

## Group 15

N, P, As, Sb, Bi

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## The elements

**N<sub>2</sub>** a colourless gas (bp: -196 °C)

**P<sub>4</sub>** yellow mp: 44 °C d: 1.84  
red mp: 600 °C d: 2.16  
black mp: 610 °C d: 3.56



chains of tetrahedra  
6:6, r, 2.23, r, 3.32 >90°

**As** gray solid, black P-structure

**Sb** gray solid, black P-structure

**Bi** gray solid, black P-structure



	N	P	As	Sb	Bi
Abundance ppm	300	800	5	1	.2
Electronegativity (H:2.2)	3.0	2.2	2.2	2.1	2.0

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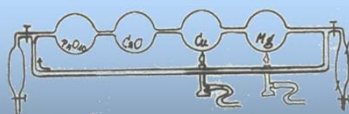
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## The atmosphere

	N <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>	Ne	H <sub>2</sub>	He	Kr	Xe
Bp /K	77.2	90.1	87.2	194.7	27.2	20.2	4.2	119.2	165.1
$\alpha_{vol}$	.7803	.2099	.0093	3·10 <sup>-4</sup>	2·10 <sup>-5</sup>	1·10 <sup>-5</sup>	5·10 <sup>-6</sup>	1·10 <sup>-7</sup>	8·10 <sup>-8</sup>



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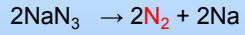
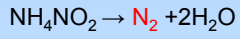
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## 1890's: discovery of noble gases

Density of atmospheric gas  
minus H<sub>2</sub>O, CO<sub>2</sub> and O<sub>2</sub>  
different from



⇒ not pure N<sub>2</sub>

Last step N<sub>2</sub> + Mg → Mg<sub>3</sub>N<sub>2</sub>

left are Ar and other Noble gases of the atmosphere



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$\Delta H^{\circ}_{\text{diss}} / \text{kJ} \cdot \text{mol}^{-1}$

- N<sub>2</sub> 945
- O<sub>2</sub> 495
- F<sub>2</sub> 159
- Cl<sub>2</sub> 242
- H<sub>2</sub> 436

	≡	=	-
CC	810	600	350
CN	850	620	240
CO	1050	700	360
NN	945	400	160

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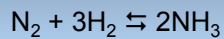
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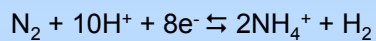
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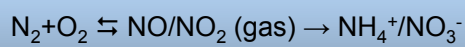
## Nitrogen fixation



metal oxide catalyst gas (400 °C, 100+ atm)



nitrogenases gas/sol (10 °C, 0.8 atm)



lightening gas (high energy, 0.8/0.2 atm)

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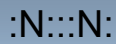
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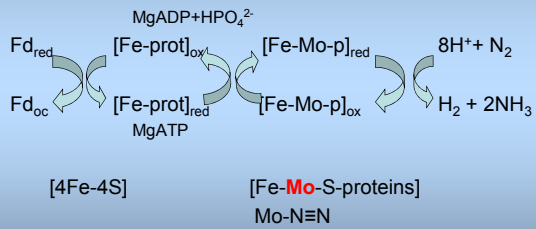
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### Nitrogen fixation by bacteria



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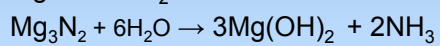
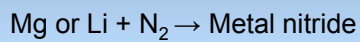
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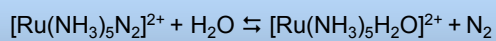
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### Nitrogen reactions



1960's:



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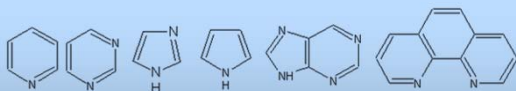
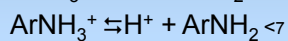
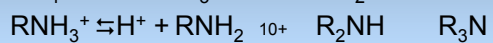
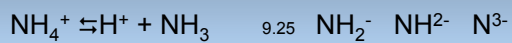
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### Amines



.....etc

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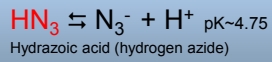
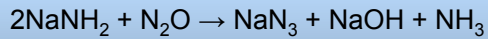
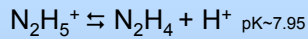
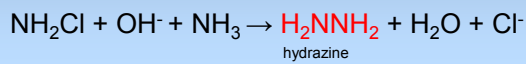
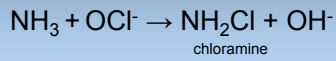
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## N - H



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## N - O

$\text{N}_2\text{O}$	$\text{NH}_4\text{NO}_3$	laugh	$\text{N}=\text{N}=\text{O}$	nitrous oxide
$\text{NO}$	$\text{N}_2 + \text{O}_2$	radical	$\cdot\text{N}=\text{O}$	nitric oxide*
$\text{NO}_2$	$\text{N}_2 + \text{O}_2$	brown	$\text{O}^+ \text{N}=\text{O}$	nitrogen dioxide
$\text{N}_2\text{O}_4$	$2\text{NO}_2$	colour less	$\text{O} \text{N} - \text{N} \text{O}$	dinitrogen tetraoxide
$\text{N}_2\text{O}_3$	$\text{HNO}_2$	blue s <sup>#</sup>	$\text{O} \text{N} - \text{N} \text{O}$	dinitrogen trioxide
$\text{N}_2\text{O}_5$	$\text{HNO}_3$	colour less	$\text{O} \text{N} - \text{O} - \text{N} \text{O}$	dinitrogen pentaoxide

\*Short living signal molecule causing dilation of blood vessels

<sup>#</sup>unstable, dissociates into NO and NO<sub>2</sub> above mp -100

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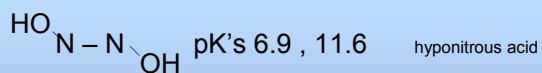
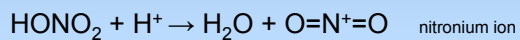
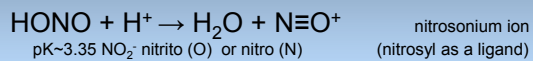
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## Acids



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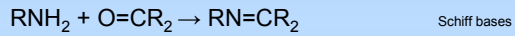
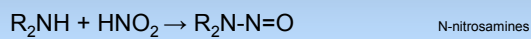
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## Other N functions



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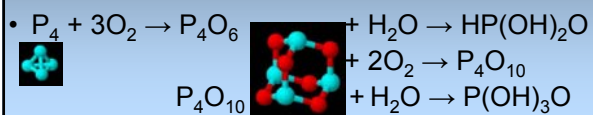
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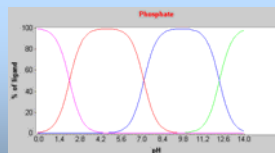
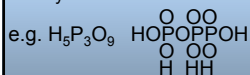
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## P-O-H



$\text{H}_x\text{P}_y\text{O}_z$ : P tetrahedral!



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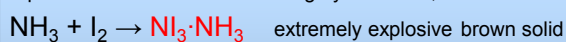
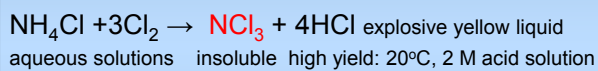
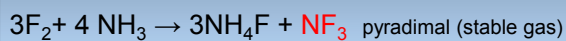
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## N – halides



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## Halides

- $2P + 3Cl_2 \rightarrow PCl_3$  stable liquid: chlorinating agent
- $P + xsCl_2 \rightarrow PCl_5$  :  $[PCl_4][PCl_6]_s \rightarrow PCl_5 g$
- $[PBr_4]Br$
- $AsCl_3 l$   $SbCl_3 s$   $BiCl_3 s$

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## Trihydrides

	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	BiH <sub>3</sub>
Name Systematic	Ammonia (azane)	phosphine phosphane	arsine arsane	stibine stibane	Bismuthane
Bp °C	-34.5	-87.5	-62.4	-18.4	
Dipol moment	1.47	0.57	0.2	0.12	
ligand	medium, strong	soft, weak	soft, more weak	soft, weaker	soft, very weak

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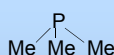
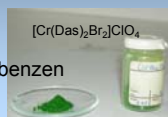
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## Other ligands

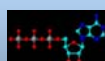


1,2-bis(dimethylarsine)benzen



ATP

cyclic or linear poly phosphates



ROPO<sub>3</sub><sup>2-</sup>

phosphate esters

RPO<sub>3</sub><sup>2-</sup>

phosphonates

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## Analysis

- $\text{NH}_3/\text{NH}_4^+ : + \text{OH}^- \rightarrow \text{NH}_3(\text{g}) + \text{phenolphthalein}$  **red**
- $\text{NO}_2^- : + \text{H}^+ + \text{SC}(\text{NH}_2)_2 \rightarrow \text{SCN}^- + \text{Fe}^{3+}$  **red**
- $\text{NO}_3^- : + \text{Zn} + \text{H}^+ \rightarrow \text{NH}_4^+ \rightarrow \text{phenolphthalein}$  **red**
  
- $\text{H}_x\text{PO}_4^{(3-x)-} : (\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  **yellow ppt**
- $\text{H}_x\text{AsO}_4^{(3-x)-} : \text{As}_2\text{S}_3$  **yellow ppt** in acid
- $\text{Sb}(\text{OH})_6^- : \text{Sb}_2\text{S}_3$  **orange ppt** in acid

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