_4$ — tests for SO_2.
- **Bleaches by reduction** (temporary — the colour returns in air); chlorine bleaches by oxidation (permanent).
- Bent molecule (sp^2, about 119°) with two equal S–O bonds by resonance.

Sulphuric acid — contact process

1. Burn sulphur or roast sulphide ores → SO_2.
2. $2SO_2 + O_2 \rightleftharpoons 2SO_3$, ΔH = −196.6 kJ; V_2O_5 catalyst, about 720 K, 2 bar.
3. Absorb SO_3 in conc. $H_2SO_4 \rightarrow H_2S_2O_7$ (oleum); dilute oleum with water → H_2SO_4 (96–98%). SO_3 is not absorbed directly in water because it forms an acid mist.

Property	Example
Strong dibasic acid	Ka_1 very large; $Ka_2 = 1.2 \times 10^{-2}$
Dehydrating agent	Chars sugar: $C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$; dries gases (not NH_3 or H_2S)
Oxidising agent (hot, conc.)	$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$; $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
Low volatility	Displaces volatile acids: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

Oxoacids of sulphur

Acid	Formula	Feature
Sulphurous	H_2SO_3	S +4; exists in solution only
Sulphuric	H_2SO_4	S +6; tetrahedral
Thiosulphuric	$H_2S_2O_3$	One O replaced by S
Pyrosulphuric (oleum)	$H_2S_2O_7$	S–O–S bridge
Peroxomonosulphuric (Caro's acid)	H_2SO_5	One O–O bond
Peroxodisulphuric (Marshall's acid)	$H_2S_2O_8$	S–O–O–S peroxo bridge

SOLVED EXAMPLE 03 — SO_2 VERSUS CL_2 AS BLEACHES

Why is the bleaching by SO_2 temporary but by Cl_2 permanent?

SOLUTION

1. $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$; nascent hydrogen reduces the dye to a colourless form.
2. In air the reduced dye is slowly re-oxidised, and the colour returns.
3. $Cl_2 + H_2O \rightarrow HCl + HOCl \rightarrow$ nascent [O] oxidises the dye irreversibly.

ANSWER SO_2 bleaches by reduction (reversible); Cl_2 by oxidation (permanent).

CHECK YOURSELF

C5 What is the catalyst in the contact process?

C6 What is the transition temperature between rhombic and monoclinic sulphur?

Answers at the end of the chapter.

SECTION I

Advanced problems

I

Each needs two ideas from the chapter.

SOLVED EXAMPLE 04 — NH_3 VS PH_3

Explain why NH_3 is more basic than PH_3 and has a larger bond angle.

SOLUTION

1. N is smaller and more electronegative; its lone pair is in a compact sp^3 orbital and is readily donated.
2. P's lone pair is in a larger, more diffuse orbital (largely s character), and is less available.
3. In NH_3 the bonding pairs are close to N and repel strongly (107.8°); in PH_3 they are farther away and P uses almost pure p orbitals (93.6°).

ANSWER Higher electron density and a more available lone pair make NH_3 more basic; stronger bond-pair repulsion gives a larger angle.

SOLVED EXAMPLE 05 — VOLUME OF OXYGEN

What volume of O_2 at STP is produced by heating 12.25 g of $KClO_3$ completely? ($KClO_3$ = 122.5 g mol^{-1})

SOLUTION

1. $2KClO_3 \rightarrow 2KCl + 3O_2$: 2 mol $KClO_3$ → 3 mol O_2.
2. 12.25 g = 0.100 mol → 0.150 mol O_2.
3. 0.150 × 22.4 L.

ANSWER 3.36 L of O_2.

SOLVED EXAMPLE 06 — HYDROLYSIS PRODUCTS

Compare the products of complete hydrolysis of PCl_3 and PCl_5, and give the basicity of each acid formed.

SOLUTION

1. $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ — phosphorous acid, dibasic.
2. $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ — orthophosphoric acid, tribasic.

ANSWER H_3PO_3 (dibasic, P +3) and H_3PO_4 (tribasic, P +5).

SOLVED EXAMPLE 07 — WHY N_2 IS SO UNREACTIVE

Explain why dinitrogen is almost inert at room temperature while white phosphorus catches fire in air.

SOLUTION

1. N_2 has a triple bond (one σ, two π) with a very high bond enthalpy, 941.4 kJ mol^{-1}.
2. P_4 has six single P–P bonds in a strained tetrahedron with 60° angles, which break easily.

ANSWER The N≡N triple bond is very strong; the strained P–P bonds of P_4 are weak and reactive.

SOLVED EXAMPLE 08 — OZONE ESTIMATION

O_3 is passed through excess moist KI, and the iodine liberated needs 20.0 mL of 0.100 M $Na_2S_2O_3$. Find the moles of O_3.

SOLUTION

1. $O_3 + 2KI + H_2O \rightarrow 2KOH + I_2 + O_2$: 1 mol O_3 → 1 mol I_2.
2. $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$: 1 mol I_2 ≡ 2 mol thiosulphate.
3. Thiosulphate = 2.00×10^{-3} mol → I_2 = 1.00×10^{-3} mol.

ANSWER 1.00×10^{-3} mol of O_3.

SOLVED EXAMPLE 09 — CONCENTRATED H_2SO_4 AS AN OXIDANT

Write the reactions of hot concentrated H_2SO_4 with copper, carbon and sulphur.

SOLUTION

1. $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$.
2. $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$.
3. $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$.

ANSWER In each case H_2SO_4 is reduced to SO_2.

SOLVED EXAMPLE 10 — ACID STRENGTH OF H_2E

Why is H_2Te a stronger acid than H_2O, although O is more electronegative?

SOLUTION

1. Acid strength of binary hydrides down a group is decided by H–E bond strength.
2. The H–Te bond is long and weak; the H–O bond is short and strong.

ANSWER Weaker H–Te bond releases H^+ more easily: $H_2O < H_2S < H_2Se < H_2Te$.

SECTION J

Exam trap gallery

J

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
NCl_5 exists like PCl_5.	No — N has no d orbitals; max covalency 4.
WHY Only PCl_3-type NCl_3 forms.	

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
PH_3 has a larger bond angle than NH_3.	NH_3 107.8° > PH_3 93.6°.
WHY Bond pairs are closer to the small N atom.	

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
NH_3 has the lowest b.p. of the group 15 hydrides.	PH_3 has the lowest; NH_3 is raised by H bonding.
WHY H bonding only in NH_3.	

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
H_3PO_3 is tribasic.	Dibasic (two P–OH).
WHY The P–H hydrogen does not ionise.	

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Cu + dilute HNO_3 gives NO_2.	Dilute gives NO; concentrated gives NO_2.

WHY Concentration changes the reduction product.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Oxygen has a more negative electron gain enthalpy than sulphur.	S (−200) is more negative than O (−141).

WHY Compact 2p subshell of O.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
H_2O is the strongest acid among group 16 hydrides.	H_2Te is the strongest; H_2O the weakest.

WHY H–E bond weakens down the group.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
SO_2 bleaches by oxidation.	By reduction (temporary).

WHY Cl_2 bleaches by oxidation.

✗ TRAP 09 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
SO_3 is dissolved directly in water in the contact process.	It is absorbed in H_2SO_4 to form oleum.

WHY Direct absorption forms an acid mist.

✗ TRAP 10 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Ozone is paramagnetic like O_2.	O_3 is diamagnetic.

WHY All electrons are paired.

✗ TRAP 11 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
White phosphorus is stored in kerosene.	White P is stored under water (Na is stored in kerosene).

WHY White P catches fire in air.

✗ TRAP 12 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Concentrated H_2SO_4 can dry NH_3.	It reacts with NH_3 (and oxidises H_2S).

WHY Use CaO for NH_3.

MEMORY HOOK

"N small: no NCl_5, high b.p. NH_3."

"Basicity counts OH, not H."

"Dilute copper gives NO, concentrated gives NO_2."

"SO_2 reduces, Cl_2 oxidises."

SECTION K

K

Practice MCQs

Levels: Easy, Moderate, Tough.

Q01 Laughing gas is: [EASY]

(a) NO
(b) N_2O
(c) NO_2
(d) N_2O_3

Q02 The brown gas formed when Cu reacts with conc. HNO_3: [EASY]

(a) NO
(b) N_2O
(c) NO_2
(d) N_2

Q03 Most basic hydride: [EASY]

(a) NH_3
(b) PH_3
(c) AsH_3
(d) BiH_3

Q04 Catalyst in the Ostwald process: [EASY]

(a) Fe
(b) V_2O_5
(c) Pt/Rh
(d) Ni

Q05 Ozone is prepared by: [EASY]

(a) heating O_2
(b) silent electric discharge
(c) electrolysis of water
(d) burning sulphur

Q06 Stable form of sulphur at room temperature: [EASY]

(a) monoclinic
(b) rhombic
(c) plastic
(d) S_2

Q07 Basicity of H_3PO_2: [EASY]

(a) 1
(b) 2
(c) 3
(d) 0

Q08 Which cannot form a pentahalide? [MODERATE]

(a) P
(b) As
(c) Sb
(d) N

Q09 Bond angle order of group 15 hydrides: [MODERATE]

(a) $NH_3 < PH_3$
(b) $PH_3 > AsH_3 > NH_3$
(c) $NH_3 > PH_3 > AsH_3$
(d) all 109.5°

Q10 Lowest boiling point: [MODERATE]

(a) NH_3
(b) PH_3
(c) AsH_3
(d) SbH_3

Q11 Paramagnetic oxide of nitrogen: [MODERATE]

(a) N_2O
(b) NO
(c) N_2O_5
(d) N_2O_3

Q12 Zn + dilute HNO_3 gives mainly: [MODERATE]

(a) NO_2
(b) N_2O
(c) H_2
(d) NO

Q13 Structure of PCl_5 in the solid state: [MODERATE]

(a) PCl_5 molecules
(b) $[PCl_4]^+[PCl_6]^-$
(c) $[PCl_6]^+[PCl_4]^-$
(d) P_2Cl_{10} dimer

Q14 Strongest acid: [MODERATE]

(a) H_2O
(b) H_2S
(c) H_2Se
(d) H_2Te

Q15 Brown ring in the nitrate test is due to: [MODERATE]

(a) NO_2
(b) $[Fe(H_2O)_5(NO)]^{2+}$
(c) $FeSO_4$
(d) Fe_2O_3

Q16 SO_2 turns acidified $K_2Cr_2O_7$: [MODERATE]

(a) yellow
(b) green
(c) colourless
(d) blue

Q17 Oleum is: [MODERATE]

(a) H_2SO_4
(b) $H_2S_2O_7$
(c) $H_2S_2O_8$
(d) H_2SO_5

Q18 PH_3 is obtained by heating white P with: [MODERATE]

(a) HCl
(b) NaOH solution
(c) H_2SO_4
(d) water only

Q19 Number of P–OH bonds in pyrophosphoric acid: [TOUGH]

(a) 2
(b) 3
(c) 4
(d) 5

Q20 In PCl_5, the axial bonds are: [TOUGH]

(a) shorter than equatorial
(b) longer than equatorial
(c) equal
(d) absent

Q21 Marshall's acid is: [TOUGH]

(a) H_2SO_5
(b) $H_2S_2O_8$
(c) $H_2S_2O_7$
(d) $H_2S_2O_3$

Q22 Oxidation state of P in H_3PO_3: [TOUGH]

(a) +1
(b) +3
(c) +5
(d) −3

Q23 Volume of O_2 at STP from 12.25 g $KClO_3$: [TOUGH]

(a) 1.12 L
(b) 2.24 L
(c) 3.36 L
(d) 6.72 L

Q24 Which acid reduces $AgNO_3$ to Ag? [TOUGH]

(a) H_3PO_4
(b) H_3PO_3
(c) $H_4P_2O_7$
(d) HNO_3

Q25 O_3 with moist KI gives: [TOUGH]

(a) KIO_3
(b) I_2
(c) KI_3 only
(d) HI

Answer key with explanations

Q01 **(b) N_2O** — Nitrous oxide.

Q02 **(c) NO_2** — Concentrated acid.

Q03 **(a) NH_3** — Most available lone pair.

Q04 **(c) Pt/Rh** — Pt/Rh gauze.

Q05 **(b) silent electric discharge** — Avoids decomposition.

Q06 **(b) rhombic** — Below 369 K.

Q07 **(a) 1** — One P–OH.

Q08 **(d) N** — No d orbitals.

Q09 **(c) $NH_3 > PH_3 > AsH_3$** — Decreases down.

Q10 **(b) PH_3** — No H bonding, smallest.

Q11 **(b) NO** — Odd electron.

Q12 **(b) N_2O** — More reactive metal, dilute acid.

Q13 **(b) $[PCl_4]^+[PCl_6]^-$** — Ionic solid.

Q14 **(d) H_2Te** — Weakest H–E bond.

Q15 **(b) $[Fe(H_2O)_5(NO)]^{2+}$** — Nitrosyl complex.

Q16 **(b) green** — Cr(VI) → Cr(III).

Q17 **(b) $H_2S_2O_7$** — Pyrosulphuric acid.

Q18 **(b) NaOH solution** — Disproportionation.

Q19 **(c) 4** — Tetrabasic.

Q20 **(b) longer than equatorial** — More repulsion at 90°.

Q21 **(b) $H_2S_2O_8$** — Peroxodisulphuric acid.

Q22 **(b) +3** — 3(+1) + x + 3(−2) = 0.

Q23 **(c) 3.36 L** — 0.15 mol O_2.

Q24 **(b) H_3PO_3** — P–H bond.

Q25 **(b) I_2** — Used to estimate ozone.

Check-yourself answers

C1 NO and NO_2 (odd-electron molecules).

C2 It has an unpaired electron; pairing two NO_2 molecules gives N_2O_4 with all electrons paired.

C3 White P exists as strained P_4 tetrahedra (60° angles); red P is polymeric and more stable.

C4 Two.

C5 V_2O_5.

C6 369 K.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Group 15

- ns^2np^3; −3 to +5; Bi^{3+} stable
- N: no d, max covalency 4, N≡N
- NH_3 > PH_3 > … basicity and bond angle
- b.p. PH_3 lowest; NH_3 H-bonded

N_2, NH_3, HNO_3

- $NH_4Cl + NaNO_2 \rightarrow N_2$; $Ba(N_3)_2$ pure N_2
- Haber: Fe, 200 atm, 700 K
- Ostwald: Pt/Rh; $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
- Cu dil → NO; conc → NO_2; Zn dil → N_2O

Phosphorus

- White P_4 (water), red polymeric
- $P_4 + NaOH \rightarrow PH_3 + NaH_2PO_2$
- PCl_5 TBP; solid $[PCl_4]^+[PCl_6]^-$
- H_3PO_2 1, H_3PO_3 2, H_3PO_4 3 (P–OH)

Group 16

- O: −2; H-bonding; ΔegH O < S
- $H_2O \rightarrow H_2Te$: acidity, reducing ↑
- O_3: silent discharge; bent 117°; oxidant
- Oxides: acidic, basic, amphoteric, neutral

Sulphur and SO_2

- Rhombic ⇌ monoclinic at 369 K
- SO_2: reducing; $K_2Cr_2O_7$ green
- Bleach: SO_2 reduces (temporary)
- $Na_2SO_3 + HCl \rightarrow SO_2$

H_2SO_4

- Contact: V_2O_5, 720 K, 2 bar
- SO_3 → oleum $H_2S_2O_7$
- Dehydrating, oxidising (Cu → SO_2)
- Caro H_2SO_5; Marshall $H_2S_2O_8$

END OF NOTES · RAMGOVINDYADAV.COM