5. Nitrogen Group

Content

Group 15 or VA

7 N	*1772*
15 P	*1669*
33 As	*antiquity*
51 Sb	*antiquity*
83 Bi	*1753*
115 Mc	*2003*

„Penteles“

5.1 Occurrence

Except Phosphorus all Penteles also Occur Elementary

<u>Nitrogen (nitrogenium)</u>	N_2 (78.1% in air)
Latin: lye salt	$NaNO_3$ Chile saltpetre
	KNO_3 Saltpetre
<u>Phosphorus (phosphoros)</u>	$Ca_5(PO_4)_3(OH,F)$ Apatite
Greek: light carrier	$Ca_3(PO_4)_2$ Phosphorite
	$Fe_3(PO_4)_2 \cdot 8H_2O$ Vivianite
<u>Arsenic (arsenikos)</u>	FeAsS Arsenopyrite
Greek: male	As_4S_4 Realgar
	As_4S_3 Bright yellow
<u>Antimony (antimonium)</u>	Sb native
Stibium = latin: eye cosmetics	Sb_2S_3 gray spear gloss
<u>Bismuth (bismutum)</u>	Bi native
German: Wismut “in the meadows”	Bi_2S_3

5.2 Group Properties

Whereas Nitrogen Exhibits the Typical Properties of A Non-Metal, Bismuth Is Solely Metallic

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
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]$4f^{14}$ $5d^{10} 6s^2 6p^3$
Electronegativity	3.0	2.1	2.2	1.8	1.7
Ionisation energy [eV]	14.5	11.0	9.8	8.6	7.3
Electronic affinity [eV]	-0.3	0.6	0.7	0.6	> 0.7
Character of oxides	acidic	acidic	amphoteric	amphoteric	alkaline
Oxidation states			-3, ……, +5		

With increasing atomic number, the oxidation state +3 becomes more stable, whilst the oxidation state +5 becomes instable. In conclusion does this behaviour lead to a higher oxidising potential

5.3 Physical Properties

Only Nitrogen Is a Gas, the Other Penteles are solids

	N	P	As	Sb	Bi
Colour (non-metallic)	transparent	white	yellow	yellow	-
Colour (metallic)	-	black	steel grey	silvery white	silvery white
Melting point [° C]	-210	44	817	630	271
Boiling point [° C]	-196	280	616	1635	1580
Conductivity [µΩ·cm]	-	10^{17}	33	42	120

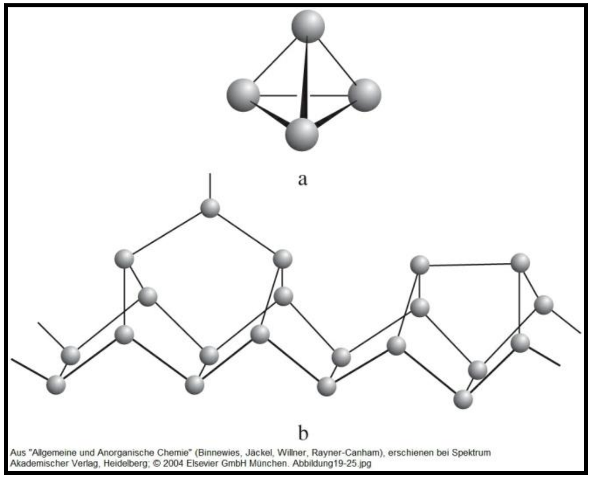
<u>Polymorphism of P, As and Sb</u>

a) Tetrahedral P_4, As_4, Sb_4

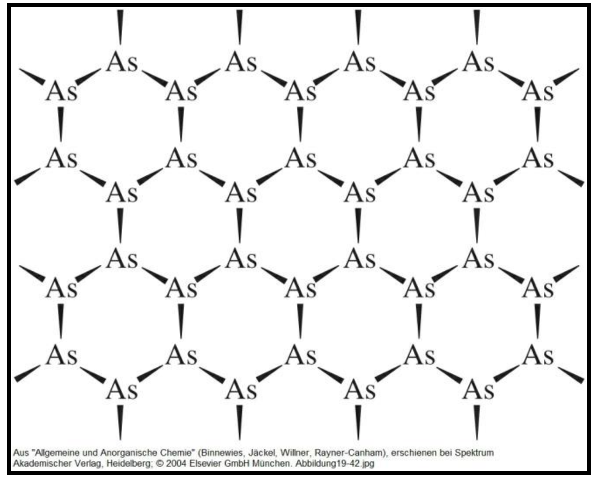
b) Rhombohedral P, As (black)

c) Amorphous P (red), As (black)

d) Rhombohedral P, As, Sb (grey)



d) Rhombohedral P, As, Sb (grey)



5.4 Synthesis

Technical Methods

Nitrogen

Linde-Process $\rightarrow$ (s.a. general chemistry) at the laboratory: $NH_4NO_2 \rightarrow 2\ H_2O + N_2$

$2\ NaN_3 \rightarrow 2\ Na + 3\ N_2$

Phosphorus

$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow 6\ CaSiO_3$ (slag) $+ 10\ CO\uparrow + P_4\uparrow$

Arsenic

Thermal treatment of arsenopyrite: $FeAsS \rightarrow FeS + As$

Antimony

Precipitation process: $Sb_2S_3 + 3\ Fe \rightarrow 3\ FeS + 2\ Sb$

Reduct. roasting process: $Sb_2S_3 + 5\ O_2 \rightarrow Sb_2O_4 + 3\ SO_2\uparrow$ $Sb_2O_4 + 4\ C \rightarrow 4\ CO\uparrow + 2\ Sb$

Bismuth

Reduction of oxidic ores: $Bi_2O_3 + 3\ C \rightarrow 3\ CO\uparrow + 2\ Bi$

5.5 Chemical Behaviour

Nitrogen

- Highly inert, due to extremely stable N≡N bonds: $N_2 \rightleftharpoons 2\ N$: $\Delta H^0 = -946$ kJ/mol
  That is why the earth's crust is made up mostly of oxidic but not nitric minerals
  Exception: Si_2N_2O sinoite (impactmineral)
- N_2 is isoelectronic to C≡O, $N{\equiv}O^+$, and $C{\equiv}N^-$ and also forms complexes with transition metals: $[Ru^{II}(H_2O)(NH_3)_5]^{2+} + N_2 \rightarrow [Ru^{II}(N_2)(NH_3)_5]^{2+} + H_2O$

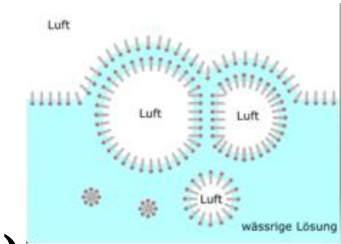
Phosphorus

- White phosphorus is highly reactive and pyrophoric in air: $P_4 + 3\ O_2 \rightarrow P_4O_6 + h\nu$
- All other modifications of phosphorus are by far less reactive
- The bonding energy of P-P bonds is significantly higher than those of N-N or As-As bonds $\Rightarrow$ P tends to form chains and/or cyclic systems

Arsenic, Antimony and Bismuth

- Thermodynamically stable are the grey metallic modifications of As and Sb. The non-metallic modifications are transformed into the metallic ones at room temperature, already
- As, Sb and Bi are stable in air at room temperature. Only upon heating they combust and form the trioxides Me_2O_3

5.6 Application

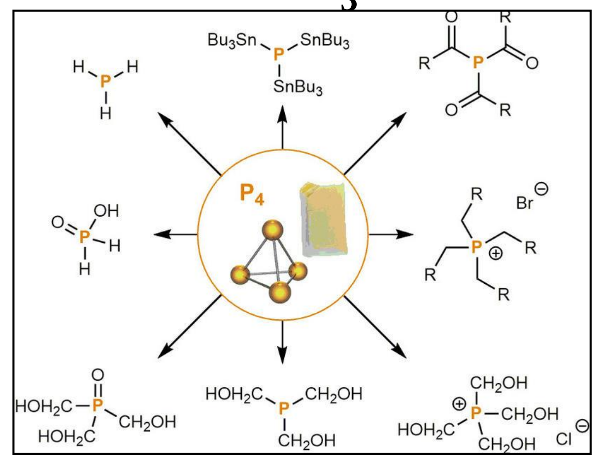


Nitrogen

- Inert gas for synthetic chemistry
- Fertilizer: ammonium compounds and nitrates
- Frothing agents: cream, whipped egg white
- AlN-GaN-InN in UV-A and blue emitting light diodes (210-520 nm)

Phosphorus

- Matches: striking surface P_{red} + glass powder, matchstick head $KClO_3$ + S
- Fertilizer: phosphates
- Pesticides
- White phosphor as precursor material

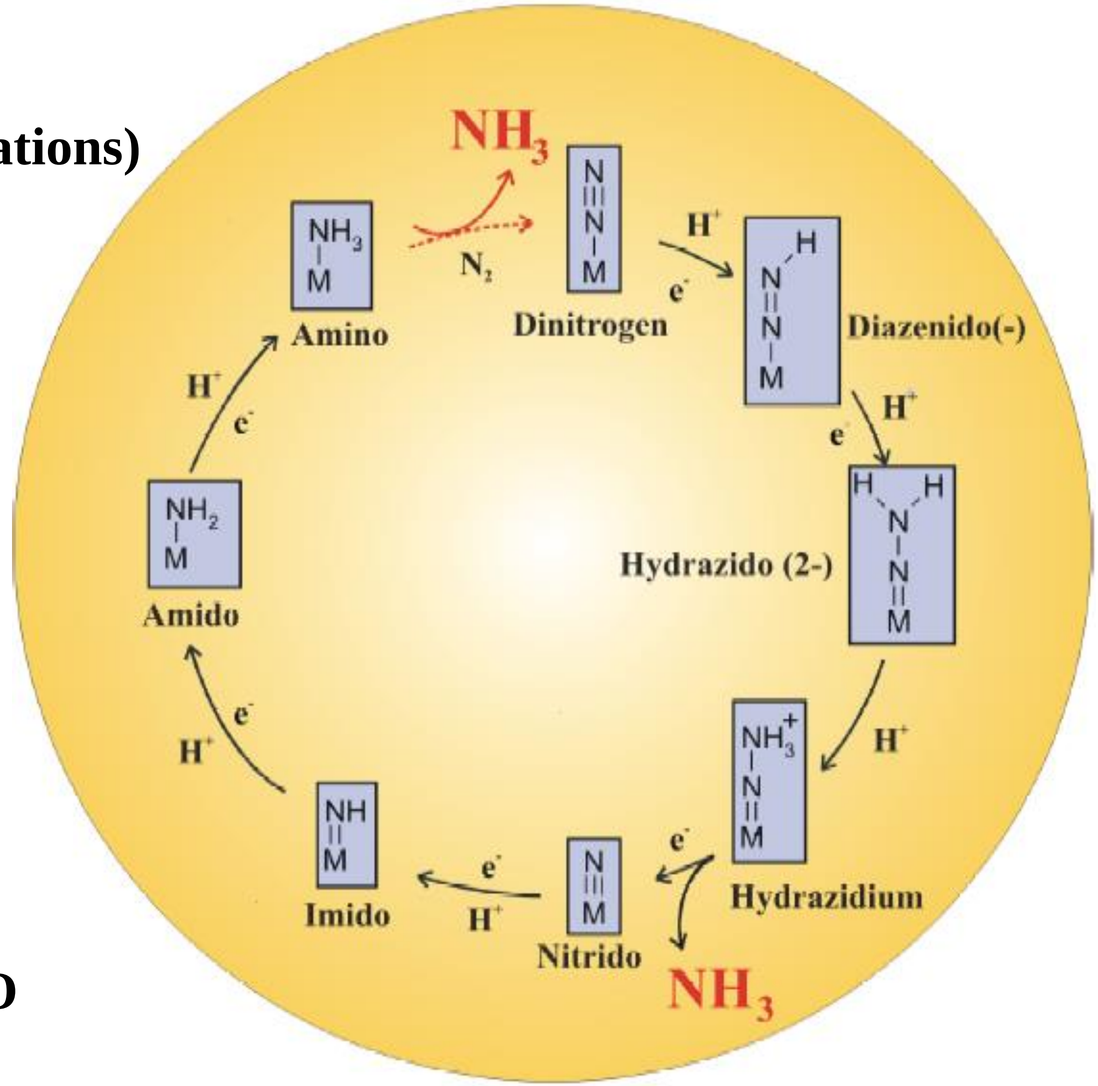


Arsenic, Antimony and Bismuth

- GaAs/GaSb solar cells
- GaAs in IR-A and red emitting light diodes
- As component in low-melting alloys, e.g. Wood's metal (50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd) ⇒ melting point about 70 °C

5.7 Chemistry of Elemental Nitrogen

Reactions with Nitrogen



a) Fixation of nitrogen (→ presentations)

$N^{0}_2 \rightarrow N^{-III}H_3$

b) As complexing agent

Mo, Fe and Ru complexes →

c) Formation of nitrides

$3\ Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

Nitrides	Imides	Amides
N^{3-}	NH^{2-}	NH_2^-

↓ hydrolysis with H_2O

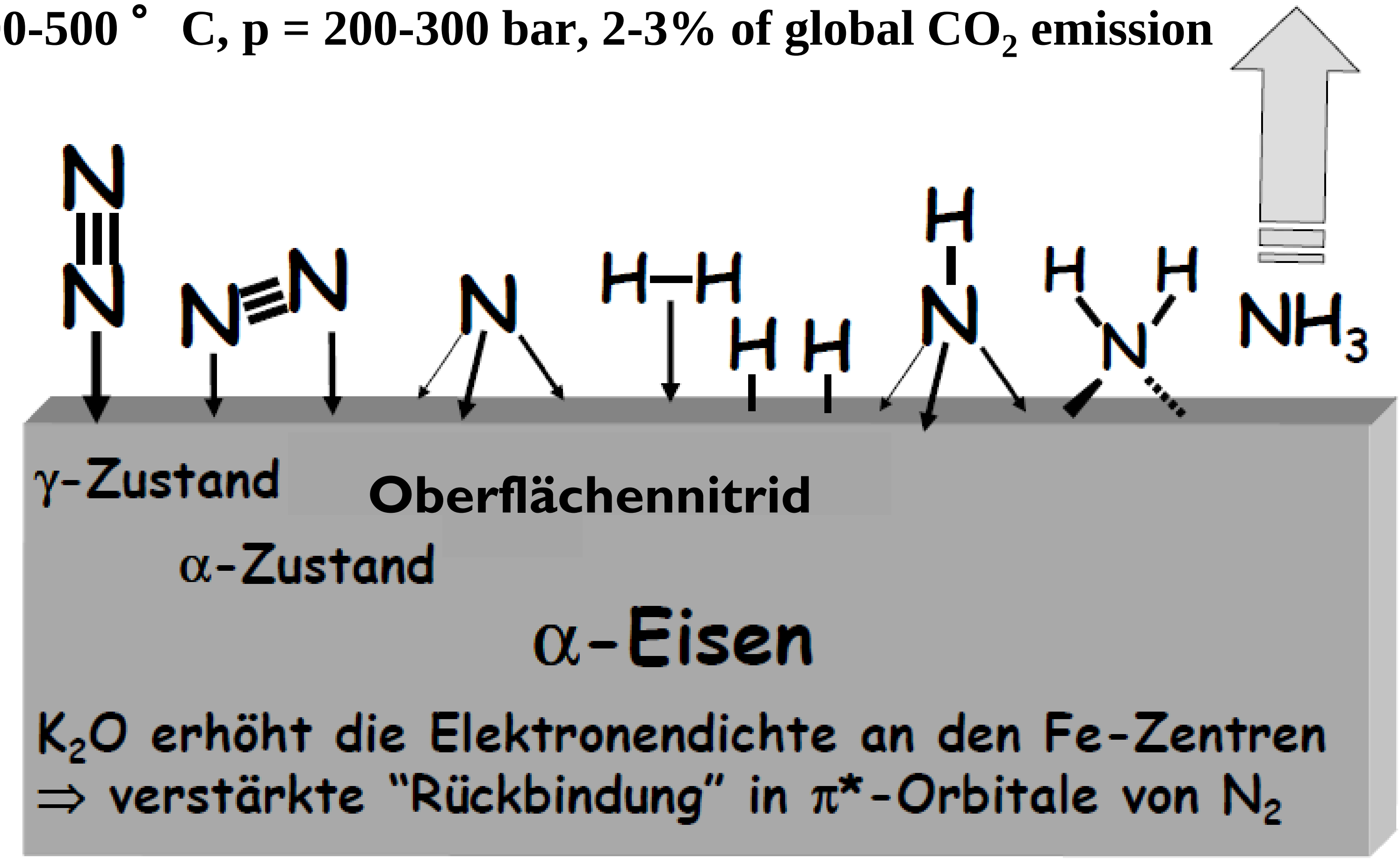
NH_3

5.7 Chemistry of Elemental Nitrogen

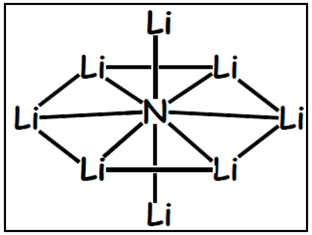
Reactions with Nitrogen

d) Ammonia synthesis (Haber-Bosch-Process): α-Fe + K_2O + Al_2O_3 + CaO

T = 400-500 °C, p = 200-300 bar, 2-3% of global CO_2 emission



5.7 Chemistry of Elemental Nitrogen



1. Ionic (salt-like) Nitrides

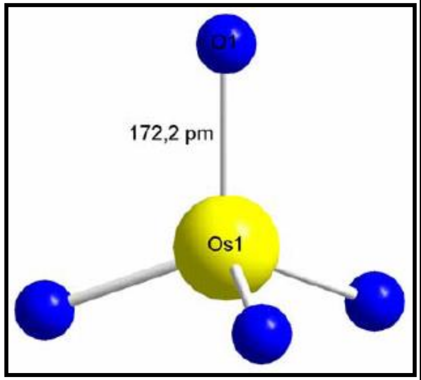
Alkaline metals Li_3N

Alkaline earth metals M_3N_2 (M = Be – Ba)

Group IB, IIB M_3N (M =Cu, Ag) and M_3N_2 (M = Zn, Cd, Hg)

2. Covalent (molecular) Nitrides

With non-metals: S_4N_4, S_2N_2, P_3N_5, $(CN)_2$



3. Complexes with the Nitrido, N^{3-}, Ligand

With transition metals in high oxidation states

$Os^{VIII}O_4 + NH_3 + OH^- \rightarrow [Os^{VIII}O_3N^-] + 2\ H_2O$

4. Nitrides with diamond-like structure (III-V semi-conductors)

With elements of the 3rd main group: BN, AlN, GaN, InN, BiN

Synthesis from gas phase: $NH_3(g) + Ga(CH_3)_3(g) \rightarrow GaN(s) + 3\ CH_4(g)$

5.7 Chemistry of Elemental Nitrogen

5. Metallic Nitrides (Intercalation compounds)

- The small nitride anions can occupy interstices within the hexagonal or cubic close packages of the metal lattices
- Typical compositions are (roughly) MN, M_2N, M_4N
- Analogous to that do carbides and borides exist

Nitride	T_m [° C]	Mohs Hardness	Carbide	T_m [° C]	Mohs Hardness
TiN	3220	8-9	TiC	3410	8-9
ZrN	3250	8	ZrC	3800	8-9
TaN	3360		TaC	4150	

(TaC and HfC possess the two highest melting points known)

Properties	Applications
• Great hardness	⇒ nitration of metallic materials
• Chemically inert	by heating in NH_3 atmosphere
• Conductive	through salt baths (cyanates)
• Opaque	through treatment in a plasma (glow discharge in N_2 atmosphere)

5.8 Compounds Made of Nitrogen and Hydrogen

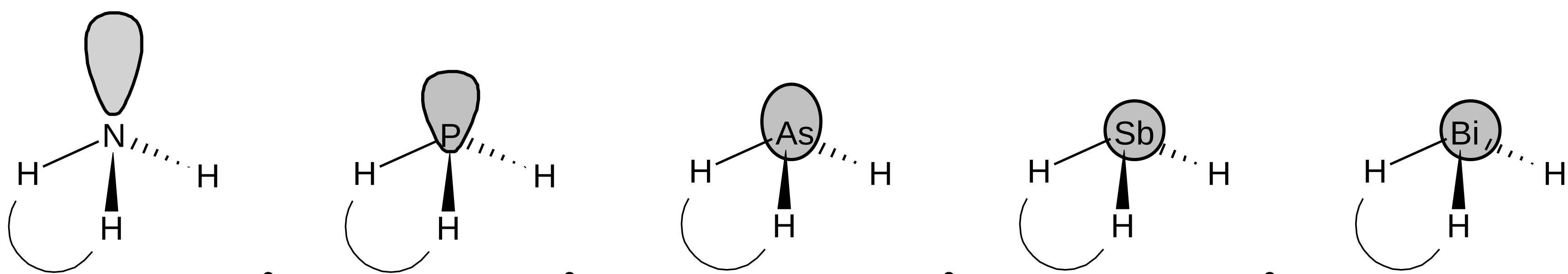
At Room Temperature Ammonia, NH_3, Hydrazine, N_2H_4, and Hydrazoic Acid, HN_3 are Stable. At Low Temperatures even Diimine N_2H_2 and Tetrazene N_4H_4 can be Isolated

<u>NH_3 Ammonia</u>

Synthesis

- **Nature: N_2 assimilation by micro organisms (→ presentations)**
- **Technical: $N_2 + 3\ H_2 \rightarrow 2\ NH_3$ Haber-Bosch-Process (→ presentations)**
- **Laboratory: $NH_4Cl \xrightarrow{>350\ °C} NH_3 + HCl \xrightarrow{<350\ °C} NH_4Cl$ (apparent sublimation)**

Structure

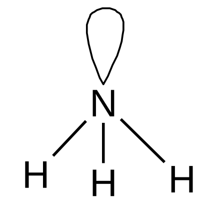


~90° **107.2°** **93°** **91.8°** **91°**

s-Character of lone pair →

5.8 Compounds Made of Nitrogen and Hydrogen

Properties of Ammonia NH_3



- Polar solvents (T_m = -78 °C, T_b = -33 °C), which dissolves alkaline metals and solvates electrons: $NH_3(l) + Na(s) \rightarrow [Na(NH_3)_n]^+ + [e \cdot (NH_3)_m]^-$ (blue)

- Readily soluble in water, because of the formation of hydrogen bonds

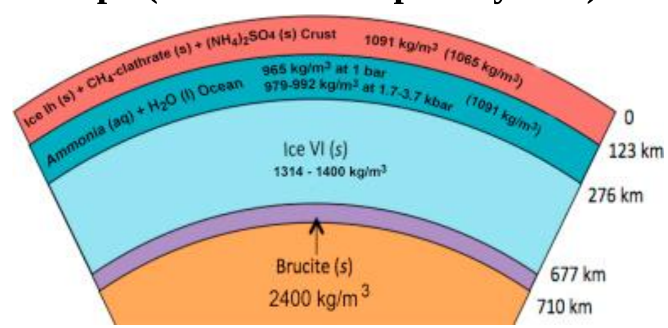
- Auto protolysis: $2\ NH_3(l) \rightleftharpoons NH_2^- + NH_4^+$ $K = 1.0 \cdot 10^{-30}$

- Weak base in water
  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $K = 1.8 \cdot 10^{-5}$

- Weak acid
  $2\ NH_3(l) + 2\ Li(s) \rightleftharpoons 2\ Li^+(aq) + 2\ NH_2^-(aq) + H_2$

- Decomposition
  - Thermal $2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$
  - Oxidation $4\ NH_3 + 3\ O_2(g) \rightarrow 2\ N_2 + 6\ H_2O(l)$

Europa (Ice moon in Jupiter system)



5.8 Compounds Made of Nitrogen and Hydrogen

Hydrazine, N_2H_4, (transparent, greasy liquid, $T_m = 2.0$ °C, $T_b = 113$ °C)

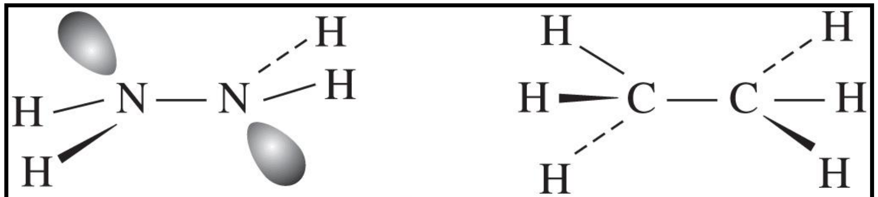
Synthesis

a) Raschig-Synthesis
1. $NaOCl + NH_3 \rightarrow NaOH + NH_2Cl$ (chloramine)
2. $NH_2Cl + NaOH + NH_3 \rightarrow NaCl + H_2O + N_2H_4$

b) Bayer-Process
1. $NaOCl + 2\ NH_3 + 2\ CH_3\text{-}CO\text{-}CH_3 \rightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + NaCl + 3\ H_2O$
2. $(CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 2\ H_2O \rightarrow N_2H_4 + 2\ CH_3\text{-}CO\text{-}CH_3$

Properties and structure

- Base: $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$
  $N_2H_5^+ + H_2O \rightarrow N_2H_6^{2+} + OH^-$
- Strong reducing agent:
  $N_2H_4 + 2\ I_2 \rightarrow 4\ HI + N_2$
  $N_2H_4 + 2\ Cu^{2+} \rightarrow 2\ Cu + 4\ H^+ + N_2$
- Thermal decomposition: $3\ N_2H_4 \rightarrow 4\ NH_3 + N_2$



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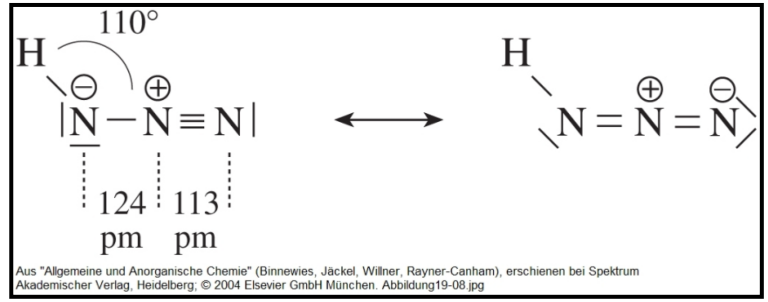
Applications

- Rocket propellant in the form of dimethyl hydrazine $(CH_3)_2N\text{-}NH_2$
- Anti corrosion agent in water circulation systems $\Rightarrow$ formation of magnetite (Fe_3O_4)

5.8 Compounds Made of Nitrogen and Hydrogen

Hydrazoic Acid, HN_3 (transparent, explosive liquid, T_b = 36 °C)



Synthesis

$NaN^{-III}H_2 + N^{+I}{}_2O \rightarrow NaN_3 + H_2O$

$NaN_3 + H^+ \rightarrow HN_3 + Na^+$

Properties and structure

- Highly explosive: $2\ HN_3(l) \rightarrow H_2(g) + 3\ N_2(g)$
- Weak acid: $HN_3 + H_2O \rightarrow N_3^- + H_3O^+$ (pK_s = 4.55)
- Strong oxidising agent: $Zn + HN_3 + 2\ H^+ \rightarrow Zn^{2+} + NH_3 + N_2$
- N_3^- is isoelectronic to CO_2
- Photolysis in water: $2\ N_3^- \rightarrow 3\ N_2\uparrow + 2\ e^-$ $2\ H^+ + 2\ OH^- + 2\ e^- \rightarrow H_2\uparrow + 2\ OH^-$

Application of the salts (azides)

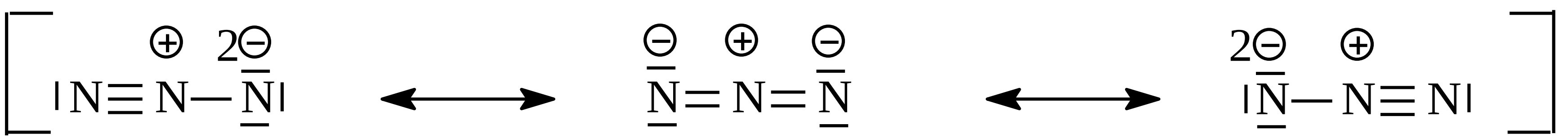
- Starting substance for azide chemistry
- Detonator, e.g. $Pb(N_3)_2$

5.8 Compounds Made of Nitrogen and Hydrogen

Azides MeN_3

Ionic azides

- **Examples: NaN_3, $Ba(N_3)_2$**
- **Stable because of resonance structures**

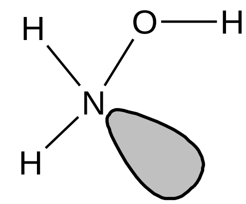


Covalent azides

- **Examples:** AgN_3, $Pb(N_3)_2$ **(schwerlöslich)**
- **Chlorineazides:** $N_3^- + Cl_2 \rightarrow Cl\text{-}N_3 + Cl^-$
- **Iodineazides:** $AgN_3 + I_2 \rightarrow I\text{-}N_3 + AgI$
- **Explosive, since the azide ion is polarised by the covalent bond (symmetrical distribution of electrons in the linear azide anion is disturbed)**

5.9 Nitrogen Compounds with Oxygen

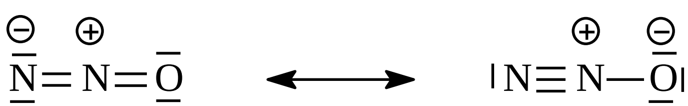
Hydroxylamine, NH_2OH (Transparent Crystals, T_m = 32 ° C)

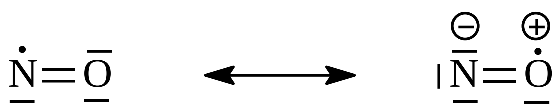


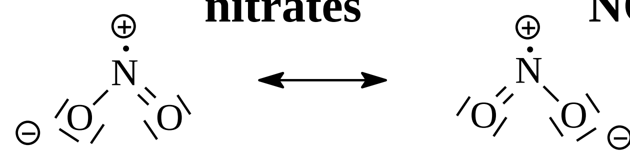
Synthesis: 2 $N^{+II}O(g) + 3\ H_2(g) \rightarrow 2\ N^{-I}H_2OH$ (Pt catalyst)
Thermal decomposition: 3 $N^{-I}H_2OH(l) \rightarrow N^{0}{}_2(g) + N^{-III}H_3(g) + 3\ H_2O(l)$
Application: NH_2OH + cyclohexanone → oxim → ε-caprolactam → polyamides

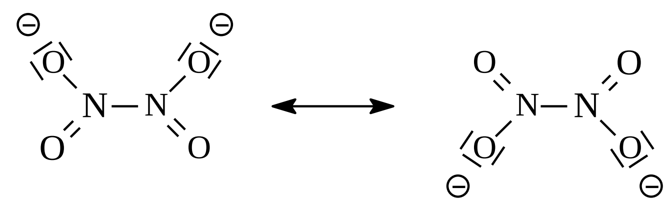
Nitrogen Oxides and Oxo Acids

Oxidation state	Oxide	Acids	Salt	Anion
+I	N_2O	$H_2N_2O_2$	hyponitrites	$N_2O_2^{2-}$
+II	NO, N_2O_2			
+III	N_2O_3	HNO_2	nitrites	NO_2^-
+IV	NO_2, N_2O_4			
+V	N_2O_5	HNO_3	nitrates	NO_3^-









5.9 Exkursion: The Autocatalyst

Heterogeneous Catalysis

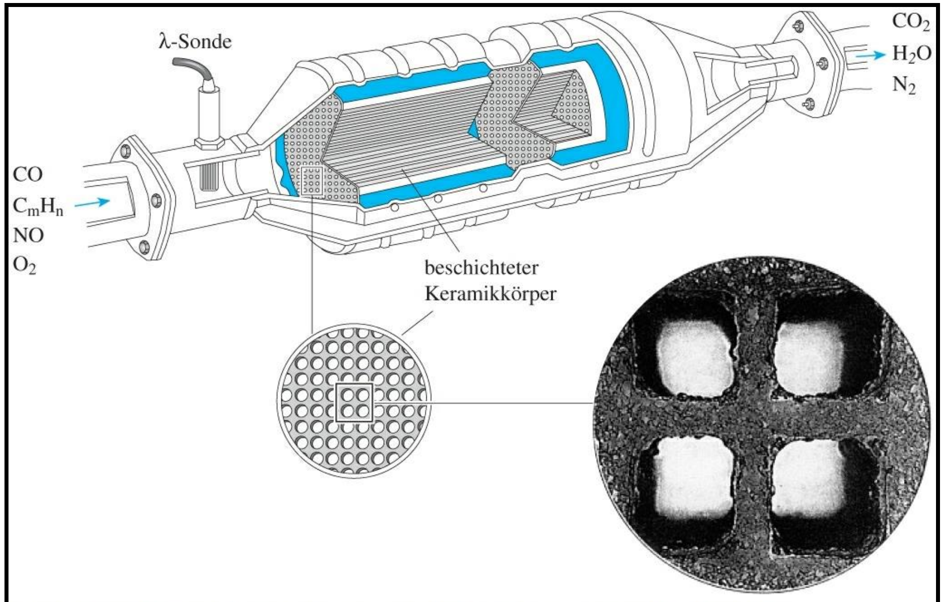
Autocatalyst Pd/Pt pigment

On ceramic substrate

$2\ CO + O_2 \rightarrow 2\ CO_2$

$C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$



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Regulation of oxygen by CeO_2

$2\ CeO_2 \rightleftarrows Ce_2O_3 + ½\ O_2$

Combustion of carbon by CeO_2

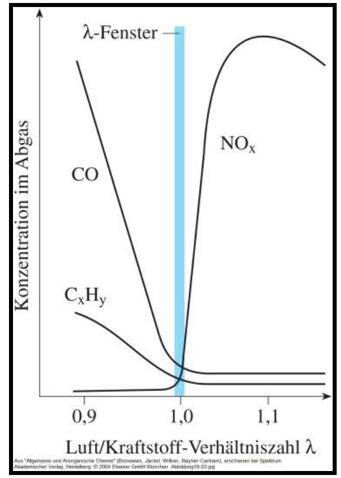
$C + 2\ CeO_2 \rightarrow CO + Ce_2O_3$

(Diesel-powered vehicles, project at Peugeot + Rhodia)

Measurement of oxygen conc. via λ probe

Electrochemical chain in order to measure the O_2 partial pressure within the catalyst

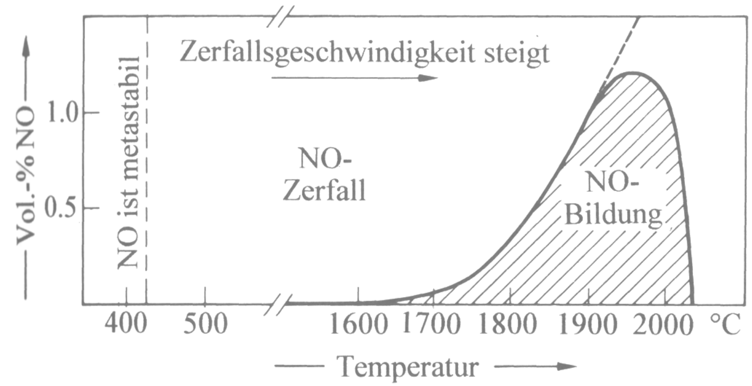
⇒ oxygen ion conductor $ZrO_2:Y^{3+}$



5.9 Nitrogen Compounds with Oxygen

Synthesis, Properties and Importance of the Oxides

Temperature dependence of nitrogen monoxide yields for the synthesis in air



N_2O (nitrous oxide, laughing gas)

Synthesis: $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(l)$

Properties: transparent, sluggish, isoelectronic to CO_2

Medical relevance: anaesthetic

NO, N_2O_2 (nitrogen monoxide)

Synthesis: $N_2 + O_2 \rightarrow 2\ NO$ (lightning bolts + high temperatures)

$3\ Cu(s) + 8\ HNO_3(l) \rightarrow 3\ Cu(NO_3)_2(s) + 2\ NO(g) + 4\ H_2O(l)$

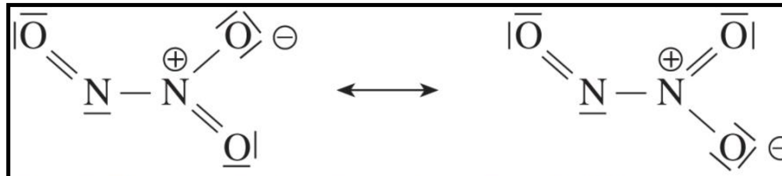
Properties: transparent, radical, highly reactive, ready formation of $|N{\equiv}O|^+$ (nitrosyl cations)

Biological relevance:

- **Relaxes smooth muscle tissue, lowers high blood pressure, triggers uterine contractions and erections, facilitates memory functions and the digestive system (neurotransmitter)**
- **NO sources: nitro glycerine (cardiac drugs), nitrogen monoxide synthase (from Arginine)**

5.9 Nitrogen Compounds with Oxygen

Synthesis, Properties and Importance of the Oxides



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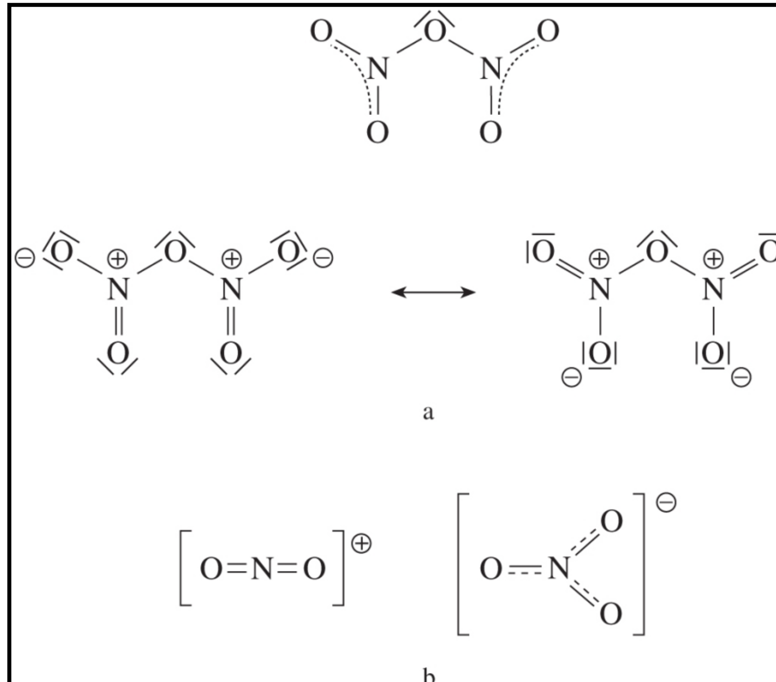
N_2O_3 (dinitrogen trioxide)

Synthesis: $NO(g) + NO_2(g) \rightarrow N_2O_3(l)$ at T < -30 ° C

Properties: $N_2O_3(l) + H_2O(l) \rightarrow 2\ HNO_2(aq)$



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NO_2, N_2O_4 (nitrogen dioxide)

Synthesis: $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H^0 = 57\ kJmol^{-1}$

Properties: brown, radical, acidic oxide, disproportionation into H_2O

$2\ N^{+IV}O_2(g) + H_2O(l) \rightarrow HN^{+III}O_2(aq) + HN^{+V}O_3^-(aq)$

Relevance: formation of ozone in the troposphere (→ fundamental chemistry)

N_2O_5 (dinitrogen pentoxide)

Synthesis: $4\ HNO_3(l) + P_4O_{10} \rightarrow 2\ N_2O_5(g) + 4\ HPO_3$

Properties: anhydride of nitric acid

solid with a formula as following $NO_2^+NO_3^-$ (nitryl nitrate)

5.9 Nitrogen Compounds with Oxygen

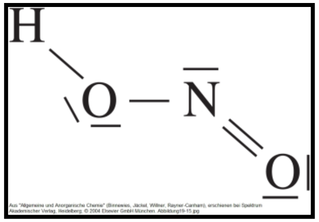
Oxo Acids of Nitrogens

$H_2N_2O_2$ (hyponitrous acid)

Synthesis: $2\ NaNO_2 + 4\ Na + 2\ H_2O \rightarrow\ Na_2N_2O_2 + 4\ NaOH$

Properties: unstable, N_2O is only on paper a anhydride of $H_2N_2O_2$, weak acid

Structure: Only in trans-configuration a acid, salts known in cis- and trans-configuration



HNO_2 (nitrous acid)

Synthesis: $Ba(NO_2)_2 + H_2SO_4 \rightarrow 2\ HNO_2 + BaSO_4\downarrow$

Properties:

- Unstable and disproportionates readily
- Weak oxidising agent: $2\ NO_2^- + 2\ I^- + 4\ H_3O^+ \rightarrow I_2 + 2\ NO\uparrow + 6\ H_2O$
- Reductive agent: $5\ NO_2^- + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ NO_3^- + 2\ Mn^{2+} + 3\ H_2O$

Relevance:

Nitrites as preservatives (nitrite salting mix) $\Rightarrow$ formation of NO

$\Rightarrow$ prevents growth of botulismus bacteria

$\Rightarrow$ hinders oxidation of Fe^{2+} in myoglobin to Fe^{3+} through formation of complexes

5.9 Nitrogen Compounds with Oxygen

Oxo Acids of Nitrogen

HNO_3 (nitric acid)

Synthesis: Ostwald-Process (→ presentations)

$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

$4\ NO_2(g) + 2\ H_2O(l) + O_2(g) \rightarrow 4\ HNO_3(l)$

Properties:

- Decomposition by light: $4\ HNO_3 \rightarrow 4\ NO_2 + 2\ H_2O + O_2$ (storage in brown flasks)
- Strong oxidising agent, which dissolves Cu, Ag and Hg ($E^0 < 0.96$ V), but not Au and Pt
- Thermal decomposition of nitrates:

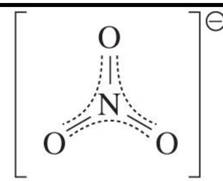
  $2\ KNO_3(s) \rightarrow 2\ KNO_2(s) + O_2(g)$

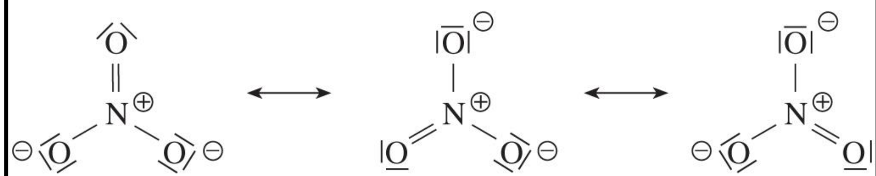
  $Pb(NO_3)_2(s) \rightarrow PbO(s) + 2\ NO_2(g) + ½\ O_2(g)$

Relevance:

- Annual production ca. 30 mio. t
- For the synthesis of fertilizers → NH_4NO_3
- For the synthesis of explosives in the form of nitration acid

  $HNO_3 + 2\ H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2\ HSO_4^-$





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5.10 Nitrogen Compounds with Halides

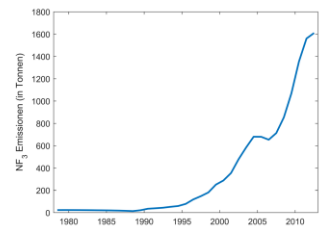
Binary Compounds of Nitrogen and Halides

Compound	F	Cl	Br	I
NX_3 Nitrogen trihalide	NF_3 transparent gas stable	NCl_3 yellow oil explosive	NBr_3 red crystals explosive	$NI_3 \cdot NH_3$ black crystals explosive
$X_2N\text{-}NX_2$ Dinitrogen tetrahalides	N_2F_4 transparent gas stable	-	-	-
X-N=N-X Dinitrogen dihalides	trans-N_2F_2 cis-N_2F_2 transparent gas	-	-	-
N=N=N-X Halide azide	N_3F green/yellow gas	N_3Cl transparent gas	N_3Br orange/red liquid	N_3I transparent solid

Greenhouse gas NF_3

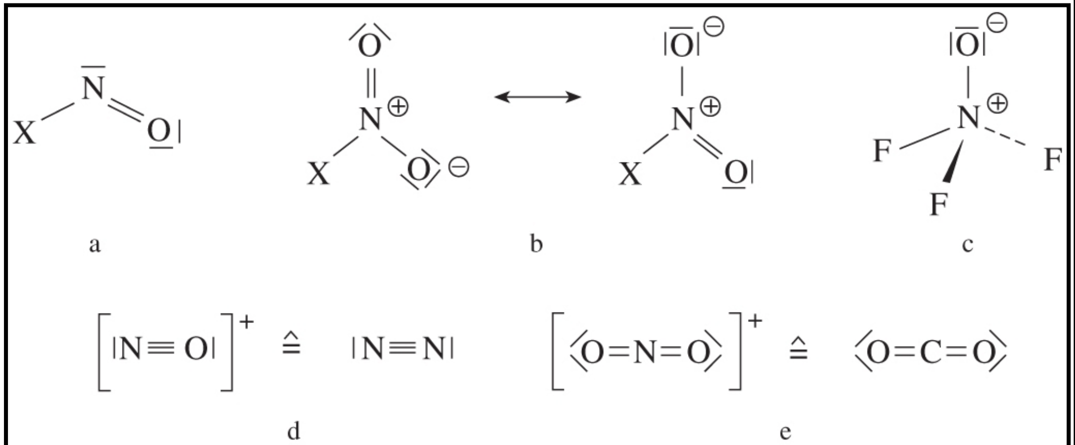
Synthesis via Cu-catalyst: $4\ NH_3 + 3\ F_2 \rightarrow NF_3$

Application: In LCD & Solar cell industry to remove SiO_2 from PECVD equipment after coating experiments



5.10 Nitrogen Compounds with Halides

Nitrogen Oxo Halides



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Nitrogen oxo trifluoride

Synthesis: $2\ NF_3(g) + O_2(g) \rightarrow 2\ ONF_3(g)$
(in electrical discharges)

Nitrosyl halides NOX (X = F, Cl, Br)

Synthesis: $2\ NO + X_2 \rightleftharpoons 2\ NOX$

Properties:

- $NOX + H_2O \rightarrow HNO_2 + HX$
- $NOCl(g) + SbCl_5(l) \rightarrow NO^+[SbCl_6]^-(s)$

Nitryl halides NO_2X (X = F, Cl, Br)

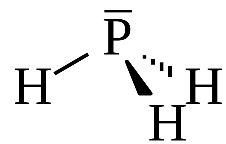
Synthesis: $HNO_3(l) + HSO_3Cl(l) \rightarrow NO_2Cl(g) + H_2SO_4(l)$
$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$

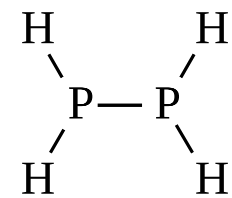
Properties:

- $NO_2F(g) + BF_3(g) \rightarrow NO_2^+[BF_4]^-(s)$

5.11 Phosphorus/Hydrogen Compounds

Phosphan PH_3 and Diphosphan P_2H_4





Synthesis

1. $6\ Ca + P_4 \rightarrow 2\ Ca_3P_2$ (+ Ca_2P_2 as side product)
2. $Ca_3P_2(s) + 3\ H_2O \rightarrow 3\ Ca(OH)_2(s) + 2\ PH_3(g)$

   $Ca_2P_2(s) + 2\ H_2O \rightarrow 2\ Ca(OH)_2(s) + P_2H_4(g)$ "topotactic reaction"

Properties of PH_3

- Transparent, highly toxic gas smelling like garlic (TLV value = 0.15 mg/m^3)
- Dissociated in liquid state $\Rightarrow T_b = -88\ °C$
- Almost insoluble in water
- Stronger reductive behavior but weaker alkaline character than NH_3

Application of PH_3

- Doping of semi-conducting silicon
- Synthesis of (Al,In,Ga)P $\Rightarrow$ red emitting LEDs
- As rodenticide (against rats and voles), whereas the toxic PH_3 is formed from Zn, Ca_3P_2 and moisture

5.12 Phosphorus Oxides

Important are P_4O_6 and P_4O_{10}

Synthesis

- $P_4(s) + 3\ O_2(g) \rightarrow P_4O_6(s)$ $\Delta H^0 = -2270$ kJ/mol
- $P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$ $\Delta H^0 = -3010$ kJ/mol

Propeties

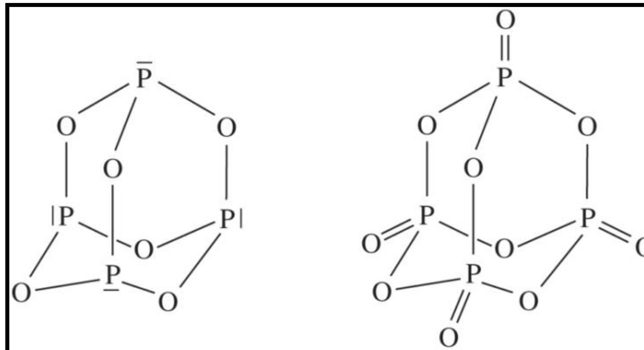
- Phosphorus oxide reacts violently with water (application as drying agents)

  $P_4O_6(s) + 6\ H_2O(l) \rightarrow 4\ H_2PHO_3(l)$ (phosphonic acid)

  $P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(l)$ (ortho-phosphoric acid) $\Delta H^0 = -378$ kJ/mol
- In contrary to N_2O_5, P_4O_{10} is no oxidising agent

Structures

- Derived from P_4
- Adamant-like cages
- P_4S_{10} is isostructural to P_4O_{10}



P_4O_6 P_4O_{10}

5.13 Oxo Acids of Phosphorus

Phosphoric Acid and Phosphates

Synthesis of phosphoric acid

Technical: Apatite $\rightarrow P_4(s) \rightarrow P_4O_{10}(s) \rightarrow H_3PO_4(l)$

Laboratory: $Ca_3(PO_4)_2(s) + 3\ H_2SO_4(aq) \rightarrow 3\ CaSO_4(s) + 2\ H_3PO_4(aq)$

Properties of phosphoric acid

- 100% phosphoric acid: transparent, hard, odorless, crystals, readily soluble in water (T_m = 42.3 °C)
- In trade, 85% solution (T_m = 21.1 °C)
- Tipple base, medium-strength acid, that forms three kinds of salts:

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ $pK_s(1) = 2.12$

(primary phosphates: dihydrogen phosphates)

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ $pK_s(2) = 7.21$

(secondary phosphates: hydrogen phosphates)

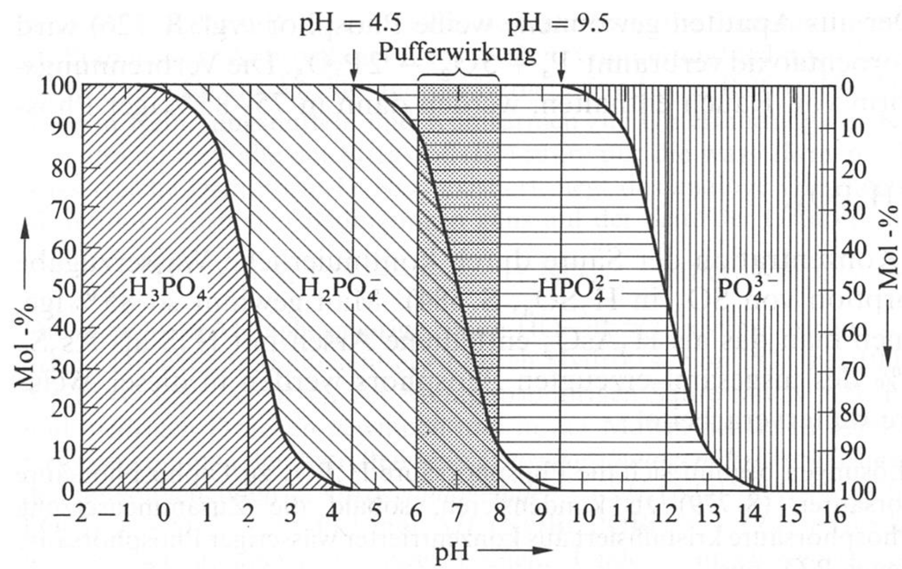
$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$ $pK_s(3) = 12.33$

(tertiary phosphates: phosphates)

5.13 Oxo Acids of Phosphorus

Application of Phosphates

Dependance of ionic concentration on pH-value in a phosphoric acid-(phosphate) solution



Primary phosphates react slightly acidic:

- **Phosphating of steel surfaces**
- **In baking soda: $Ca(H_2PO_4)_2$**
- **As double super phosphate fertilizer:**
  $Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow 3\ Ca(H_2PO_4)_2$

Secondary phosphates react slightly alkaline:

- **Emulsifier and stabilizer in food and feeding stuff: Na_2HPO_4**
- **In blood as a buffer: $H_2PO_4^-/HPO_4^{2-}$**

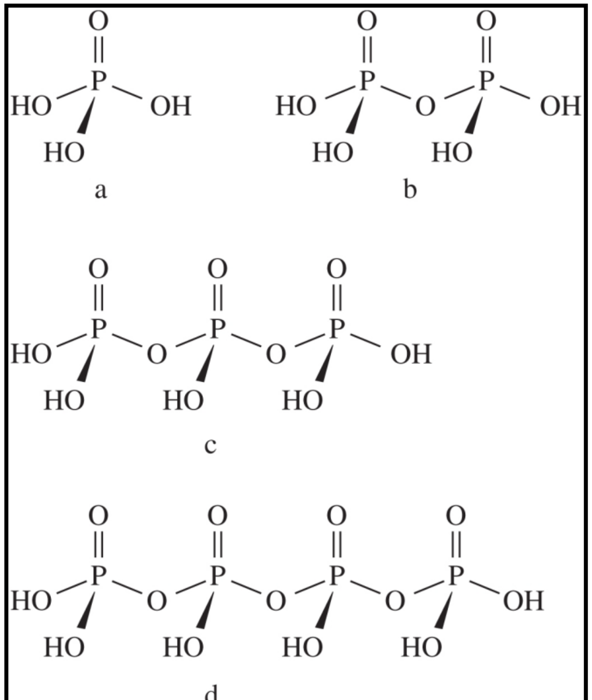
Tertiary phosphates react highly alkaline:

- **Part of washing liquids for dish washers: $Na_3PO_4 \cdot 12H_2O$**
- **As phosphors: $LaPO_4$:Ce, $LaPO_4$:Ce,Tb, $LaPO_4$:Pr, YPO_4:Ce, YPO_4:Bi, $LuPO_4$:Ce, …**

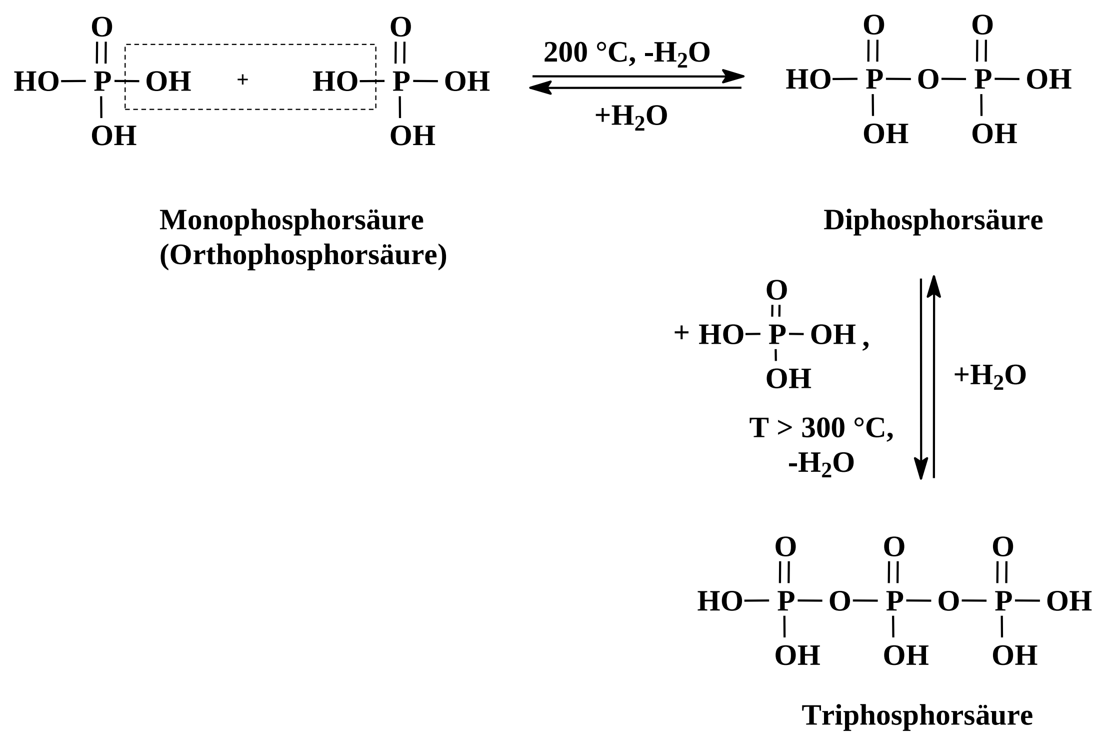
5.13 Oxo Acids of Phosphorus

Condensed Phosphoric Acids and Their Salts

Di- (b), tri-(c), and tetra phosphoric acid (d) form upon heating of ortho-H_3PO_4 (a) at about 200 ° C in a highly exothermic reaction:



Formation of di and triphosphoric acid

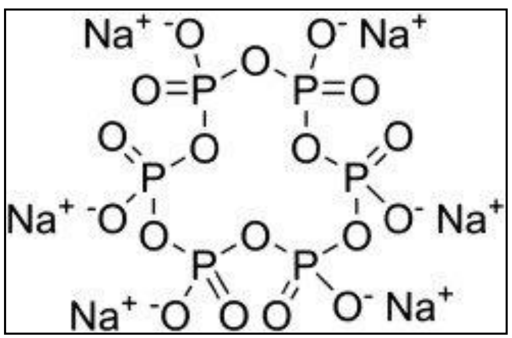


5.13 Oxo Acids of Phosphorus

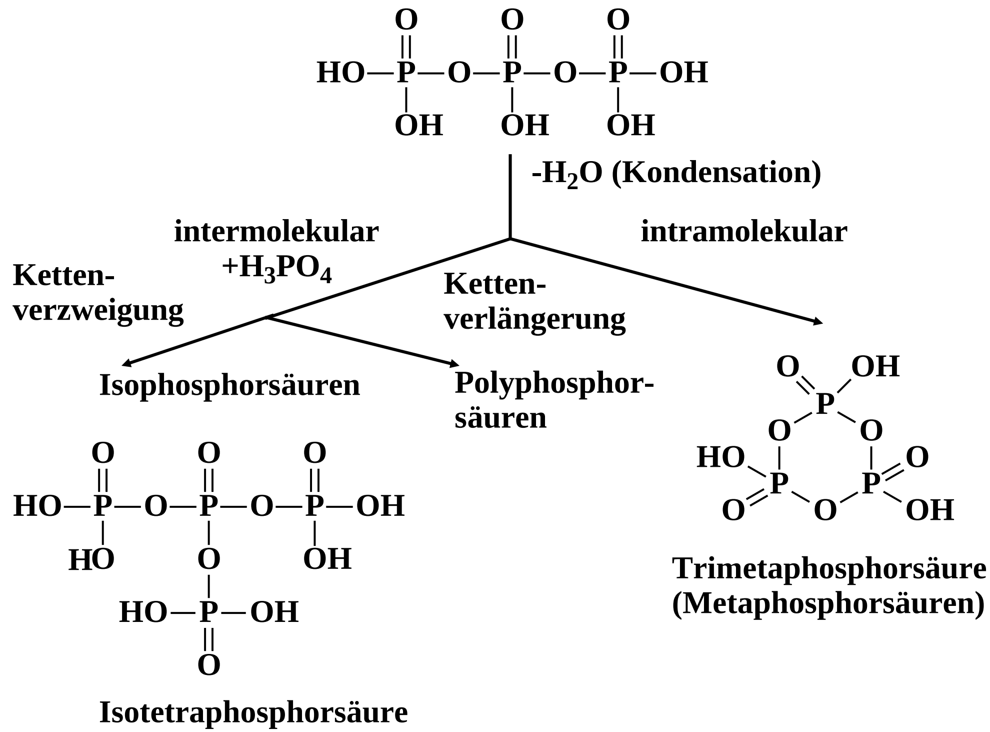
Condensed Phosphoric Acids and Their Salts

Heating of ortho-H_3PO_4 over 300 ° C leads to poly-phosphoric acids with linear, ultra-phosphoric acids with branched chains and meta-phosphoric acids (HPO_3) with cyclic molecules.

Heating of sodium salts results in the formation of ring type structures, e.g. hexanatrium hexaphosphat



Oligo- and polyphosphoric acid



5.13 Oxo Acids of Phosphorus

Condensed Phosphoric Acids and Their Salts

Heating of the salts of the phosphoric acid leads to condensation reactions, too:

$$2\ M_2HPO_4 \longrightarrow M_4P_2O_7 + H_2O\uparrow$$

$$2\ NaH_2PO_4 \xrightarrow{245\ ^\circ C} Na_2H_2P_2O_7 + H_2O\uparrow$$ (disodium dihydrogenphosphate)

$$2\ Na_2HPO_4 \xrightarrow{300 - 500\ ^\circ C} Na_4P_2O_7 + H_2O\uparrow$$ (tetrasodium diphosphate)

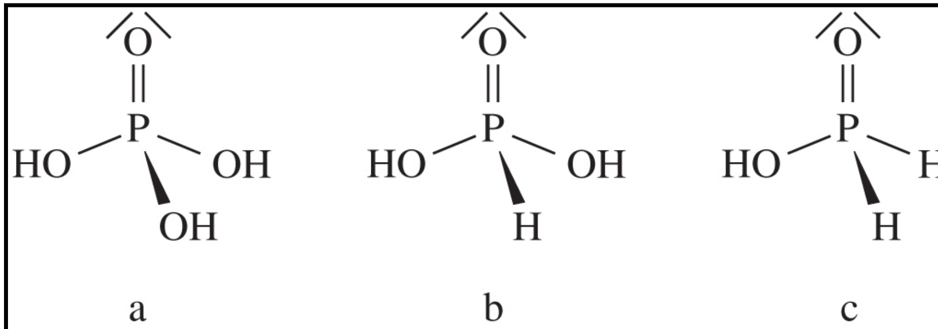
$$2\ Na_2HPO_4 + NaH_2PO_4 \xrightarrow{300 - 550\ ^\circ C} Na_5P_3O_{10} + 2\ H_2O\uparrow$$ (pentasodium triphosphate)

$$2\ Na_2HPO_4 + (n-2)\ NaH_2PO_4 \xrightarrow{> 600\ ^\circ C} Na_{n+2}P_nO_{3n+1} + (n-1)\ H_2O\uparrow$$ (Graham's salt)

Graham's salt is a polyphosphate, that can be described as a inorganic polymer of the formula H–$(NaPO_3)_n$-OH

5.13 Oxo Acids of Phosphorus

Phosphine and Phosphonic Acid



Phosphinic acid HPH_2O_2

$P_4 + 6\ H_2O \rightarrow P^{-III}H_3 + 3\ HP^{+I}H_2O_2$

- Mono basic acid $\Rightarrow$ phosphinates
- Extremely strong reducing agent
- Disproportionation upon heating:

  $3\ HP^{+I}H_2O_2 \rightarrow P^{-III}H_3 + 2\ H_2P^{+III}HO_3$

Phosphonic acid H_2PHO_3

$P^{+III}Cl_3 + 6\ H_2O \rightarrow 3\ HCl + H_2P^{+III}HO_3$

- Dibasic acid $\Rightarrow$ hydrogen phosphonates and phosphonates
- Strong reducing agent:

  $2\ Ag^+ + P^{+III}HO_3^{2-} + H_2O \rightarrow H_3P^{+V}O_4 + 2\ Ag^0\downarrow$
- Disproportionation upon heating:

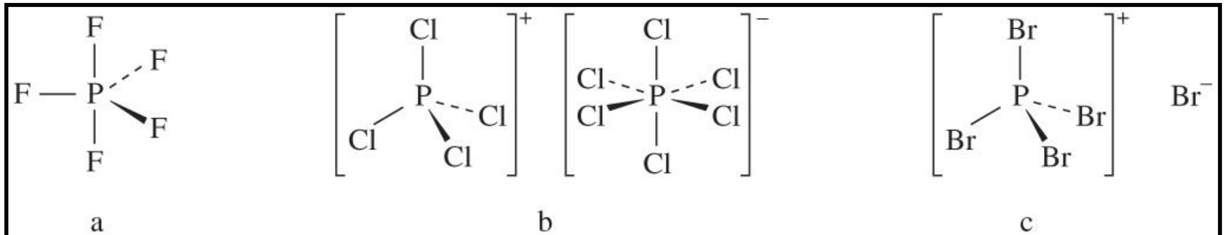
  $4\ H_2P^{+III}HO_3 \rightarrow P^{-III}H_3 + 3\ H_3P^{+V}O_4$

5.14 Phosphorus Compounds with Halides

Binary Phosphorus Halides and Phosphorus Oxo Halides

Compound	F	Cl	Br	I
PX_3	transparent gas	transparent liquid	transparent liquid	red crystals
PX_5	transparent gas	transparent crystals	red/yellow crystals	black crystals
P_2X_4	transparent gas	transparent liquid	-	light red crystals
POX_3	transparent gas	transparent liquid	transparent crystals	-

Structures of the phosphorus penthalides



PF_5 exhibits a phenomenon called pseudo rotation, leading to five equal F atoms, i.e. in ^{19}F-NMR is only one signal oserved

5.15 Arsenic, Antimony and Bismuth

Hydrogen Compounds

- The stability of the gaseous hydrides NH_3, PH_3, AsH_3, SbH_3, and BiH_3 decreases with increasing atomic number: SbH_3 and BiH_3 are thermally unstable
- Arsenic hydride (arsane) AsH_3 is a transparent and highly toxic gas (T_b = -62 °C) Precipitate is used as analytical identification tool for As, arsenic mirror (thermal decomposition and/or incomplete oxidation with oxygen from air) (→ Marsh's test)

Oxygen Compounds

- By combustion of elements:

  $2\,Me + 3\,O_2 \rightarrow 2\,Me_2O_3$ (As_2O_3 and Sb_2O_3 show polymorphism)
- $As_2O_3 + 3\,H_2O \rightarrow 2\,H_3AsO_3$ (arsenious acid)
- All compounds of As and Sb are highly toxic!
- Salts of bismuth in solution tend to form bismuthyl groups $[BiO]^+$ and hence form corresponding BiOX compounds (X = F, Cl, Br, I, NO_3)
- In the melt with alkaline oxides and oxygen, bismuthates are formed:

  $Bi_2O_3 + Na_2O + O_2 \rightarrow 2\,NaBi^{+V}O_3$

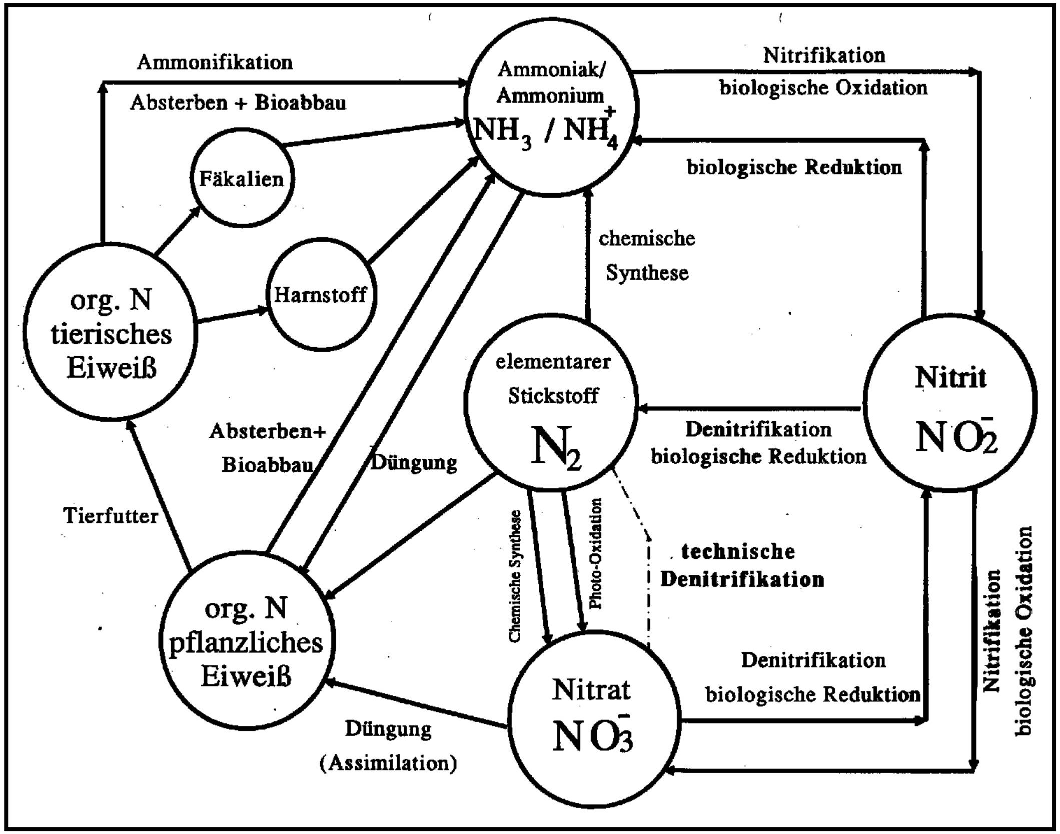
  $Bi_2O_3 + 3\,Na_2O + O_2 \rightarrow 2\,Na_3Bi^{+V}O_4$
- $Bi_4Ge_3O_{12}$ (BGO) is a fast scintillator (conversion of x-rays into visible light (λ_{max} = 480 nm, τ = 300 ns))

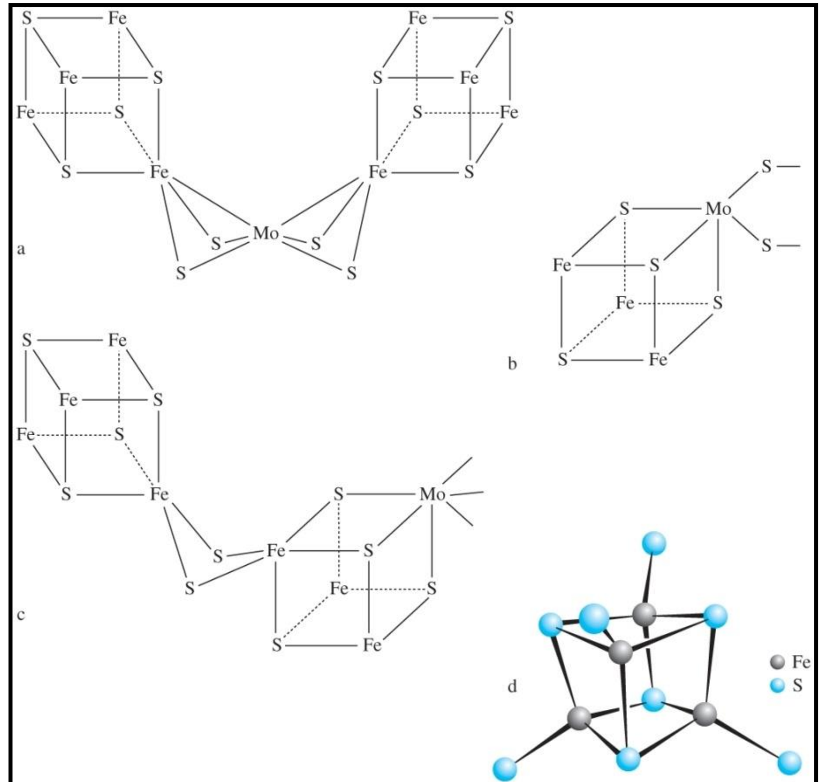
5.16 Biological Aspects

Nitrogen(cycle): The Crucial Part Is the Fixation of Nitrogen!

Technical: $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ 500 °C, 200 bar, Fe catalyst

Biochemically: $N_2(g) + 8\ H^+(aq) + 8\ e^- \rightarrow 2\ NH_3(g) + H_2$, 20 °C, 1 bar, Fe/Mo cat.





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5.16 Biological Aspects

Phosphates

- Phosphorus/phosphates are essential for all living creatures, since they are part of the genetic make-up of (DNA, RNA) as well as the energy storage molecules (ATP, ADP).
- Phosphorus is a decisive limiting factor for growth in every ecosystem!

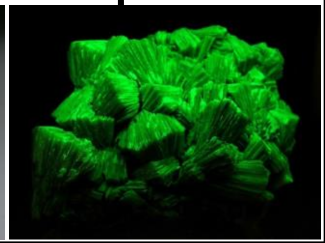
<u>Occurrence of phosphate on earth</u>

Soil	$150 \cdot 10^9$ t
Oceans	$150 \cdot 10^9$ t
Biomass (terrestrial)	$2 \cdot 10^9$ t
Biomass (marine)	$120 \cdot 10^6$ t
Human mankind (~ $8 \cdot 10^9$)	$5.6 \cdot 10^6$ t
Human	700 g

Uranium (50 - 100 ppm) is present in mineral phosphate fertiliser → 114 - 228 t Uranium per year are brought onto deutsche German fields!

daylight | upon UV

$Ca(UO_2)_2(PO_4)_2 \cdot 11H_2O$
Autunite, Daybreak Mine, WA, USA



Annual loss of marine biosphere through sedimentation on the bottom of the sea ~ $15 \cdot 10^6$ t

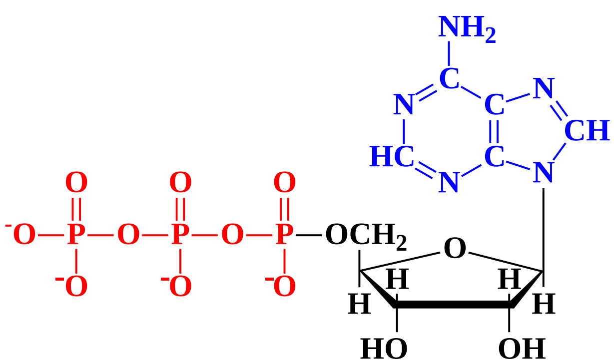
Annual decomposition of phosphate minerals ~ $75 \cdot 10^6$ t → eutrophication

5.16 Biological Aspects

Phosphates

- Many insecticides are phosphoric acid or thiophosphoric acid esters, e.g. Parathion E605
- Apatites are part of bones and teeth
- DNA and RNA are biopolymers linked by phosphate groups
- ATP is one of the most important energy storages in biology

ATP (adenosine triphosphate) is the universal energy storage in biological systems

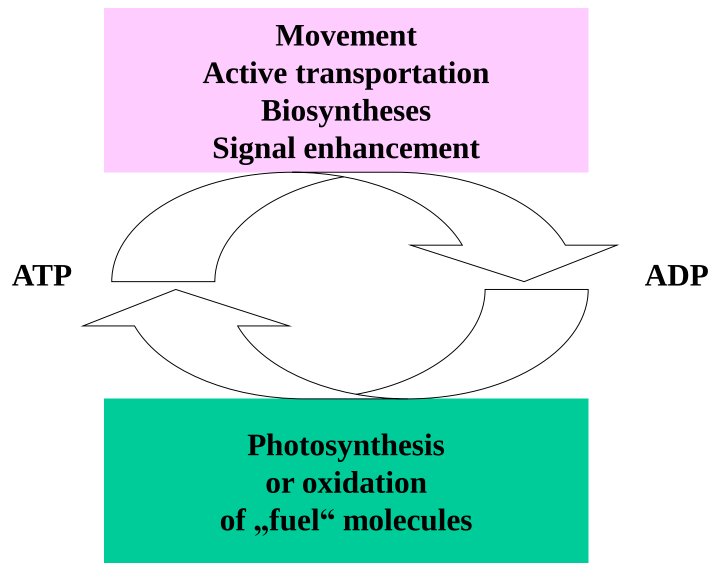


triphosphate units with two phosphoric acid anhydride bonds | ribose | adenine

$$ATP + H_2O \rightleftharpoons ADP + P_i + H^+ \quad \Delta G° = -30{,}5\ kJ/mol$$

$$ATP + H_2O \rightleftharpoons AMP + PP_i + H^+ \quad \Delta G° = -30{,}5\ kJ/mol$$

ATP is continously formed and consumed



5.16 Biological Aspects

Arsenic

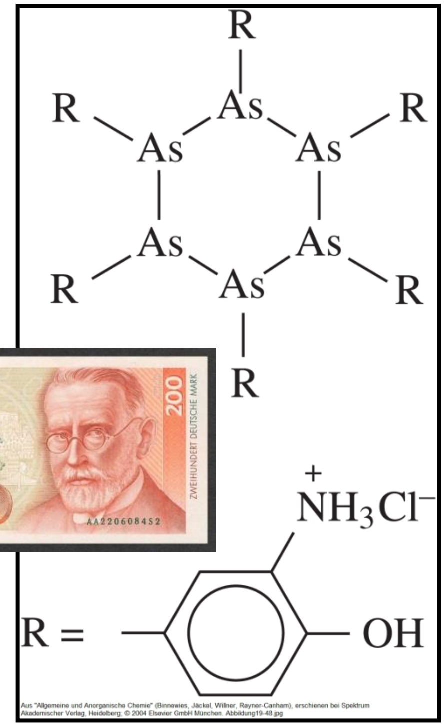
- As, in traces, is essential to humans (daily need 10 – 25 µg), but highly toxic in greater amounts, since it can blockade a number of enzymes

- The pigment "Schweinfurter green" $Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$ was used in paints the 19th century. Mildews liberate $As(CH_3)_3(g)$ from that

  ⇒ Intoxication of Bonaparte Napoleon in exile on St. Helena (south Atlantic) in 1821?

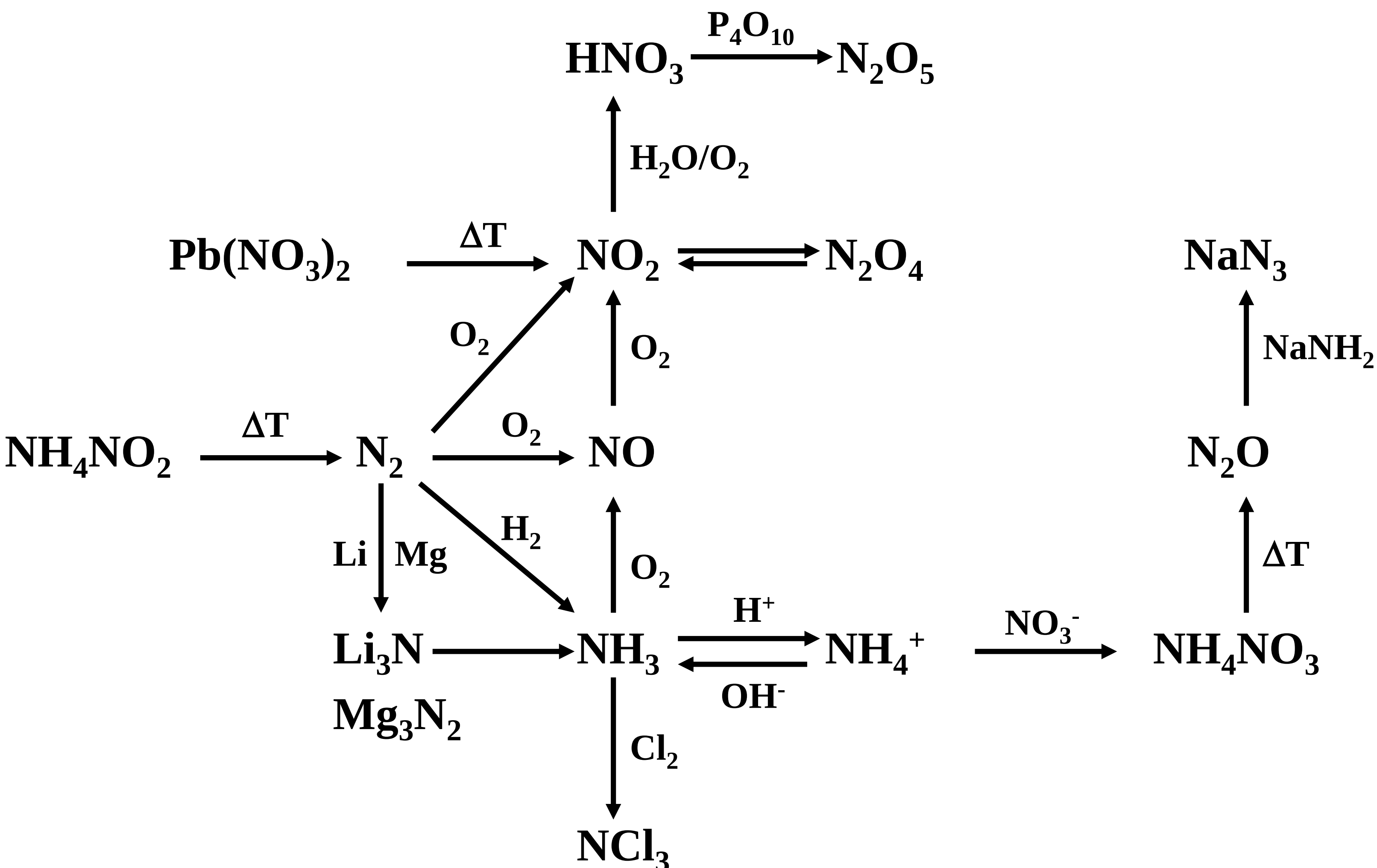
- A organo-arsenic compound of the name "Salvarsan" was used to treat syphilis in the early 20th century (Paul Ehrlich 1909)

  ⇒ one of the first antibiotics with a exceptional impact and only little side effects



Overview Nitrogen Chemistry

Oxidation States: -III, -II, 0, +I, +II, +III, +IV, +V



Overview Phosphorus Chemistry

Oxidation States: -III, -II, -I, 0, +I, +II, +III, +IV, +V