Nitrogen family Gr-15 (Pnictogens)

Physical properties of Group-15 elements and their ions :

Property	N	P	As	Sb	Bi
Atomic number, Z	7	15	33	51	83
Ground state electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Enthalpy of atomization, $\Delta_a H^\circ(298\,K)$ / kJ mol^{-1}	473‡	315	302	264	210
Melting point, mp / K	63	317	887 sublimes	904	544
Boiling point, bp / K	77	550	–	2023	1837
Standard enthalpy of fusion, $\Delta_{fus} H^\circ$(mp) / kJ mol^{-1}	0.71	0.66	24.44	19.87	11.30
First ionization energy, IE_1 / kJ mol^{-1}	1402	1012	947.0	830.6	703.3
Second ionization energy, IE_2 / kJ mol^{-1}	2856	1907	1798	1595	1610
Third ionization energy, IE_3 / kJ mol^{-1}	4578	2914	2735	2440	2466
Fourth ionization energy, IE_4 / kJ mol^{-1}	7475	4964	4837	4260	4370
Fifth ionization energy, IE_5 / kJ mol^{-1}	9445	6274	6043	5400	5400
Metallic radius, r_{metal} / pm	–	–	–	–	182
Covalent radius, r_{cov} / pm*	75	110	122	143	152
Ionic radius, r_{ion} / pm**	171 (N^{3-})	–	–	–	103 (Bi^{3+})
NMR active nuclei (% abundance, nuclear spin)	^{14}N (99.6, $I = 1$) ^{15}N (0.4, $I = \frac{1}{2}$)	^{31}P (100, $I = \frac{1}{2}$)	^{75}As (100, $I = \frac{3}{2}$)	^{121}Sb (57.3, $I = \frac{5}{2}$) ^{123}Sb (42.7, $I = \frac{7}{2}$)	^{209}Bi (100, $I = \frac{9}{2}$)

Physical properties of Group-15 elements and their ions :

	N	P	As	Sb	Bi
Melting point /°C	−210	44 (white) 590 (red)	613 (sublimes)	630	271
Atomic radius/pm	74	110	121	141	170
First ionization energy/(kJ mol^{-1})	1402	1011	947	833	704
Electrical conductivity/(10^6 S m^{-1})		10	3.33	2.50	0.77
Pauling electronegativity	3.0	2.2	2.2	2.0	2.0
Electron affinity/(kJ mol^{-1})	−8	72	78	103	91
B(E−H)/(kJ mol^{-1})	390	322	275		

Where do we utilize these elements?:

- The major nonchemical use of nitrogen gas is as an inert atmosphere in metal processing, petroleum refining, and food processing.
- Liq. N_2 is important coolant in freezing processes
- N-based chemical cyanides/azides used in motor vehicle airbags where decomposition produces N_2 to inflate the airbag (during accident)
-

$$2NaN_3(s) \xrightarrow{\Delta} 2Na + 3N_2$$



-

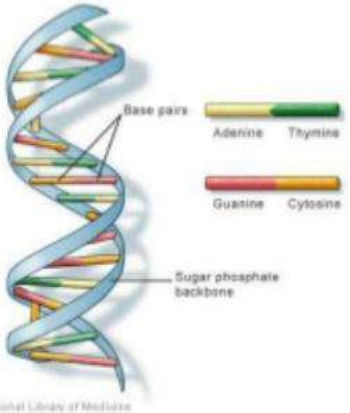
White Phosphorus is used in some explosives, including rockets. This caused an uproar because of safety concerns.



Red Phosphorus is used in match heads. You can see the texture of a match head next to the matches.



Fertilizer; Phosphorus is known for being essential to DNA and to a lesser extent fertilizer



P together with N and K is an essential plant nutrient

P crucial constituent of bones and teeth

Where do we utilize these elements?:

- **Arsenic** is used as a dopant in solid-state devices such as integrated circuits and lasers as well as semiconductors. Although As is a well-known poison it is also an essential trace element in chickens, rats, goats, and pigs, and arsenic deficiency leads to restricted growth
- **Arsenic** compounds are sometimes used as rat poisons and insecticides but their use is strictly controlled.
- As a result of its toxicity, **arsenic** compounds are used in wood preservation
- **Antimony** is used in semiconductor technologies to produce infrared detectors and light-emitting diodes. It is used in alloys, where it leads to stronger and harder products.
- Sb used in paints, adhesives and plastics, and as a flame retardant
- **Bi** used in alloys. **BiOCl** used in cosmetic products i.e. cream, hair dyes and tints
- **Bi** has use in glass, ceramics industry and for catalysts, magnets



N differs from rest of its group elements due to

- small size
- high electronegativity
- high ionization enthalpy
- non-availability of d orbitals
- has potential to form $p\pi$-$p\pi$ bond with itself and hence inert at room temperature
- $p\pi$-$d\pi$ bond formation is rare
- other elements of Group-15 are single bonded only
- maximum covalency is 4 as can not extend its bonding capacity

Chemical reactivity :

- towards Hydrogen (H_2):

Forms complexes i.e. EH_3 (E= N, P, As, Sb, Bi)

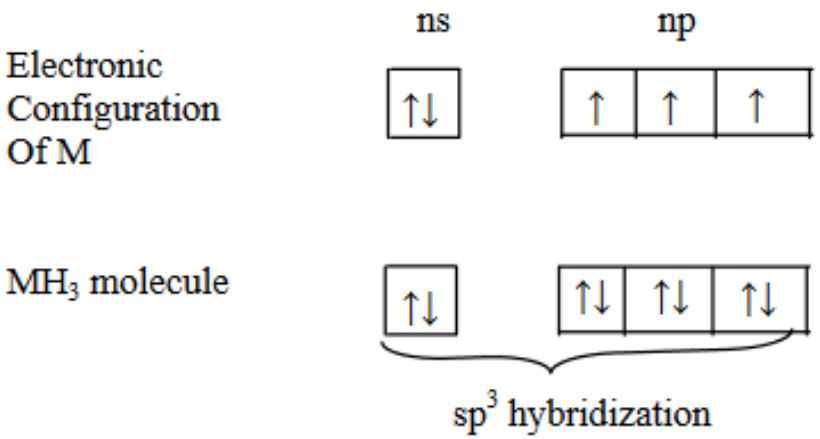
- towards Oxygen (O_2):

Forms complexes i.e. E_2O_3 and E_2O_5 (E= N, P, As, Sb, Bi)

Hydrides :

All elements form volatile hydrides of the formula MH_3.

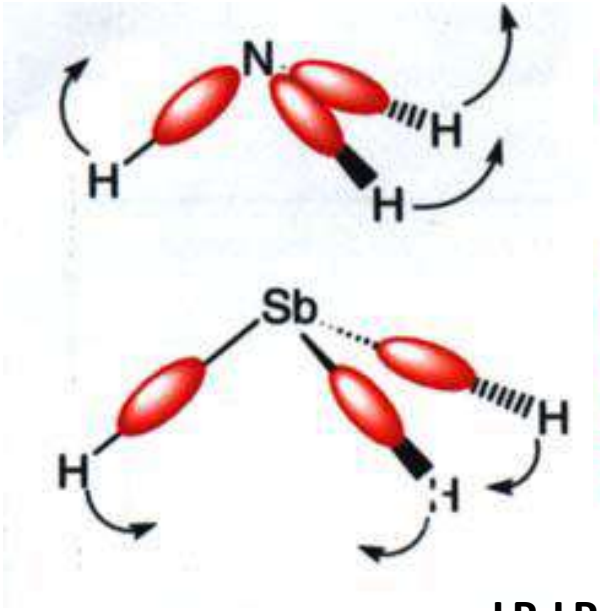
VSEPR theory predicts pyramidal structure (sp^3 hybridization with lone pair on central atom).



On moving down the group from NH_3 to BiH_3, the central atom becomes larger and effective overlap with the small 1s orbital of hydrogen decreases. Thus the stability of the hydrides decreases down the group and their reducing power increases.

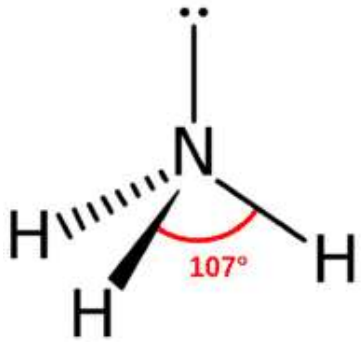
Hydride structures :

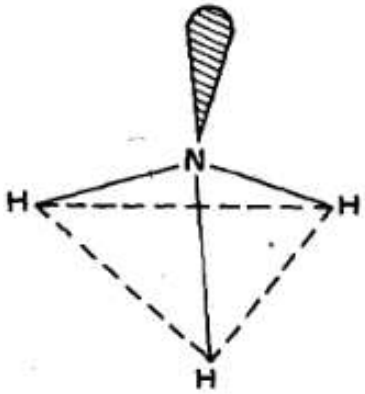
- central atoms are sp^3 hybridised
- one of the positions of the tetrahedron is occupied by lone pair giving rise to pyramidal structure (three bond pair + 1 lone pair)
- tetrahedron is distorted due to repulsion between bond pairs and lone pair of electrons



Nomenclature

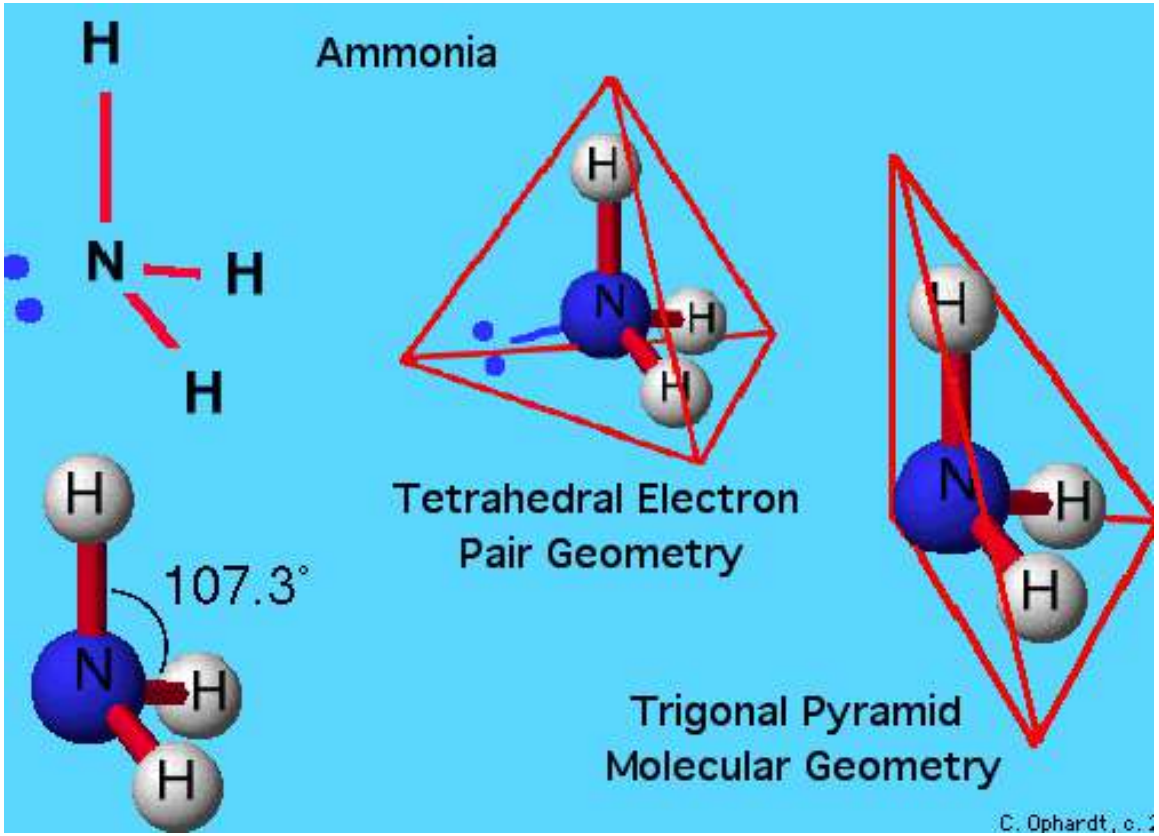
	Traditional name	IUPAC[a] name
NH_3	ammonia	azane
PH_3	phosphine	phosphane
AsH_3	arsine	arsane
SbH_3	stibine	stibane
BiH_3	bismuthine	bismuthane





LP-LP > LP-BP > BP-BP (repulsion order)

Hydride structures :

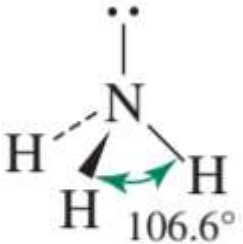


Opposite to the boron hydride trigonal planar molecular geometry as that did not have lone pair of electrons

Oxidation state of N in NH_3 = -3

$$N_2 + 3\ H_2 \xrightarrow[\text{Catalyst}]{\text{300 atm, 450 °C}} 2\ NH_3$$

Haber process of ammonia production



Ammonia

Hydride structures : Rationale

Molecule EH_3	H–E–H angle (°)
NH_3	107
PH_3	93.5
AsH_3	92
SbH_3	91.5

- All central atoms have four valence electron pairs
- The expected H-E-H bond angle likely < 109.5° (general Td) due to LP effect
- Distortion arises from the different electronic distribution in E-H bond
- Down the group electronegativity of E decreases
- Bond pairs tend to move away from E , occupying less space in its valence shell
- Reduction of repulsion between bonding pairs in the vicinity of E leading to decrease in the bond angle

Hydride properties :

- Down the group electronegativity of E decreases
- H-E-H bond angle also decreases reaching ~90°
- Indicates that , E-H bonds consist of almost pure p orbital
- Lone pair resides in almost pure s orbital i.e. in orbital which is more s type than the sp^3 type
- Lone pair in s orbital locates more closer to the nucleus and difficult to remove
- NH_3 is string base and can donate its lone pair of electrons strongly to form complexes
- So, basicity (lone pair donation capacity) also decreases down the group

All these trihydrides of Gr-15 elements are strong reducing agents

Time to assess your knowledge

Q Rationalize the trend in the H–E–H bond angles in the series of hydrides:

Molecule EH_3	H–E–H angle (°)
NH_3	107
PH_3	93.5
AsH_3	92
SbH_3	91.5

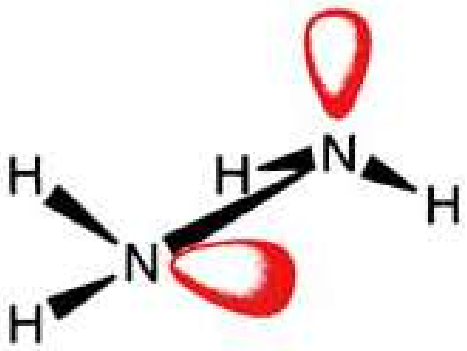
For answer check next slide

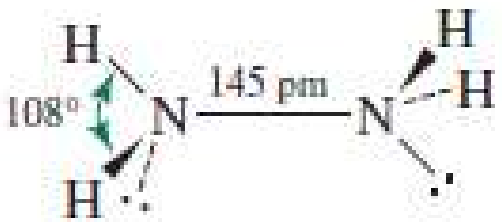
A All species have four valence pairs of electrons in the central E atom, corresponding to a tetrahedral arrangement. The H–E–H bond angles are expected to be <109.5° (the tetrahedral angle) owing to the effect of the lone pair. Distortions to the basic shape can be obtained by considering the electron distribution in the E–H bonds. The N–H bond is short (101.5 pm) and nitrogen is more electronegative than hydrogen, so the bonding pair will reside closer to the central N atom, occupying more space in its valence shell. These N–H bonding pairs will repel each other more, widening the bond angle.

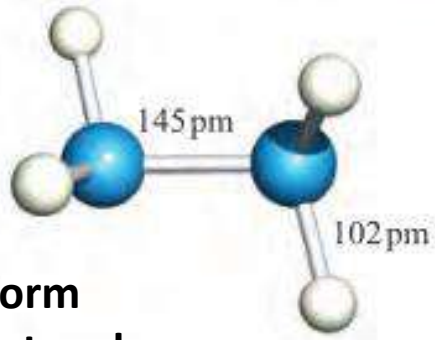
Hydrazine (N_2H_4) structure : N Oxidation State = -2

- Each nitrogen atom has a lone pair of electrons and either one or both nitrogen atoms are able to accept protons to give $N_2H_5^+$ and the less stable $N_2H_6^{2+}$

- overall complex has two lone pair of electrons

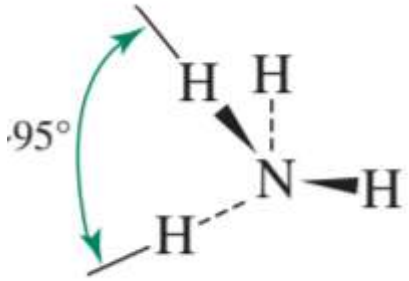




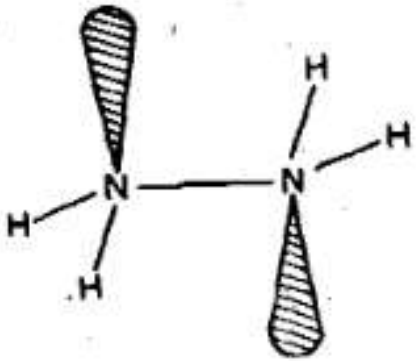


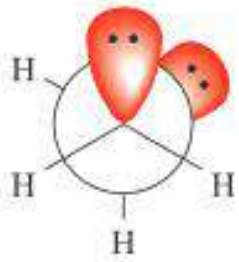
(a)

Gauche form predominant and stable

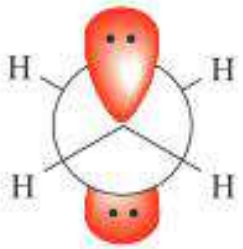


End view





Gauche



Staggered

Hydrazine structure :

- Derivative of NH_3 where one H being replaced with $–NH_2$ group

- Both N atoms are sp^2 hybridized, each having a lone pair of electrons in one of the hybrid orbitals. One hybrid orbital from each N forms the N-N bond; the remaining orbitals are engaged in N-H bonding. The N-N bond distance is 1.47 Å. The bond energy is estimated at 160 KJ mol^{-1} assuming the N-H bond energy to be the same as in NH_3.

- Both N atoms adopt pyramidal geometry

- bond energy of N-N bond is extremely small due to repulsion of the nonbonding electrons causing weakening of the N-N bond

- overall complex has two lone pair of electrons

- anomalously low bond dissociation energy due to strong repulsion between the lone pair of electrons on the adjacent N atoms

- due to small size of N weaker base than NH_3

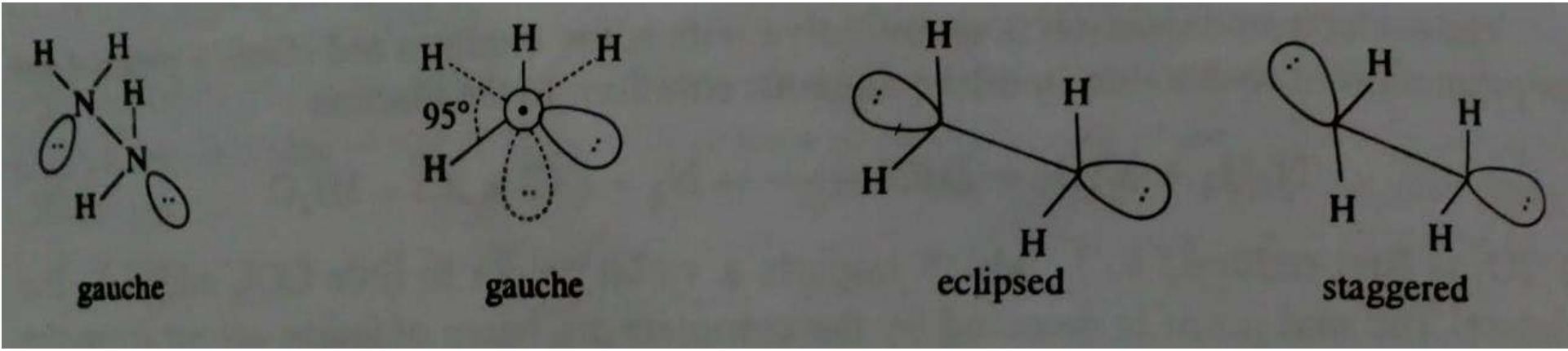
- more electronegative $–NH_2$ has –I effect on LP of N, making less basic for protonation

- may be considered as a derivative of ammonia, one hydrogen atom being replaced by an $—NH_2$ group

Hydrazine structure :

- it is exclusively present in gauche conformation, the two halves of the molecule being rotated by ~95° along the N-N bond. The HNH bond angles are 108°

- It is widely used as Rocket fuel. N_2H_4 has uses in the agricultural and plastics industries, and in the removal of O_2 from industrial water boilers to minimize corrosion, used as foam blowing agent



Hydrazine is prepared by the Raschig process, the first step of which involves the production of chloramine, NH_2Cl. The process can be summarized by the equations

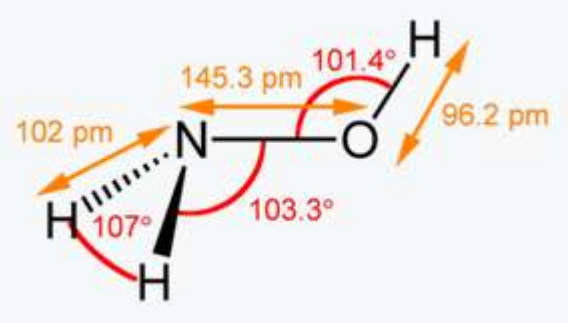
$$NH_3 + NaOCl \xrightarrow{\text{Gelatin}} NaOH + NH_2Cl$$

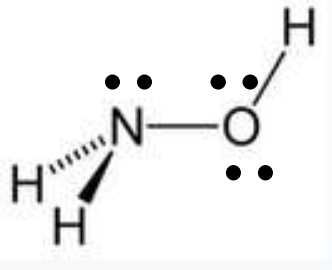
$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

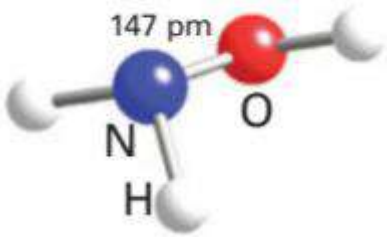
Hydroxylamine (NH_2OH) structure : N Oxidation State = -1

- Derivative of NH_3 where one H being replaced with –OH group

- weaker base than ammonia







- structure lies between hydrazine and hydrogen peroxide

- **N : sp^3 (trigonal pyramidal)**

- **O : sp^3 (bent)**

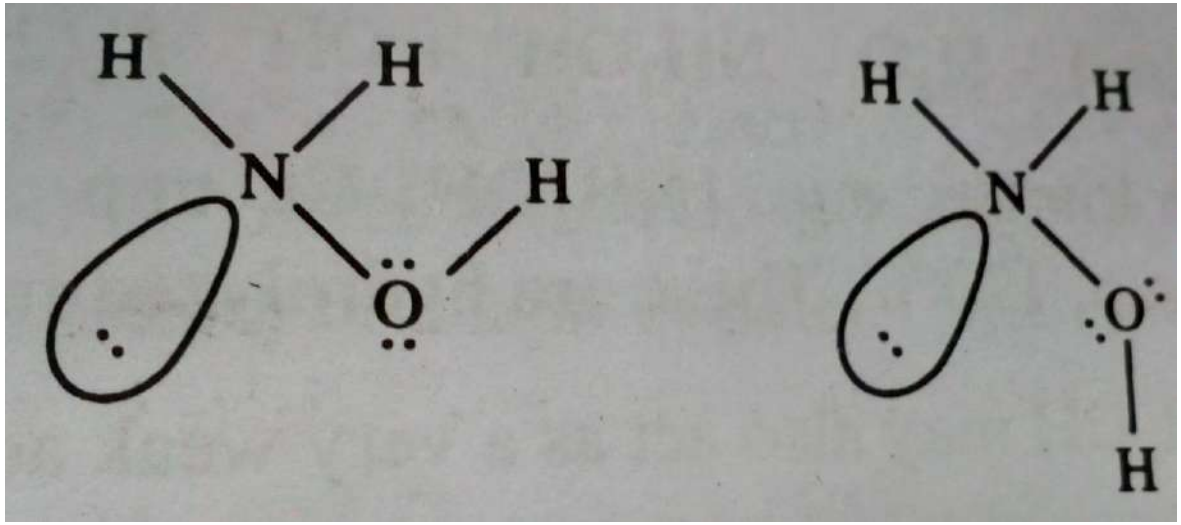
Hydroxylamine (NH_2OH) structure : N Oxidation State = -1

- Hydroxylamine is derived from ammonia by replacing one hydrogen atom by a hydroxyl group

- It is prepared by the electrolytic reduction of nitric acid, using a lead cathode

$$HNO_3 + 6H^+ + 6e^- \rightarrow NH_2OH + 2H_2O$$

- The bonding corresponds to sp^3 hybridised N atom with ne orbital occupied by a lone pair of electrons. The N-O distance is 1.47Å in conformity with expected single bond. Two configurational isomers –cis and –trans, are possible with several intermediate gauche conformations:

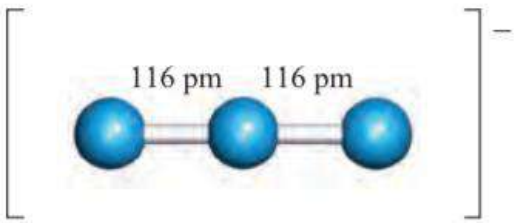


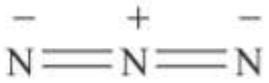
Used as an antioxidant in photographic developers, in reduction during dyeing of acrylic fibres, as absorbent in combustion analysis

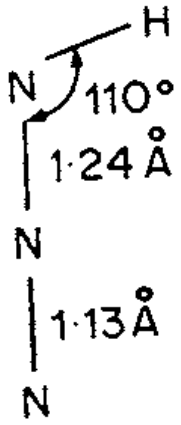
Hydrazoic acid (HN_3)/ Hydrogen azide structure :

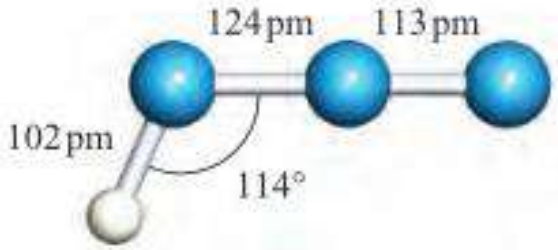
- The N-N-N group in this structure is linear

Azide ion

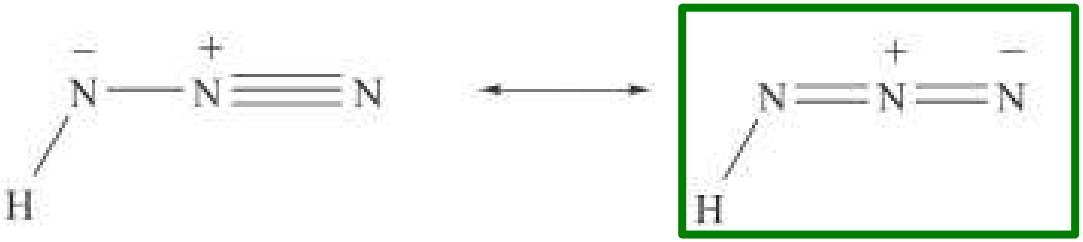












Major contributing resonance forms

✓ **Linear hybridisation (sp) for central N**

✓ **trigonal sp^2 for terminal N atoms**

Hydrazoic acid (HN_3) structure :

- The **linear** azide ion, N_3 , can be formed by deprotonation of HN_3, and is symmetrical with two identical N-N bond lengths of 116 pm.



- no resemblance to either ammonia or hydrazine

- increased stability of ionic azides is due to enhanced resonance structural forms

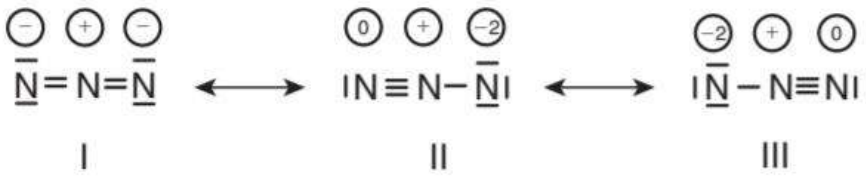
Hydrazoic acid (HN_3) preparation:

$$3\ NaNH_2 + NaNO_3 \xrightarrow{175\,^\circ C} NaN_3 + 3\ NaOH + NH_3$$

$$2\ NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

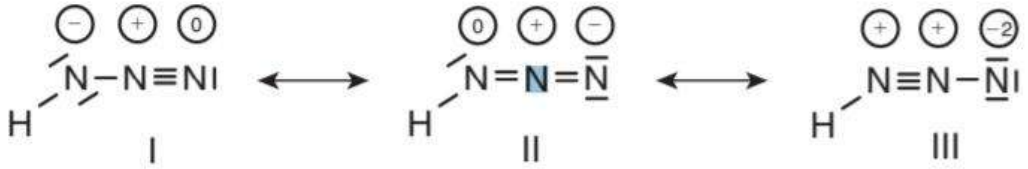
Hydrazoic acid (HN_3)/ Hydrogen azide structure :

The difference in stability of ionic and covalent azides is sometimes explained in terms of resonance structures. The azide ion, N_3^-, can be represented by the three resonance structures



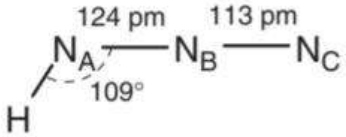
I II III

Structure I is the most important of the three. A covalent azide such as HN_3 (dipole moment = 1.70 D) can be represented by the resonance structures



I II III

Structure III makes virtually no contribution because of the positive formal charges on adjacent atoms and the overall higher formal charges. In HN_3, the bond lengths are



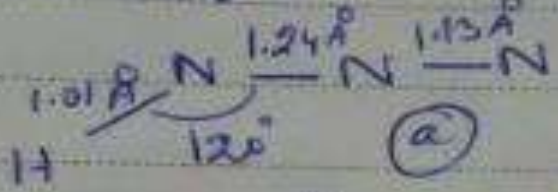
Hydrazoic acid (HN_3)/ Hydrogen azide structure / USE:

Bonds between nitrogen atoms have lengths that are normally as follows: N–N, 145 pm; N=N, 125 pm; N≡N, 110 pm. Because structure I for HN_3 shows a single bond between N_A and N_B and structure II shows a double bond between these atoms, the observed bond length should be somewhere between the values expected for those bonds (125 and 145 pm). However, it is almost the same as that for a double bond, indicating that structures I and II do not contribute equally, and that structure II is the more significant. Because the dipole moment of HN_3 is 1.70 D and the H–N bond moment is only about 1.33 D, it appears that structure II, which places a negative formal charge on N_C, is dominant. Therefore, it appears that only one resonance structure makes a significant contribution to the actual structure of HN_3, whereas in N_3^- three resonance structures contribute to the true structure. It is generally true that the greater the number of contributing resonance structures, the more stable the species (the lower the energy of the species), and ionic azides are much more stable than covalent azides. This analysis is overly simplistic because the distance between N_B and N_C is close to that expected for a triple bond as shown in structure I.

The azides are particularly useful in explosive industry. Lead azide is vigorously used in detonators.

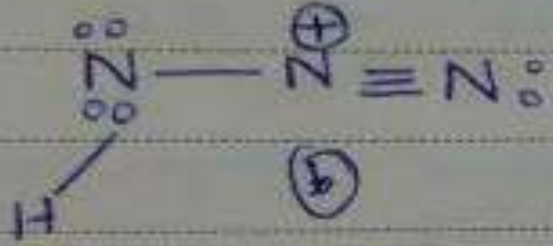
Hydrazoic acid (HN_3)/ Hydrogen azide structure :

In HN_3, the N-N-N group is linear and the structure is:—

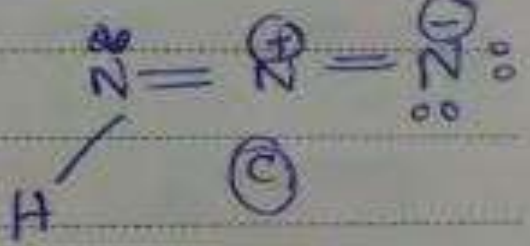


(a)

This is also true for covalent azides. Resonance contribution from the following structures appears consistent with the unequal N-N distances:—



(b)

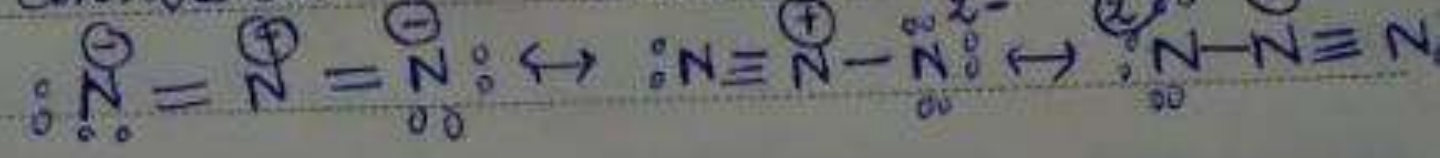


(c)

The central N is sp hybridised. The N attached to H has sp^3 and sp^2 hybrid orbital in (b) and (c) respectively

Hydrazoic acid (HN_3)/ Hydrogen azide structure :

The azide ion is symmetrical and linear with both N-N distances being equal to 116 pm. Valence bond consideration narrates as :—



The explosive nature of covalent azides contrary to ionic azides has been attributed to the relatively greater stability of the azide ion in ionic azides and to the loss of symmetry in covalent compounds.

Halides:

- Group-15 elements have preferrable +3 and +5 oxidation states

- Hence, both of their halide types : trihalides as well as pentahalides are known

- trihalides are sp^3 hybridised with distorted tetrahedral geometry and pyramidal molecular shape

- pentahalides are sp^3d hybridised and are trigonal bipyramidal in shape

- All combination of EX_3 type complexes are known (E = N, P, As, Sb, Bi and X= F, Cl, Br, I)

- Ionic nature of these trihalides increases down the group

- All EX_5 complexes are stable except NF_5 as N has only four valence orbitals

- Fluoride ligands are able to stabilize the highest oxidation state of the Group 15 elements.

Halides:

- **N has only 4 electrons in its outermost shell (one in s orbital and 3 in p) which is available for bonging. So, shows maximum covalency of 4**

- **heavier congeners have vacant d orbital in valence shell to be used for bonding**

- Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell.

- Pentahalides are more covalent than trihalides.

- In case of nitrogen, only NF_3 is known to be stable due to high polarizing nature of F-atom

- Trihalides except BiF_3 are predominantly covalent in nature. BiF_3 is ionic due to high matallic character of Bismuth.

Halides:

- EX_5 compounds become increasingly oxidizing on going down the group

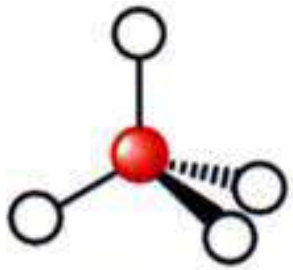
- **Structure of PCl_5 :**

Q PCl_5 crystallizes as $PCl_4^+PCl_6^-$. Predict the shapes of these ions.

A Phosphorus is in Group 15, with 5 valence electrons:

	PCl_4^+	PCl_6^-
central P atom	5 electrons	5 electrons
bonds to Cl atoms	4 electrons	6 electrons
charge	subtract 1 electron	add 1 electron
total	8 valence electrons	12 valence electrons
	4 pairs	6 pairs
shape	regular tetrahedron	regular octahedron

Structure of PCl_5 :



Td, PCl_4^+



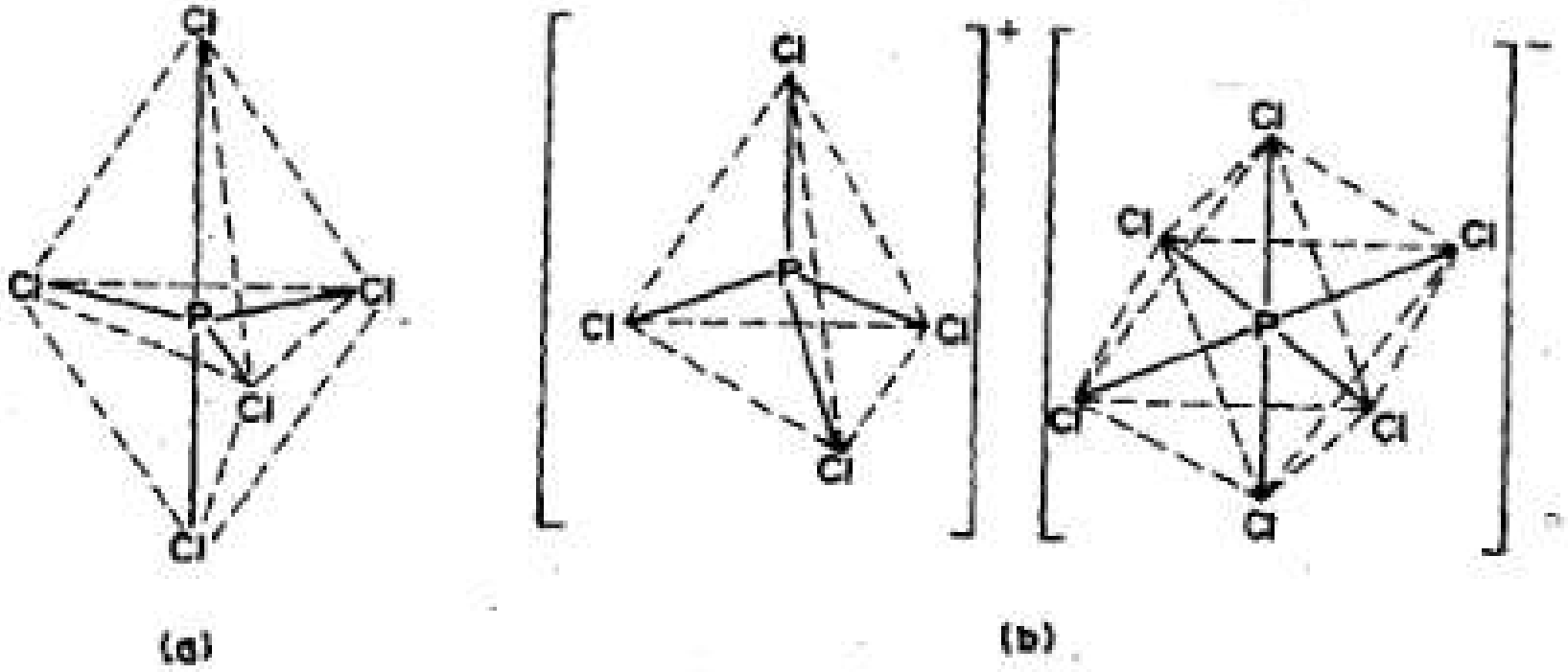


Oh, PCl_6^-

- In gas phase, pentahalide adopts trigonal bipyramidal structure as expected from VSEPR
- In solid state situation complicates due to characterisation of different phases of PCl_5
- crystallizes as ionic solid as shown beside
- another metastable form : $(PCl_4^+)_2\ (PCl_6^-)\ Cl$
- generally, EX_5 act as lewis acids to react with lewis bases (electron pair donor ligands) to form EX_6^- species
- PCl_5 is a strong Lewis acid and form stable complexes with amines and ethers
- It is an important reagent and made industrially by the reaction of PCl_3 and Cl_2

Structure of PCl_5 :

$$PX_3 + X_2 \longrightarrow PX_5$$



Structure of PCl_5 in (a) gaseous state (b) solid state

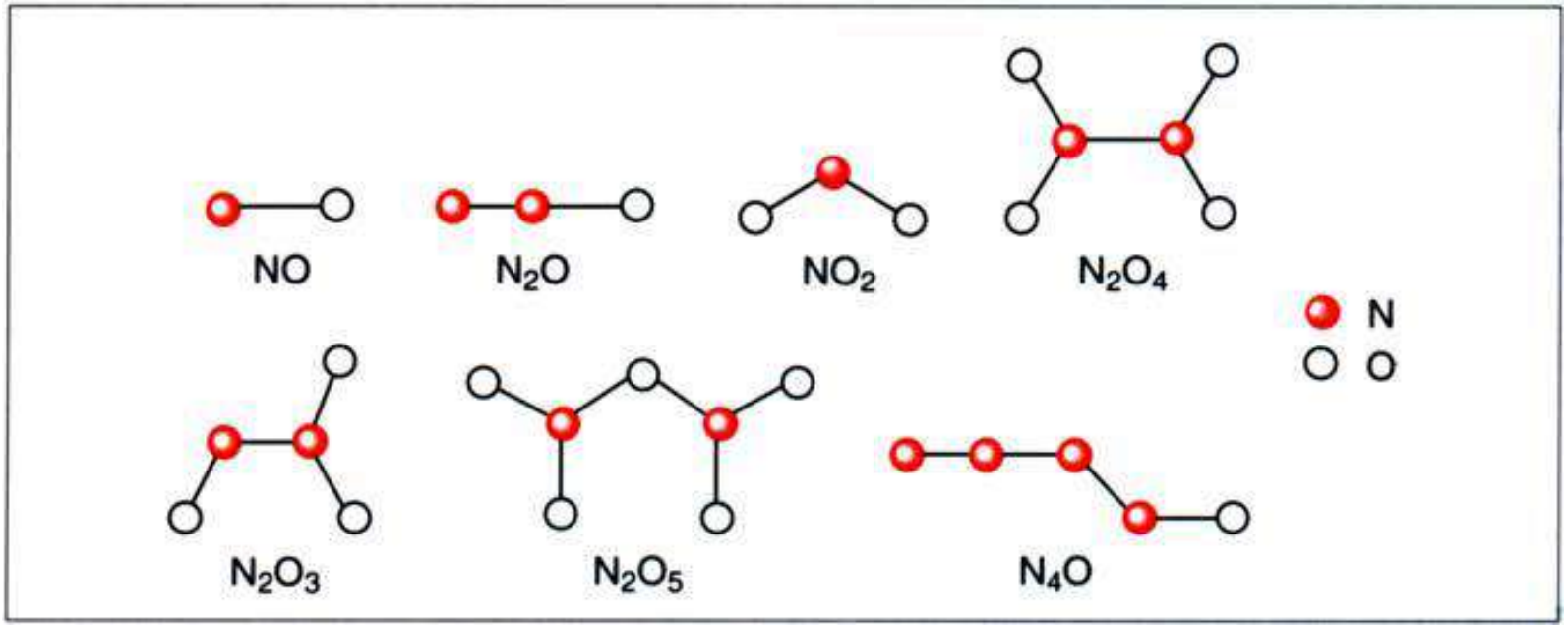
Oxides and oxoacids:

- **All Group-15 elements form wide range of oxides : N, P specially**

Element	N	P	As	Sb	Bi
Oxidation state					
+1	N_2O				
+2	NO				
+3	N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
+4	NO_2, N_2O_4				
+5	N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	

- **The *+5 oxides are found, in each case,* to be more acidic than the corresponding + 3 oxides.**

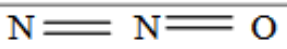
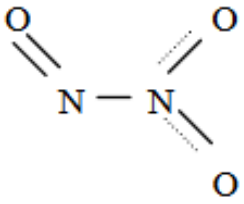
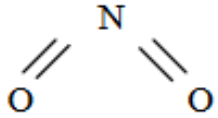
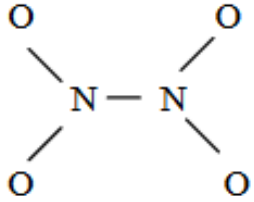
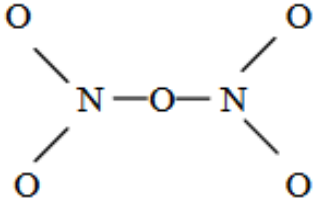
Nitrogen Oxides :



Oxides of nitrogen cover a range of oxidation states, from + 1 to *+5, and* in all compounds there is significant N-0 pπ-pπ bonding

They all exhibit pл-pл multiple bonding between nitrogen and oxygen atoms. The other elements of Group 15 cannot form such bonds and consequently nitrogen forms a number of compounds for which P, As, Sb or Bi analogues are not known. Oxides in lower oxidation state are neutral while those in higher oxidation states are acidic.

Nitrogen Oxides :

Formula	Name	Structure	Remarks
N_2O	Nitrous Oxide		Oxidn.state + 1 (O.S.)
NO	Nitric Oxide		O. S + 2 Bond order 2.5 Paramagnetic
N_2O_3	Nitrogen Sesquioxide		O.S + 3 Dissociates readily to NO & NO_2
NO_2	Nitrogen Dioxide		O.S + 4 Paramagnetic Following equilibrium presents $2NO_2 = N_2O_4$
N_2O_4	Dinitrogen Tetraoxide		O.S + 4 Dissociates to NO_2
N_2O_5	Dinitrogen Pentoxide		O.S + 5 N-O-N may be bent. Exists as $NO_2^+NO_3^-$ in solid state

Nitrogen Oxides :

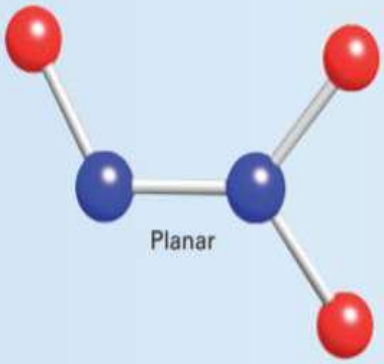
Formula	Name	Color	Remarks
N_2O	Nitrous oxide	Colorless	Rather unreactive
NO	Nitric oxide	Gas, colorless; liquid and solid, blue	Moderately reactive
N_2O_3	Dinitrogen trioxide	Blue solid	Extensively dissociated as gas
NO_2	Nitrogen dioxide	Brown	Rather reactive
N_2O_4	Dinitrogen tetroxide	Colorless	Extensively dissociated to NO_2 as gas and partly as liquid
N_2O_5	Dinitrogen pentoxide	Colorless	Unstable as gas; ionic solid
NO_3 ; N_2O_6	—	—	Not well characterized and quite unstable

Nitrogen Oxides :

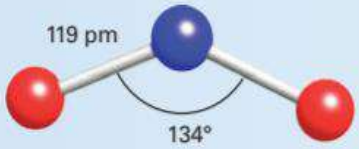
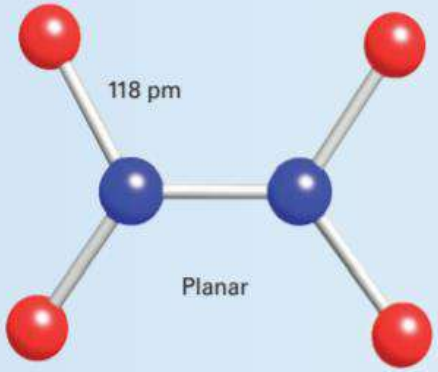
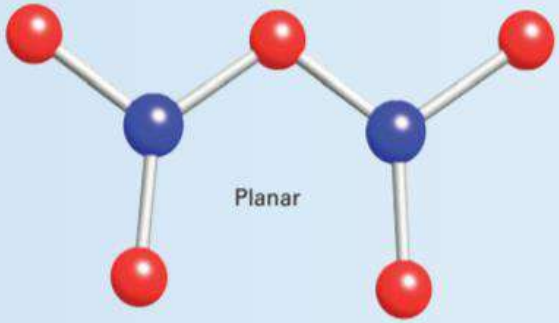
Formula	Name	Characteristics
N_2O	Nitrous oxide	Colorless gas, weak oxidizing agent
NO	Nitric oxide	Colorless gas, paramagnetic
N_2O_3	Dinitrogen trioxide	Blue solid, dissociates in gas
NO_2	Nitrogen dioxide	Brown gas, equilibrium mixture
N_2O_4	Dinitrogen tetroxide	Colorless gas
N_2O_5	Dinitrogen pentoxide	Solid is $NO_2^+NO_3^-$, gas unstable

	N_2O	NO	N_2O_3	NO_2	N_2O_4	N_2O_5
Name	Dinitrogen monoxide‡	Nitrogen monoxide‡	Dinitrogen trioxide	Nitrogen dioxide	Dinitrogen tetraoxide	Dinitrogen pentaoxide
Melting point / K	182	109	173	–	262	303
Boiling point / K	185	121	277 dec.	–	294	305 sublimes
Physical appearance	Colourless gas	Colourless gas	Blue solid or liquid	Brown gas	Colourless solid or liquid, but see text	Colourless solid, stable below 273 K
$\Delta_f H^\circ(298\,K)$ / kJ mol^{-1}	82.1 (g)	90.2 (g)	50.3 (l) 83.7 (g)	33.2 (g)	−19.5 (l) 9.2 (g)	−43.1 (s)
Dipole moment of gas-phase molecule / D	0.16	0.16	–	0.315	–	–
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic

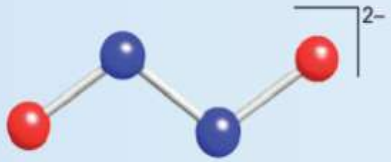
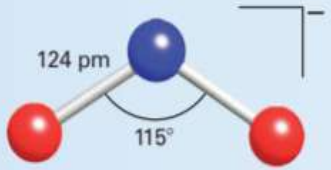
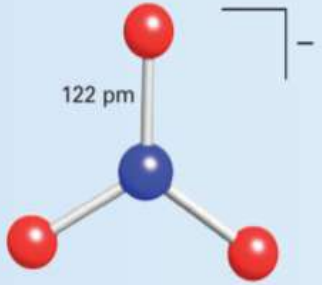
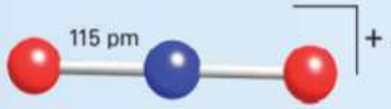
Nitrogen Oxides :

Oxidation number	Formula	Name	Structure (gas phase)	Comments
+1	N_2O	Nitrous oxide (dinitrogen oxide)		Colourless gas, not very reactive
+2	NO	Nitric oxide (nitrogen monoxide)		Colourless, reactive, paramagnetic gas
+3	N_2O_3	Dinitrogen trioxide		Blue solid (m.p. 101°C); dissociates into NO and NO_2 in the gas phase

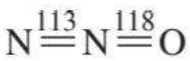
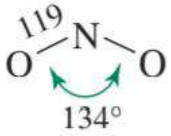
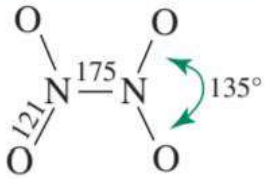
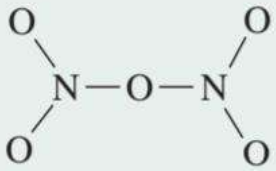
Nitrogen Oxides :

+4	NO_2	Nitrogen dioxide		Brown, reactive, paramagnetic gas
+4	N_2O_4	Dinitrogen tetroxide		Colourless liquid (m.p. −11°C); in equilibrium with NO_2 in the gas phase
+5	N_2O_5	Dinitrogen pentoxide (dinitrogen pentoxide)		Colourless, ionic solid $[NO_2][NO_3]$ (m.p. 32°C); unstable

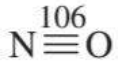
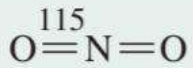
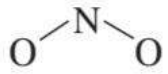
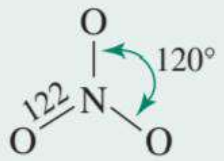
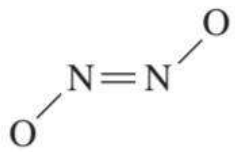
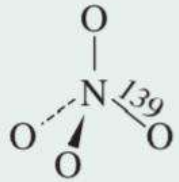
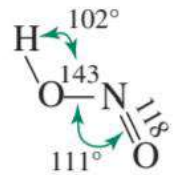
Nitrogen-Oxygen anions :

Oxidation number	Formula	Common name	Structure	Comments
+1	$N_2O_2^{2-}$	Hyponitrite		Usually acts as a reducing agent
+3	NO_2^-	Nitrite		Weak base; acts as an oxidizing agent and a reducing agent
+3	NO^+	Nitrosonium (nitrosyl cation)		Oxidizing agent and Lewis acid; π-acceptor ligand
+5	NO_3^-	Nitrate		Very weak base; an oxidizing agent
+5	NO_2^+	Nitronium (nitryl cation)		Oxidizing agent, nitrating agent, Lewis acid

N-oxides: more recapitulation :

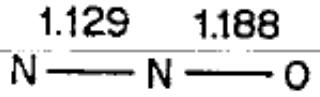
N_2O	Nitrous oxide		mp = −90.9 °C; bp = −88.5 °C
NO	Nitric oxide		mp = −163.6 °C; bp = −151.8 °C; bond order approximately 2.5; paramagnetic
NO_2	Nitrogen dioxide		Brown, paramagnetic gas; exists in equilibrium with N_2O_4; $2\,NO_2 \rightleftharpoons N_2O_4$
N_2O_3	Dinitrogen trioxide		mp = −100.1 °C; dissociates above melting point: $N_2O_3 \rightleftharpoons NO + NO_2$
N_2O_4	Dinitrogen tetroxide		mp = −11.2 °C; bp = −21.15 °C; dissociates into $2\,NO_2$ [ΔH(dissociation) = 57 kJ/mol]
N_2O_5	Dinitrogen pentoxide		N—O—N bond may be bent; consists of $NO_2^+NO_3^-$ in the solid

N-oxides: more recapitulation :

NO^+	Nitrosonium or nitrosyl		Isoelectronic with CO
NO_2^+	Nitronium or nitryl		Isoelectronic with CO_2
NO_2^-	Nitrite		N — O distance varies from 113 to 123 pm, and bond angle varies from 116° to 132° depending on cation; versatile ligand (see Chapter 9)
NO_3^-	Nitrate		Forms compounds with nearly all metals; as ligand, has a variety of coordination modes
$N_2O_2^{2-}$	Hyponitrite		Reducing agent
NO_4^{3-}	Orthonitrate		Na and K salts known; decomposes in presence of H_2O and CO_2
HNO_2	Nitrous acid		Weak acid (pK_a = 3.3 at 25 °C); disproportionates: $3\ HNO_2 \rightleftharpoons H_3O^+ + 2\ NO + NO_3^-$ in aqueous solution
HNO_3	Nitric acid		Strong acid in aqueous solution; concentrated aqueous solutions are strong oxidizing agents

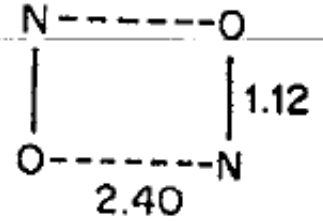
Nitrogen Oxides :

Nitrous oxide ($C_{\infty v}$)

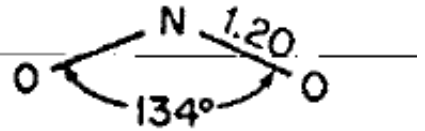


Linear (Dinitrogen oxide; N_2O)

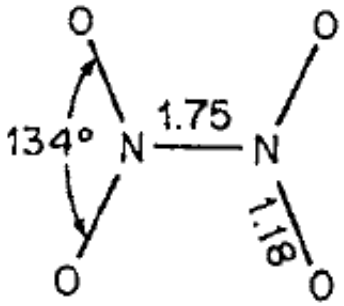
Nitric oxide in crystal (C_{2h})



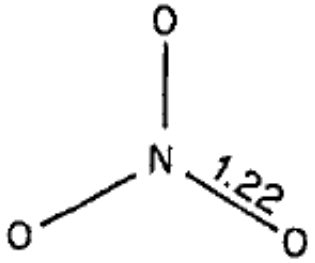
Nitrogen dioxide (C_{2v})



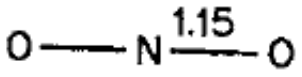
Dinitrogen tetroxide (D_{2h})
(one of several forms)



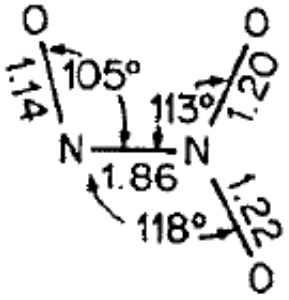
Nitrate ion (D_{3h})



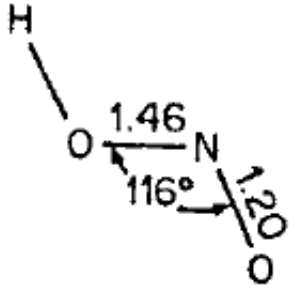
Nitronium ion ($D_{\infty h}$)



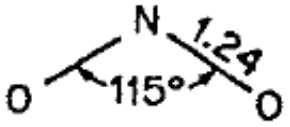
Dinitrogen trioxide (C_s)



Nitrous acid (C_s)



Nitrite ion (C_{2v})

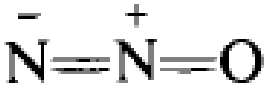


Nitrogen Oxides :

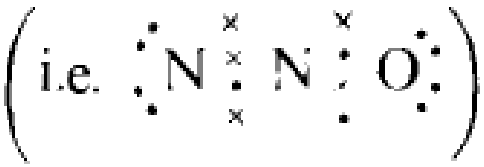
1. Linear (Dinitrogen oxide; N_2O)

- sp hybridisation for both N, sp^3 for O
- 16 electron triatomic molecule



(a) 

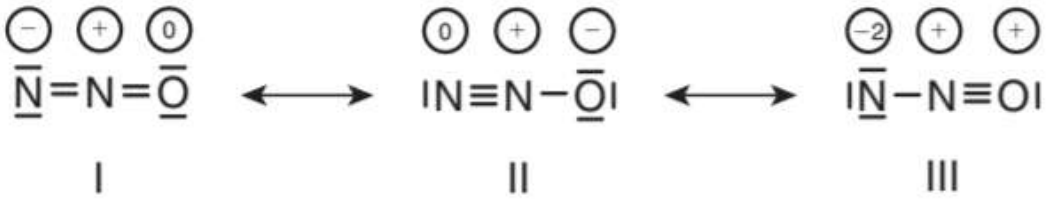
(b) 



and



Dinitrogen oxide is a colourless gas; the molecule has the *geometric* structure N—N—O, and is a resonance hybrid of the two forms the molecule being linear; in this respect it resembles the isoelectronic molecule of carbon dioxide, O=C=O. There is also a resemblance in physical properties, but the dinitrogen oxide molecule possesses a small dipole moment, unlike that of carbon dioxide.



1. Linear (Dinitrogen oxide; N_2O)

- **Preparation**

$$NH_4NO_3 \xrightarrow{450-520\ K} N_2O + 2H_2O$$

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$$

Features

- The calculated bond orders are N-N: 2.73 and N-O: 1.61
- Dinitrogen monoxide has a faint, sweet odour. It dissolves in water to give a neutral solution, but does not react to any significant extent.
- One application of N_2O is as a general anaesthetic ('laughing gas'), but its major use is in the preparation of whipped cream and as aerosol propellants
- Central N boasts sp hybrid orbital to form two σ bonds to N and O on two sides. The two p orbitals excluded from hybridisation form two π bonds to N ad O in structure and to N only in structure b in previous slide