Chemical properties of elements from VA group.
Part 1 – nitrogen and its compounds.

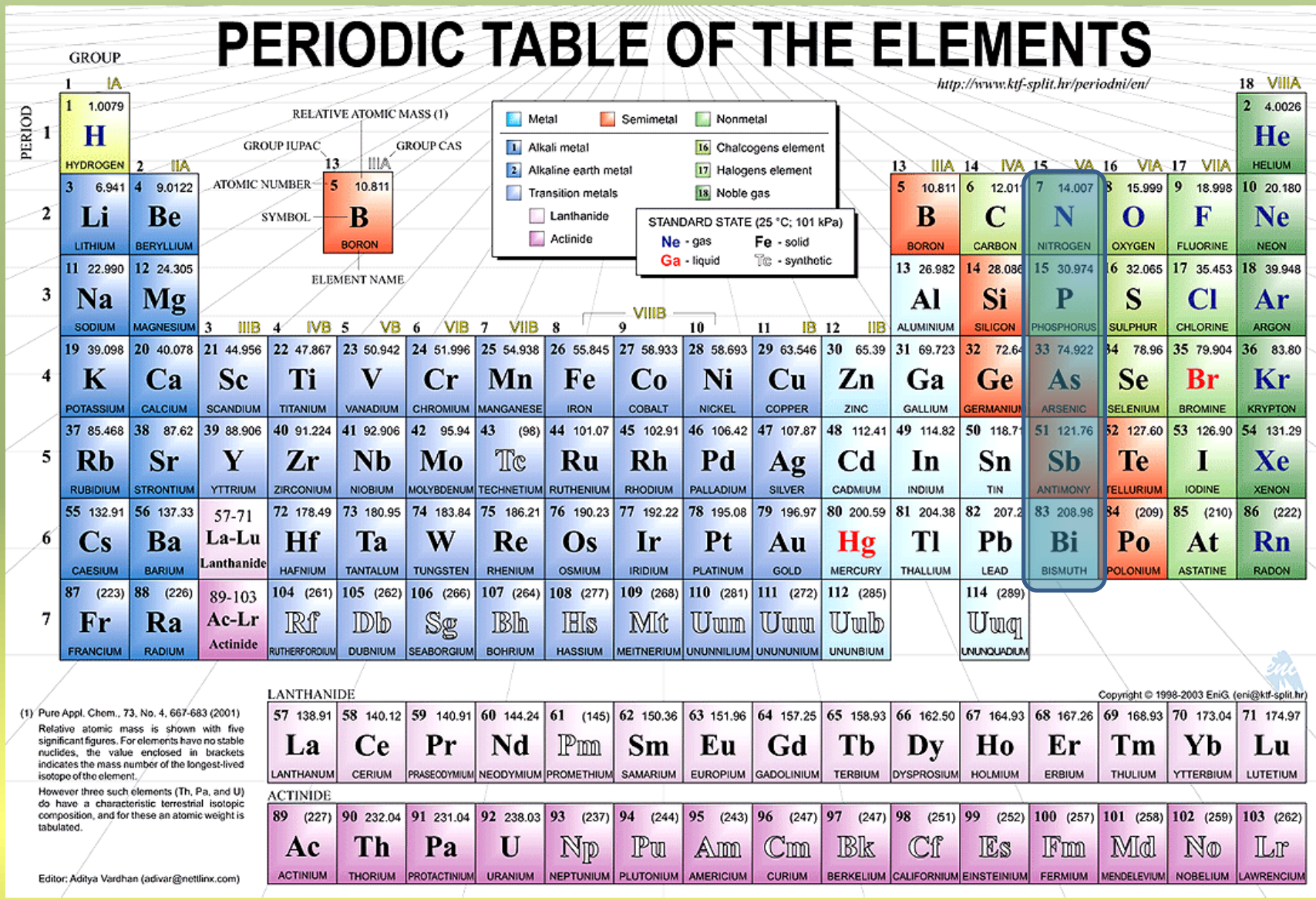
Lecture 10

The main topics of the lecture:

1. Overall characteristic of the elements from VA group.
2. Nitrogen. Chemical properties of the element.
3. Compounds of nitrogen in negative oxidation state.
4. Compounds of nitrogen in positive oxidation state.
5. The usage of nitrogen containing compounds in medicine and pharmacy.

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/



LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERBIUM	LUTETIUM

ACTINIDE

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
(227)	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netllinx.com)

Properties of elements from VA group

Properties	N	P	As	Sb	Bi
Mass percentage in the Earth crust, %	**$1 \cdot 10^{-2}$**	**$8 \cdot 10^{-2}$**	**$5 \cdot 10^{-4}$**	**$4 \cdot 10^{-5}$**	**$2 \cdot 10^{-5}$**
Molar mass, g/mol	**14,0**	**31,0**	**74,9**	**121,8**	**209,0**
Atomic radius, nm	**0,070**	**0,110**	**0,121**	**0,141**	**0,146**
Electronegativity	**3**	**2,1**	**2,0**	**1,9**	**1,8**
Oxidation states	**-3**,-2,-1 +1,+2,**+3**, +4,**+5**	-3 +3,**+5**	-3 +3,+5	-3 +3,+5	**+3**,+5
Temperature of boiling. ^{o}C	**-195,8**	**429**	**615**	**1634**	**1552**
Density, g/ml	**0,808(ж)**	**2**	**5,72**	**6,7**	**9,8**
Electrode potential (E^{+3} aq/E), V	**-**	**-**	**0,3**	**0,24**	**0,2**

Acid-base properties of some oxides and hydroxides of elements from VA group

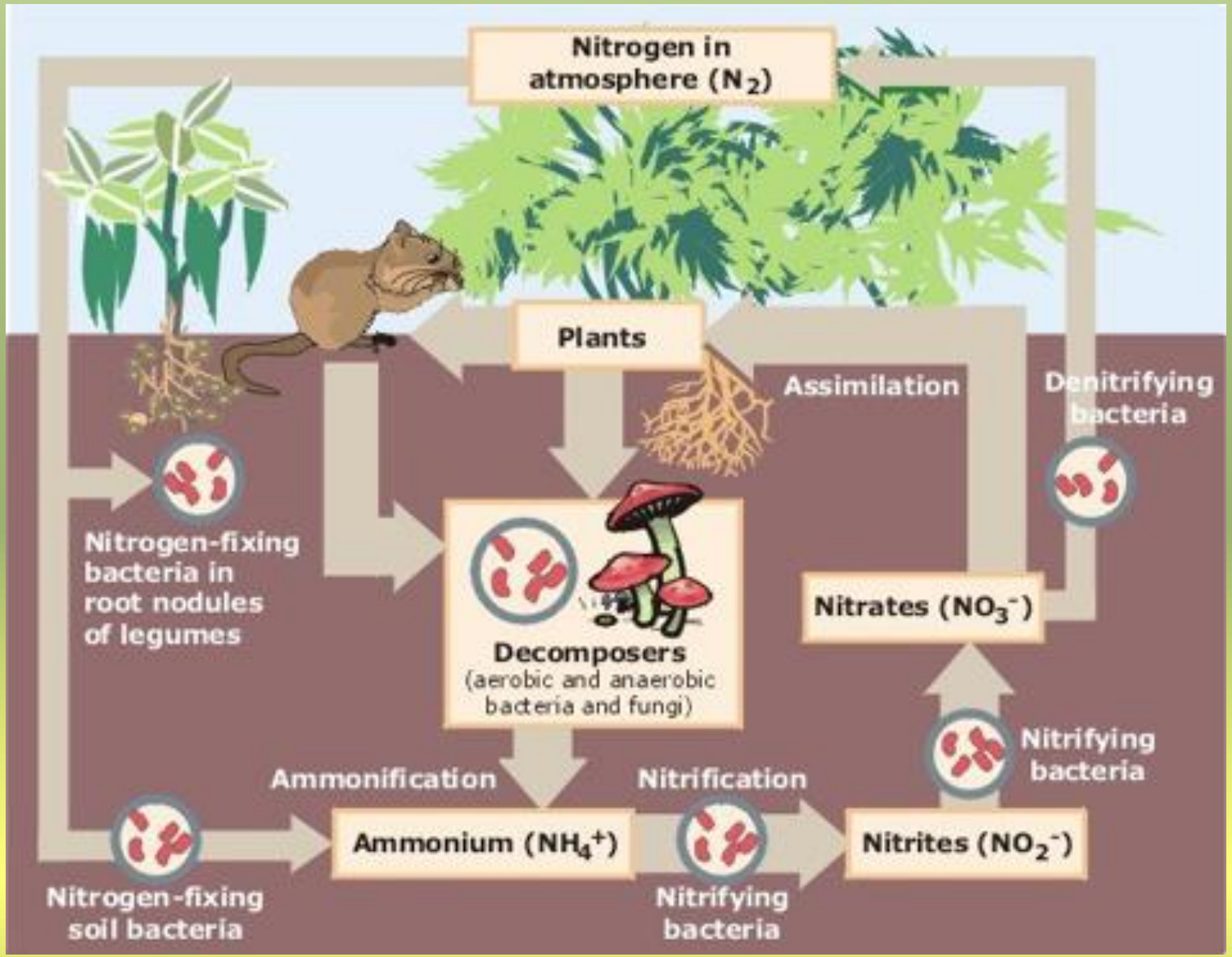
Oxides E_2O_3	Properties	The formula of hydroxide and its properties	Oxides E_2O_5	Properties	The formula of hydroxide and its properties
N_2O_3	acidic	HNO_2, weak acid	N_2O_5	acidic	HNO_3, strong acid
P_2O_3	acidic	H_3PO_3, weak acid	P_2O_5	acidic	H_3PO_4, weak acid
As_2O_3	Amphoteric, but mostly acidic	H_3AsO_3	As_2O_5	acidic	H_3AsO_4, weak acid (weaker than orthophosphoric acid)
Sb_2O_3	Amphoteric, but mostly basic	Variable content $xSb_2O_3 \cdot yH_2O$	Sb_2O_5	acidic	Variable content $xSb_2O_5 \cdot yH_2O$
Bi_2O_3	basic	$Bi(OH)_3$, weak base	Bi_2O_5	acidic	Hydroxide is unknown

Natural resources

Volume percentage in the air is **~78%**
Animals consume nitrogen as the part of amino acids and nucleotides.
Plants consume nitrogen as the part of nitrates from the soil.
Nitrogen forms such minerals, as nitrates:

Chile saltpeter **$NaNO_3$**,
Indian saltpeter **KNO_3**
Norvegian saltpeter **$Ca(NO_3)_2$**

Just nitrogen fixing bacteria can consume nitrogen from the air.


Nitrogen in atmosphere (N_2)
Plants
Assimilation
Denitrifying bacteria
Nitrogen-fixing bacteria in root nodules of legumes
Decomposers
(aerobic and anaerobic bacteria and fungi)
Nitrates (NO_3^-)
Nitrifying bacteria
Ammonification
Nitrification
Ammonium (NH_4^+)
Nitrites (NO_2^-)
Nitrogen-fixing soil bacteria
Nitrifying bacteria

Nitrogen is a colorless gas that has no taste and odor. The solubility of nitrogen in water and organic solvents is low.

$$\cdot\cdot \quad \cdot\cdot$$
$$\mathbf{N \equiv N}$$

Nitrogen cannot burn, other substances cannot burn in nitrogen, nitrogen cannot react with acids and bases.

At room temperature nitrogen reacts with lithium:

$$\mathbf{N_2 + 6Li = 2Li_3N}$$

At high temperature nitrogen reacts with active metals and forms nitrides**.**

Phosphorus nitride is formed under the electric strike:

$$6P + 5N_2 \rightarrow 2P_3N_5$$

Cyanogen is formed upon the hot coal:

$$N_2 + 2C \rightarrow (CN)_2$$

Cyanamide of calcium is formed in the reaction with nitrogen:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

Cyanamide of calcium is hydrolyzed into calcium carbonate and NH_3:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3\downarrow + 2NH_3\uparrow$$

Nitrogen reacts with fluorine:

$$N_2 + 3F_2 \rightarrow 2NF_3$$

Several ways to produce nitrogen in the laboratory: (t^oC)

- $NH_4NO_2 \rightarrow N_2 + 2H_2O$
- $2N_2O \rightarrow O_2 + 2N_2$
- $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$

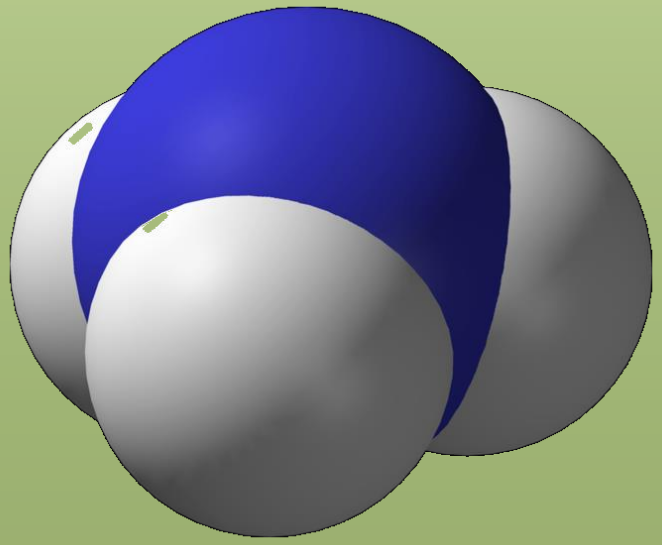
$$5Mg + 12HNO_3 \rightarrow 5Mg(NO_3)_2 + N_2\uparrow + 6H_2O$$

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2\uparrow + 3H_2O$$

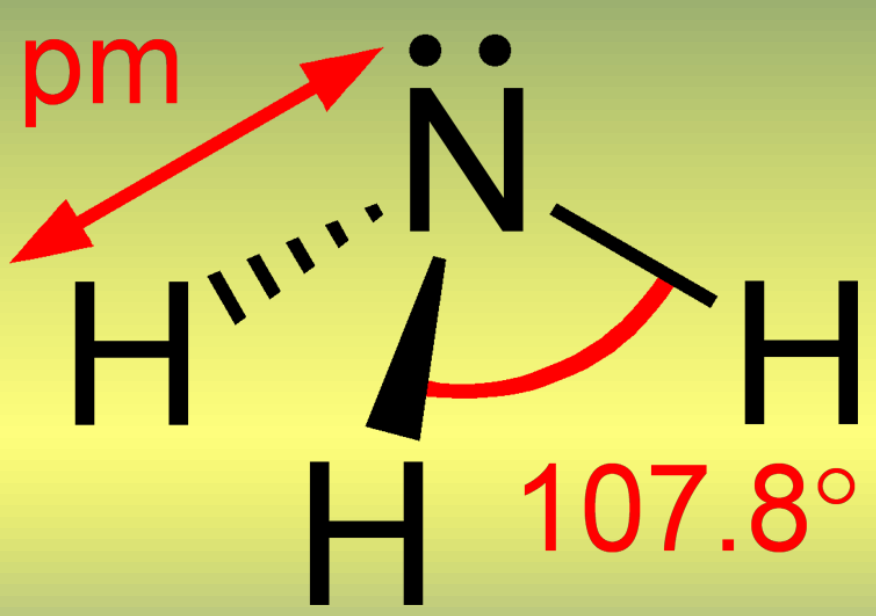
Pure nitrogen is produced by the decomposition of azides of metals:

$$\overset{-1/3}{2NaN_3} \rightarrow 2Na + 3N_2$$

Ammonia



sp^3 – hybridization



$$NH_3 + H^+ \rightarrow NH_4^+$$

$$NH_3 + HNO_3 = NH_4NO_3$$

Thermal decomposition of ammonium salts (t °C):

$$NH_4Cl \rightarrow NH_3\uparrow + HCl\uparrow$$

$$(NH_4)_2CO_3 \rightarrow 2NH_3\uparrow + CO_2\uparrow + H_2O$$

$$(NH_4)_2HPO_4 \rightarrow 2NH_3\uparrow + H_3PO_4$$

$$NH_4H_2PO_4 \rightarrow NH_3\uparrow + H_3PO_4$$

$$(NH_4)_2SO_4 \rightarrow NH_3\uparrow + NH_4HSO_4$$

$$3(NH_4)_2SO_4 \rightarrow 4NH_3\uparrow + 3SO_2 + N_2\uparrow + 6H_2O$$

$$NH_4NO_2 \rightarrow N_2\uparrow + 2H_2O$$

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2\uparrow + 4H_2O$$

$$NH_4NO_3 \xrightarrow{260^oC} N_2O\uparrow + 2H_2O$$

$$2NH_4NO_3 \xrightarrow{500^oC} N_2\uparrow + O_2\uparrow + 4H_2O$$

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

Pale blue turns to deep dark blue

$Ni(NO_3)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6](NO_3)_2$

Green turns to violet

$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad \Delta H = -1266\ kJ/mol$

$2NH_3 + 3Cl_2 = N_2 + 6HCl \qquad \Delta H = -426\ kJ/mol$

$2(NH_3 \cdot H_2O)_{conc.} + 2KMnO_4 \rightarrow$

$\rightarrow N_2\uparrow + 2MnO_2\downarrow + 4H_2O + 2KOH$

$2(NH_3 \cdot H_2O)_{conc.} + 3Br_2 \rightarrow N_2\uparrow + 6NH_4Br + 8H_2O$

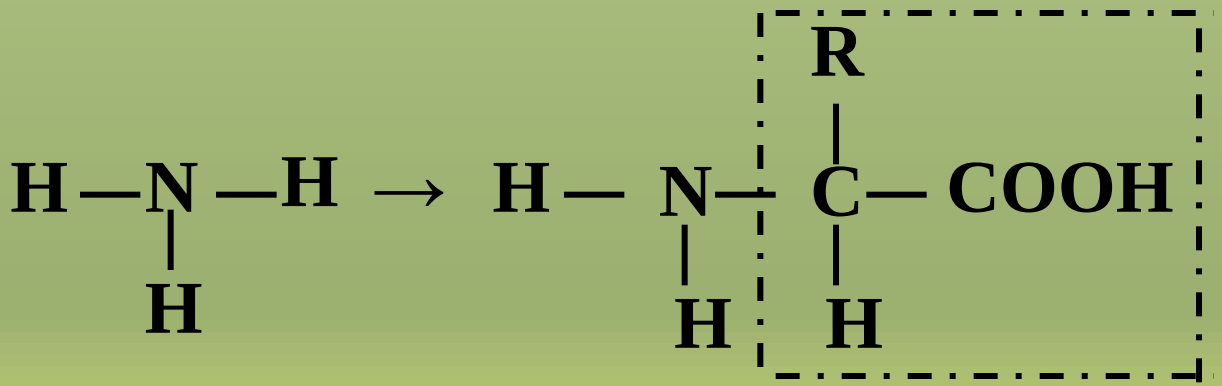
$2NH_4Cl + 3CuO \rightarrow 3Cu + 3H_2O\uparrow + 2HCl\uparrow + N_2\uparrow$

- $Na + NH_3 = NaNH_2 + 1/2\ H_2$
  sodium amide
- $2K + NH_3 = K_2NH + H_2$
  potassium imide
- $2Al + 2NH_3 = 2AlN + 3H_2$
  aluminum nitride

- $NaNH_2 + H_2O \rightarrow NaOH + NH_3$

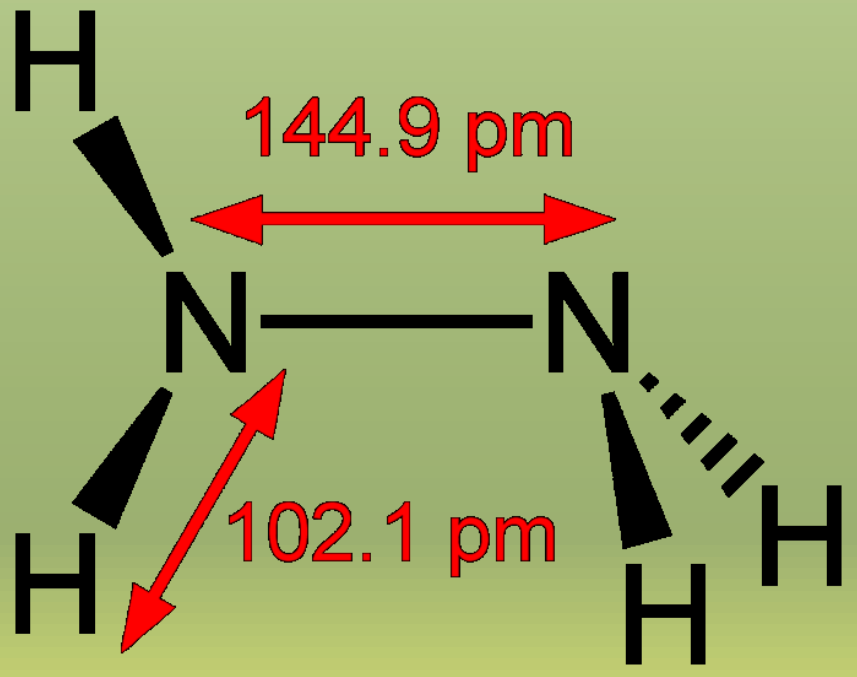
- $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

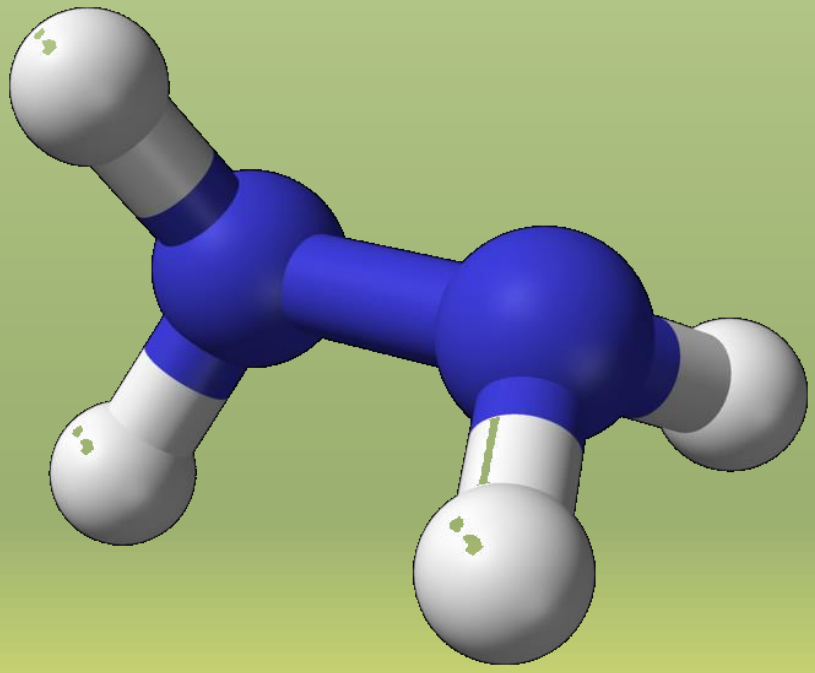
Amino acids may be described as derivatives of ammonia in which one of the hydrogen atoms is replaced by the remain of carbonic acid:



$$NH_2 - CH_2 - COOH + HCl \rightarrow Cl[H_3N - CH_2 - COOH]$$

$$2NH_3 + NaOCl = N_2H_4 + NaCl + H_2O$$





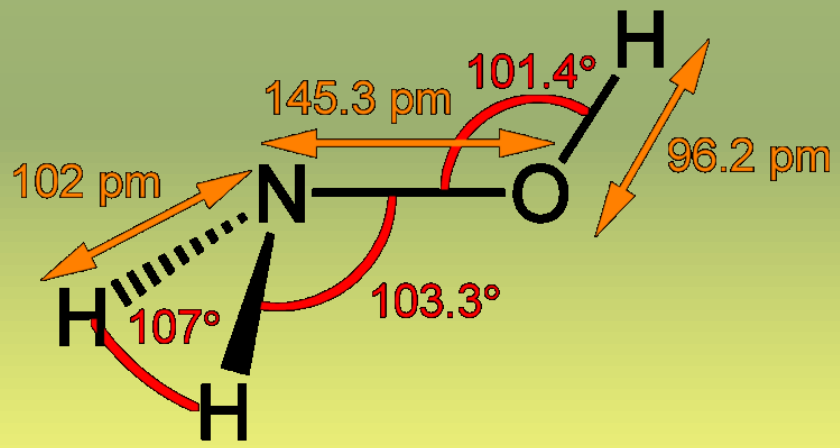
Hydrazine (N_2H_4) is a colorless, volatile liquid, that is poisonous, and bursts in the presence of oxygen.

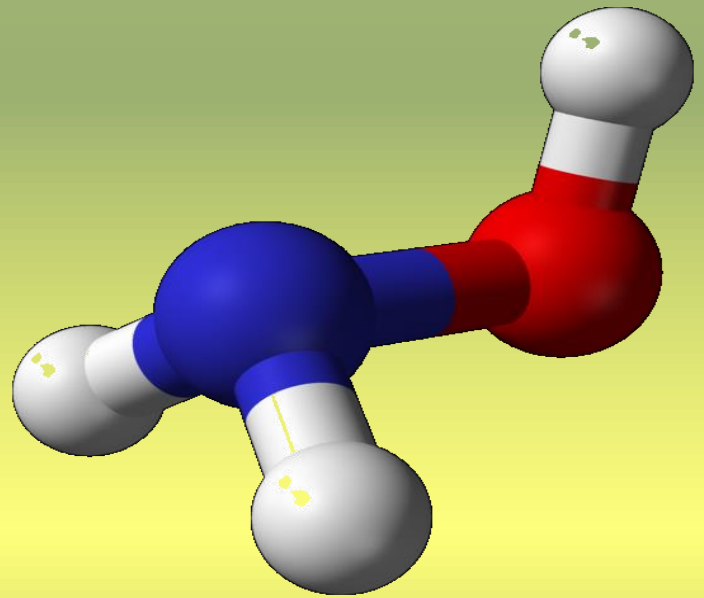
$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

Nitric acid can be reduced by atomic hydrogen into the hydroxylamine:

$$HNO_3 + 6H = \overset{-1}{NH_2OH} + 2H_2O$$

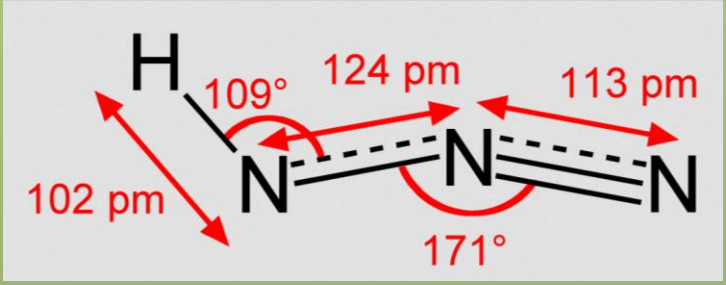
$$2NH_2OH + I_2 + 2KOH = N_2 + 2KI + 4H_2O$$

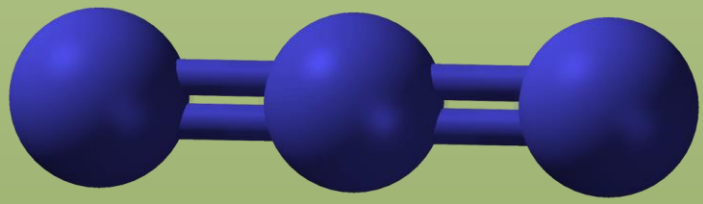




Hydrazoic acid, azoimide, HN_3

$$HN_3 + H_2O \rightarrow N_2 + NH_2OH$$





$$Cu + 3HNN_2 \rightarrow Cu(NN_2)_2 + N_2 + H_3N$$

pKa = 4.59

Salts of hydrazoic acid are called azides

HN_3 can be produced in the reaction between orthophosphoric acid and sodium azide **NaN_3**, while the last one is synthesized from sodium amide:

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

$$3NaN_3 + H_3PO_4 \rightarrow 3HN_3 + Na_3PO_4$$

Oxygen containing compounds of nitrogen

Oxidation state	Oxides			Hydr-oxides	Acids	Salts
	formula	name	properties	formula	The name	The name
+1	N_2O	Nitrogen (I) oxide	Cannot form salts	-	-	-
+2	NO	Nitrogen (II) oxide	Cannot form salts	-	-	-
+3	N_2O_3	Nitrogen (III) oxide	Acidic	HNO_2	Nitrous	Nitrites
+4	NO_2	Nitrogen (IV) oxide	Acidic. Reacts with water with redox process	HNO_2 HNO_3	Nitrous Nitric	Nitrites Nitrates
+5	N_2O_5	Nitrogen (V) oxide	Acidic	HNO_3	Nitric	Nitrates

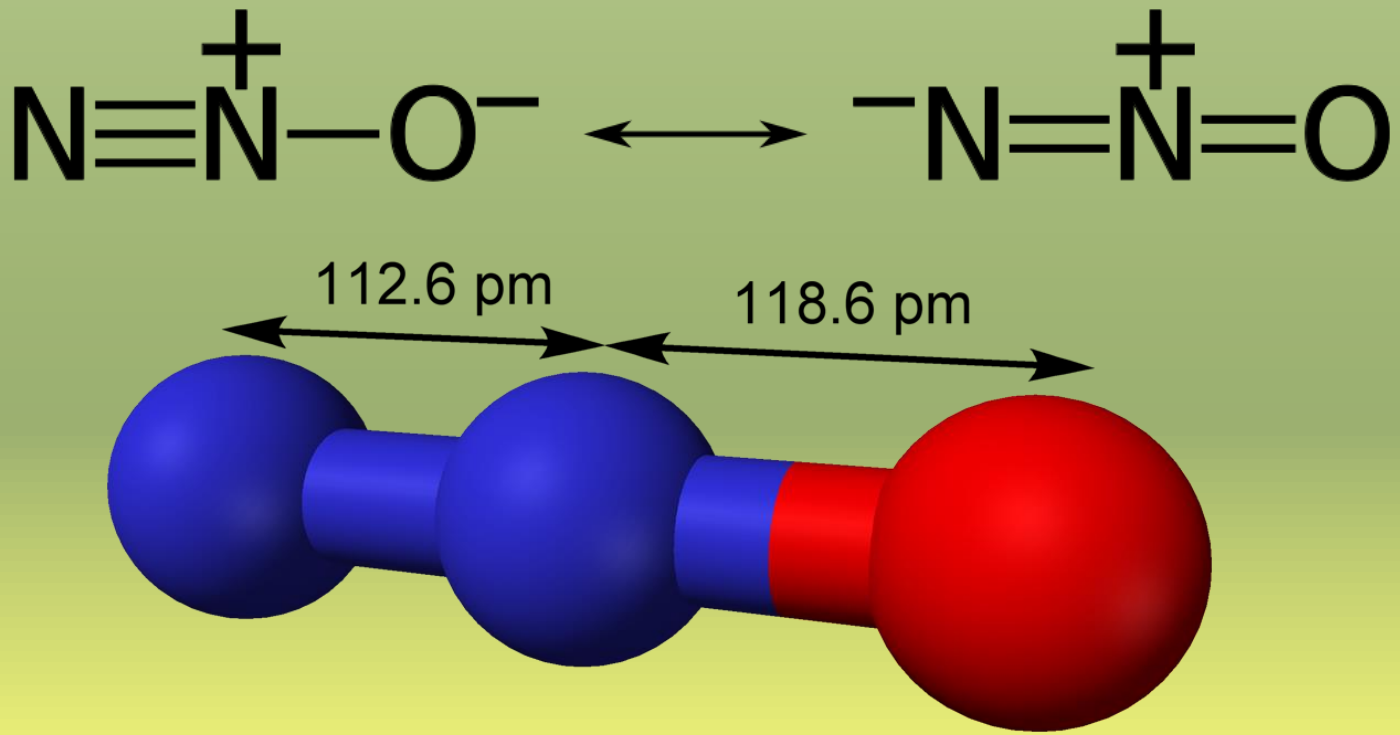
- ***Nitrogen (I) oxide*** **N_2O** cannot form salts.
- It is used fro narcosis in the mixture with oxygen.
- In small doses it causes the desire to laugh (due to intoxication). In high concentration N_2O causes narcosis.
- **$NH_4NO_3 \rightarrow N_2O\uparrow + 2H_2O$**
- At high temperature it becomes more active and begins to be able to oxidize sulfur, hydrogen, carbon and copper, as well as organic compounds:

$Cu + N_2O = CuO + N_2$

700 °C

$2N_2O \rightarrow 2N_2 + O_2$

The structure of N_2O



Nitrogen (II) oxide **NO** cannot form salts. **NO** demonstrates both oxidative and reductive properties.

Nitrogen *(II) oxide* is easily oxidized by oxygen from the air up to nitrogen (IV) oxide

$$2NO + O_2 = 2NO_2 \quad (\Delta H°_{298} = -113.4 \text{ кДж/моль}).$$

Also it is reduced by hydrogen up to the molecular nitrogen:

$$2NO + 2H_2 = N_2 + 2H_2O$$

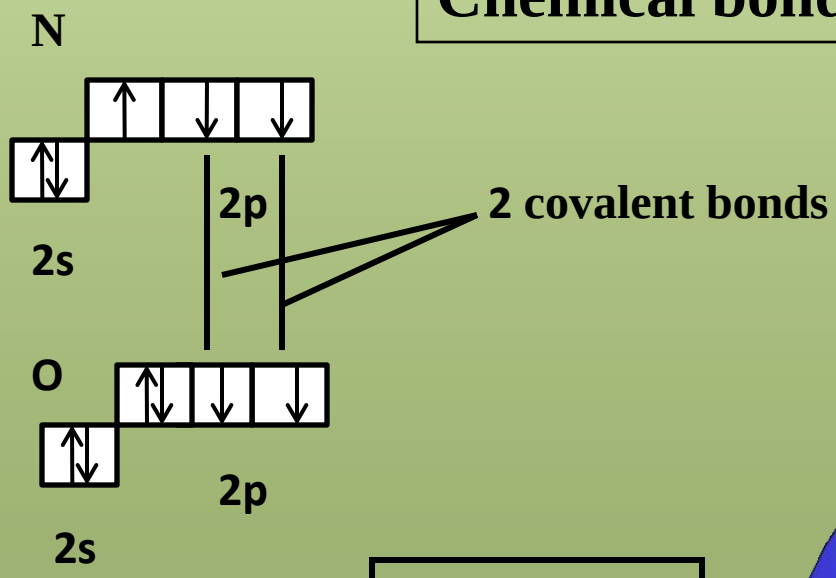
Production: $2NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

A wire made from platinum and rhodium is a catalyst for this process

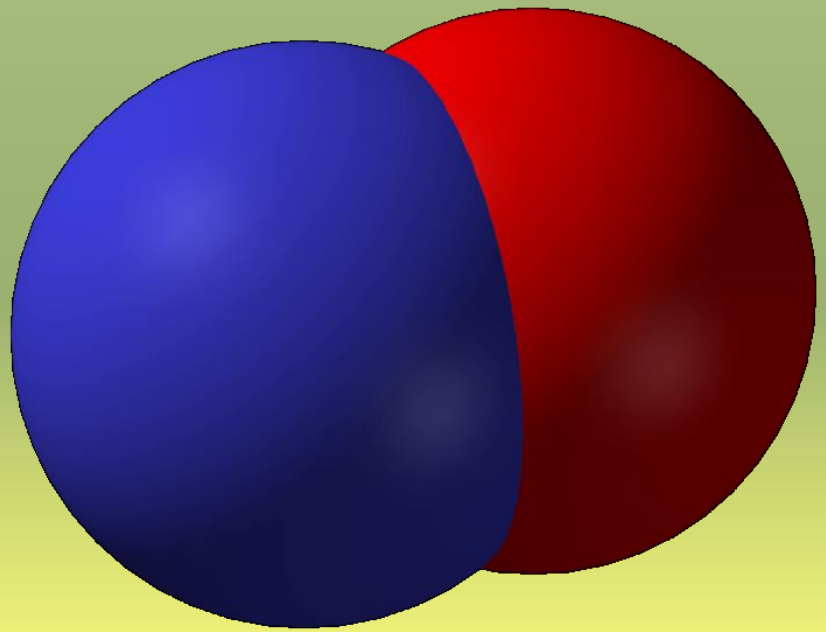
Water solutions of **NO** are neutral. Nitrogen monoxide can be reduced by halogens up to **nitrosyl halides:**

$$2NO + Cl_2 = 2NOCl$$

Chemical bonds in the molecule of NO



$$\cdot N = O$$



Secondary messandger
Vasodepressor

NO can play a role of a ligand in complexes. NO produces brown complex in the reaction with iron (II) sulfate:

$$[Fe(H_2O)_6]SO_4 + NO \rightarrow [Fe(H_2O)_5NO]SO_4 + H_2O$$

NO – is colorless. It is produced in the laboratory from 30% nitric acid in the reaction with copper:

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

NO_2, that is a subproduct of this reaction, is removed by the way of the passing of this gas through the water.

At high temperature NO oxidizes many substances (**C, P, S, SO_2, H_2** and some **metals**).

Nitrogen (III) oxide $\mathbf{N_2O_3}$ exists at low temperatures as a dark-blue liquid, but it is decomposed at 0°C:

$\mathbf{N_2O_3 \rightarrow NO + NO_2}$; $\mathbf{\Delta H°298 = - 41.2\ кДж/моль.}$

Production: $\mathbf{2HNO_3\ (50\%) + As_2O_3 = 2HAsO_3 + NO + NO_2}$

$\mathbf{HNO_2}$ ($\boldsymbol{K_{dissociation} = 4 \cdot 10^{-4}}$ **mol/L).**

Nitrous acid exists only in dilute solutions.

Production: $\mathbf{NO + NO_2 + H_2O = 2HNO_2}$

At storage and heating $\mathbf{HNO_2}$ disproportionates:

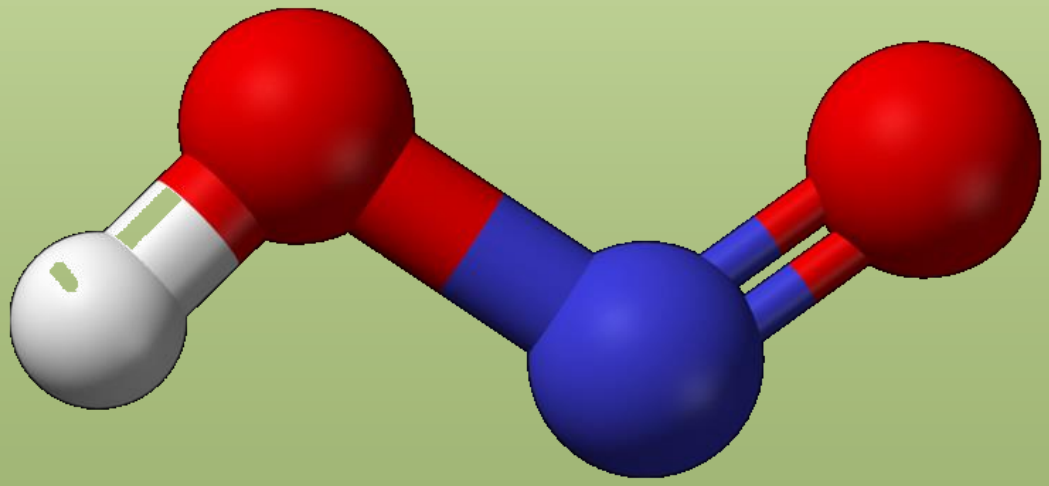
$$\mathbf{3HNO_2 = HNO_3 + 2NO + H_2O}$$

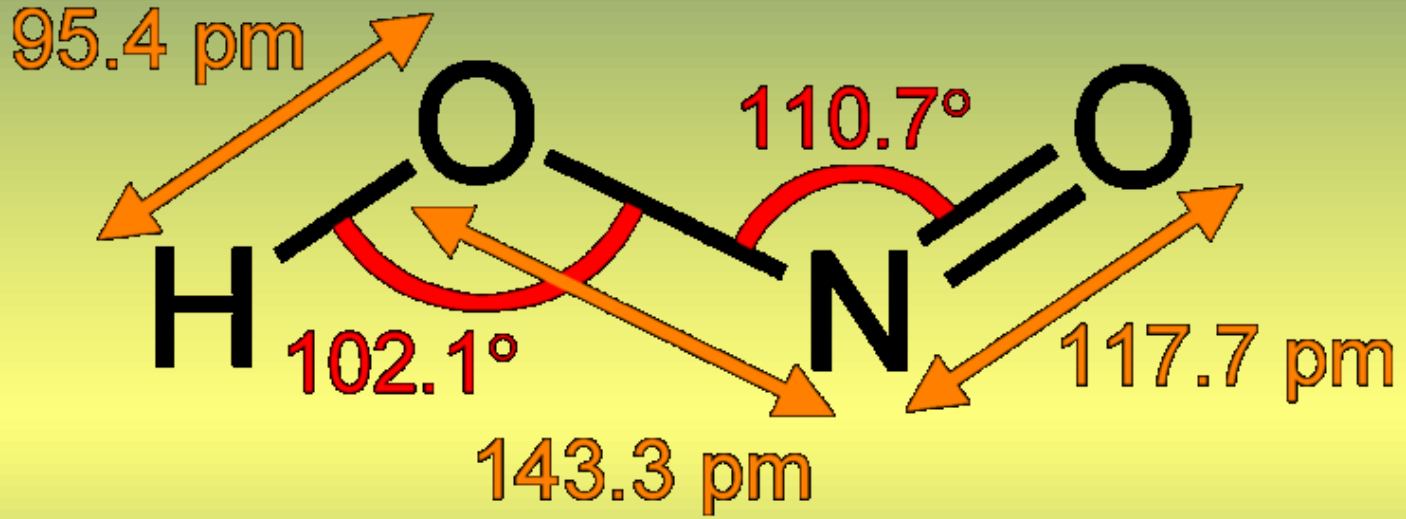
Nitrous acid demonstrates oxidative properties:

$\mathbf{2HNO_2 + 2HI = I_2 + 2NO + 2H_2O}$

$\mathbf{2HNO_2 + H_2S = S + 2NO + 2H_2O}$

HNO_2





Salts of nitrous acid are called — ***nitrites***

$$2NaNO_2 + 2KI + 2H_2SO_4 = I_2 + 2NO + K_2SO_4 + Na_2SO_4 + 2H_2O$$

Oxidizer

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O$$

Reducer

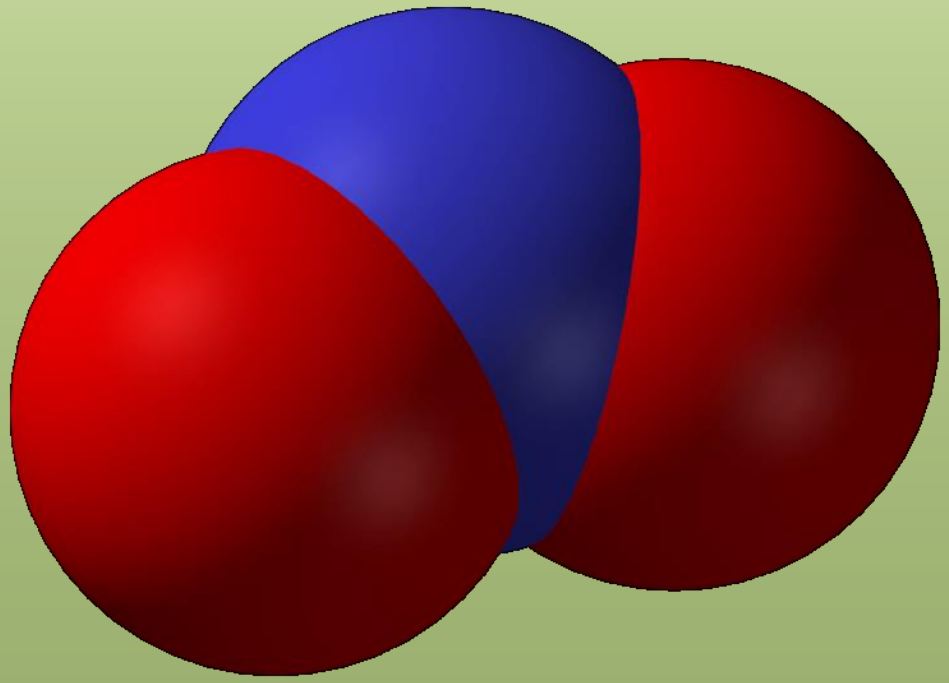
$$3KNO_2 + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3KNO_3 + K_2SO_4 + 4H_2O$$

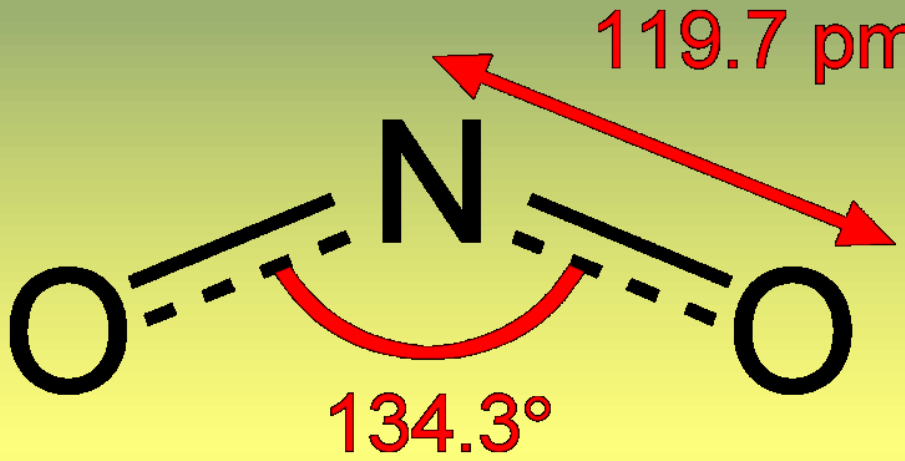
Reducer

Nitrites of transition metals show low solubility in water. At heating they disproportionate:

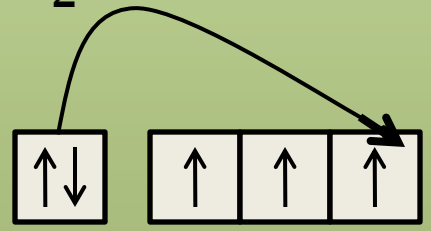
$$2AgNO_2 \rightarrow AgNO_3 + Ag + NO\uparrow$$

Nitrogen (IV) oxide





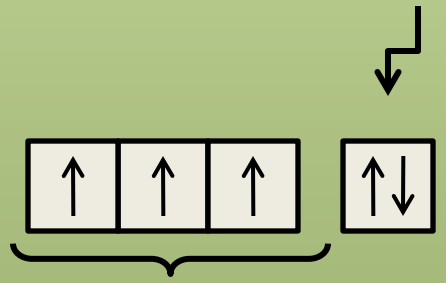
NO_2



2s 2p

sp^2-hybridization

2p-orbital



sp^2 orbitals

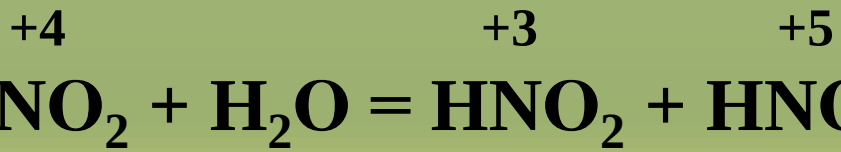
$2NO_2 \leftrightarrow N_2O_4$;
$\Delta H°_{298}{}^{=}$ - 58 kJ

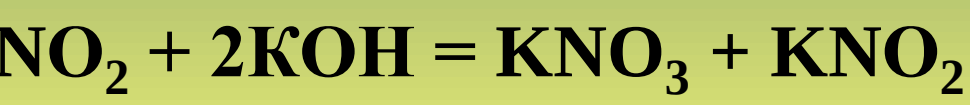
NO_2 – nitrogen (IV) oxide

Production:

$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$.

Nitrogen dioxide disproportionates when it reacts with water and water solution of alkali:





NO_2 can be produced in the laboratory this way:

$$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + NO + NO_2 + H_2O$$

Then NO will be oxidized by oxygen down to NO_2.

Many substances can be burnt in NO_2

$$NO_2 + SO_2 = SO_3 + NO; \quad \Delta H°_{298} = -42\ kJ/mol$$

At the temperature higher than 150°C nitrogen dioxide decomposes:

$$2NO_2 = 2NO + O_2$$

Nitrogen (V) oxide N_2O_5

$$[NO_2^+][NO_3^-] \rightleftharpoons N_2O_5$$

Production:

a) Dehydration of **HNO_3** by phosphoric anhydrate:

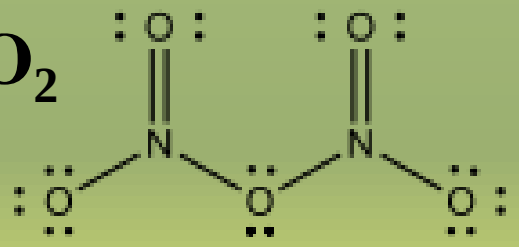
$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5$

b) Oxidation of **N_2O_3** by ozone:

$N_2O_3(liquid)+2O_3 \rightarrow N_2O_5(solid)+2O_2$

c) Oxidation of silver nitrate by chlorine:

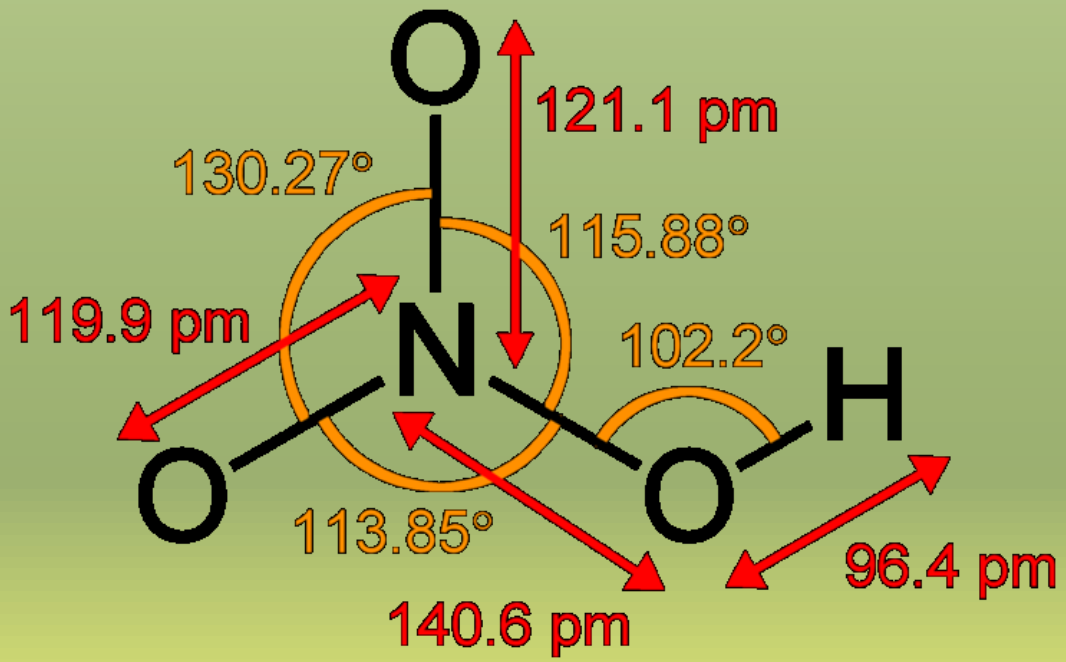
$4AgNO_3+2Cl_2 \rightarrow 4AgCl\downarrow+2N_2O_5+O_2$

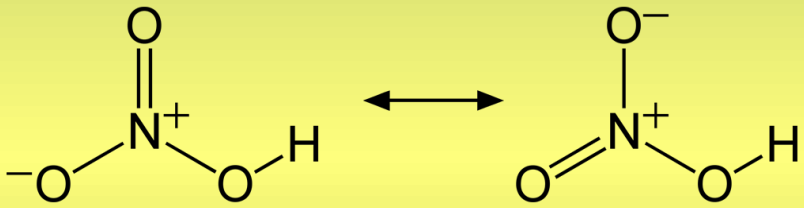


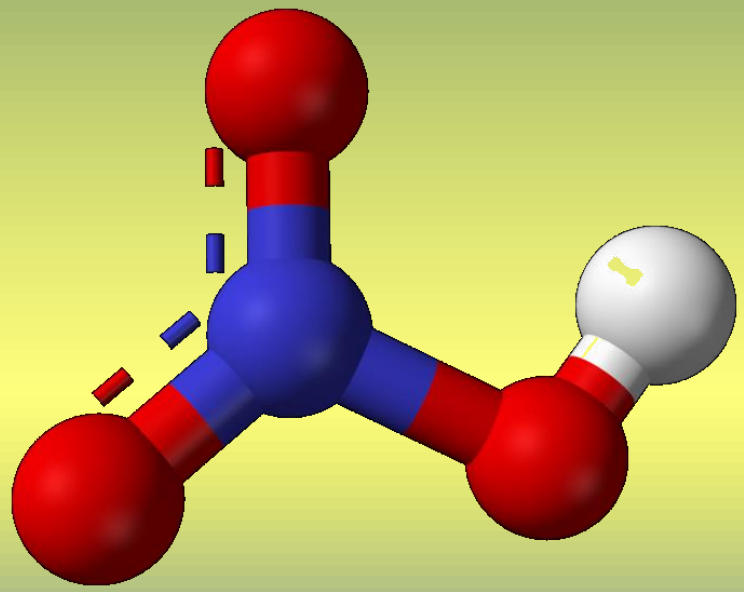
Dinitrogen pentoxide **N_2O_5** is a strong oxidizer. When it dissolves in water, nitric acid is formed:

$N_2O_5 + H_2O = 2HNO_3$

Nitric acid


O
121.1 pm
130.27°
115.88°
119.9 pm
N
102.2°
H
O
O
113.85°
96.4 pm
140.6 pm


O
N+
−O
O
H
O−
N+
O
O
H



HNO_3 can be produced in the laboratory by the way of heating sodium nitrate with sulfuric acid

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$$

In industry nitric acid is produced in 3 steps

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad \Delta H°_{298} = -904\ kJ$$

$$2NO + O_2 = 2NO_2$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

$$4HNO_3 \xrightarrow{\text{into the light}} 4NO_2 + 2H_2O + O_2$$

Concentrated **HNO_3** is a strong oxidizer.

Au, Pt, Rh, Ir, Ti, Ta are resistant
to concentrated nitric acid

Al, Cr, Fe, Ni, Co are **"passivated"** (at low temperature) by concentrated nitric acid.

Corresponding salt, water and a mixture of the following products of nitric acid reduction are formed in the reaction between a metal and HNO_3: **NH_3, N_2, NO, N_2O, NO_2**.

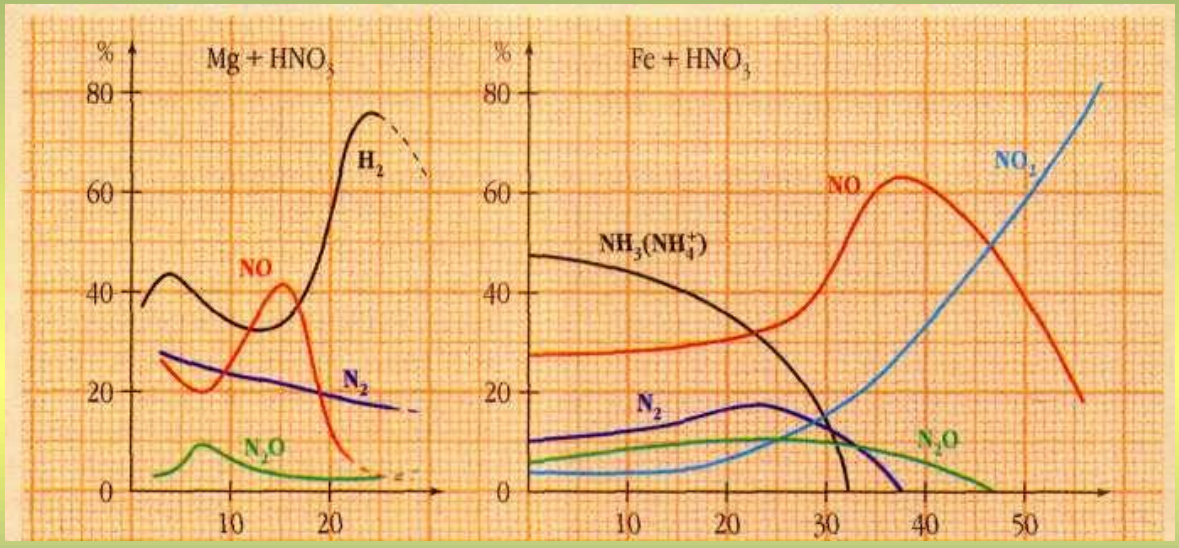
The more **dilute** the acid, the higher the percentage of a product of deeper reduction.

The content of products of HNO_3 reaction with metals

Me / $w(HNO_3)$, %	Li, Cs, Rb, K, Ba, Sr, Ca*, Na, Mg*, Al*	Mn*, Zn, Cr*, Fe*, Cd, Co*, Ni*, Sn, Pb*	Bi*, Cu, Ru, Hg, Ag, Rh, Pd	Ir, Pt, Au
> 80%	NO_2	NO_2	NO_2	—
45 – 75%	N_2O	NO	NO_2	—
10 – 40%	N_2	N_2O	NO	—
<5%	NH_4NO_3	N_2	—	—

$2NO + 2H_2 = N_2 + 2H_2O$

$N_2O + H_2 = N_2 + H_2O$



$$HNO_3 + \text{Metal} \rightarrow$$

All sulfides are oxidized up to higher acids or hydroxides by concentrated nitric acid **HNO_3** (conc.):

$As_2S_3 + 28HNO_3(conc.) =$

$= 2H_3AsO_4 + 3H_2SO_4 + 28NO_2 + 8H_2O$

Tzar's vodka dissolves gold and other inert metals (**Pd, Pt, Os, Ru**):

$Au + HNO_3 + 4HCl \rightarrow H[AuCl_4] + NO + 2H_2O$

HNO_3 oxidizes almost all nonmetals:

$S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$

$C + 4HNO_3 = 4NO_2 + CO_2 + 2H_2O$

$2KNO_3 + 3C + S = N_2 + 3CO_2 + K_2S$

Nitrates are produced in reactions between **HNO_3** with metals, oxides, hydroxides and carbonates.

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O$$

Thermal decomposition of **HNO_3** salts.

Nitrates
$MeNO_3$

- **before Mg** → **$MeNO_2 + O_2$**
- **Mg - Cu** → **$MeO + O_2 + NO_2$**
- **after Cu** → **$Me + O_2 + NO_2$**

t°>700°C

$2NaNO_2 \rightarrow Na_2O + NO + NO_2$

The usage of nitrogen containing compounds in medicine and pharmacy.

Water solution of ammonia **NH_4OH (10% by mass)** is used for awaking from the loss of consciousness.

Nitrogen (I) oxide (N_2O) is known as laughing gas and used in anesthesiology for putting a patient into deep narcosis.

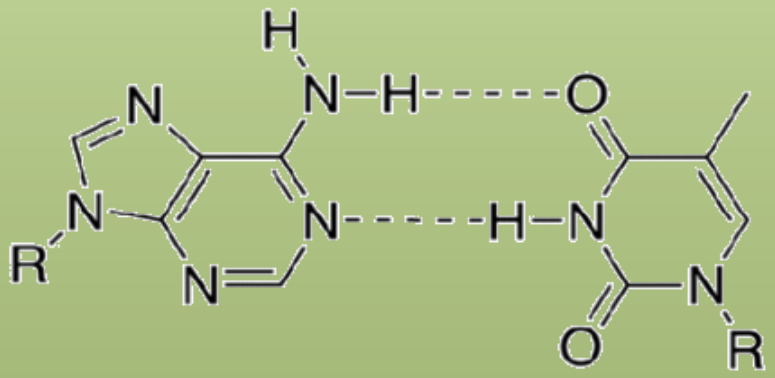
Nitrites are used for conservation of meet products like sausages. Nitrites are deaminating agents which can cause nucleotide mutations in DNA and RNA.

$A \rightarrow I \rightarrow G$
$C \rightarrow U \rightarrow T$

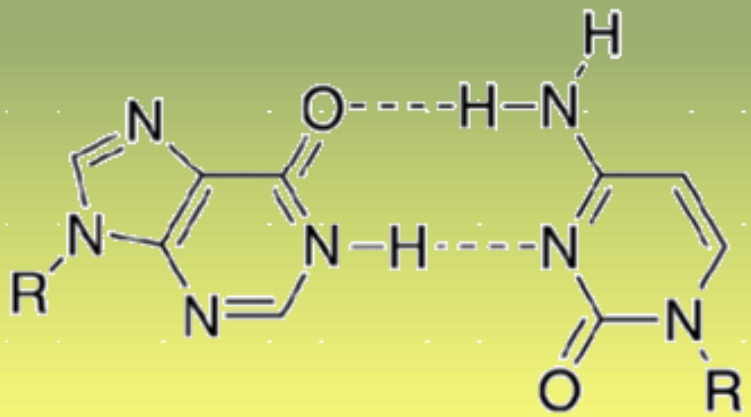
At high concentration nitrites can turn hemoglobin into methemoglobin:

$$\mathbf{HbFe^{2+} + NO_2^- \rightarrow HbFe^{3+} + NO}$$

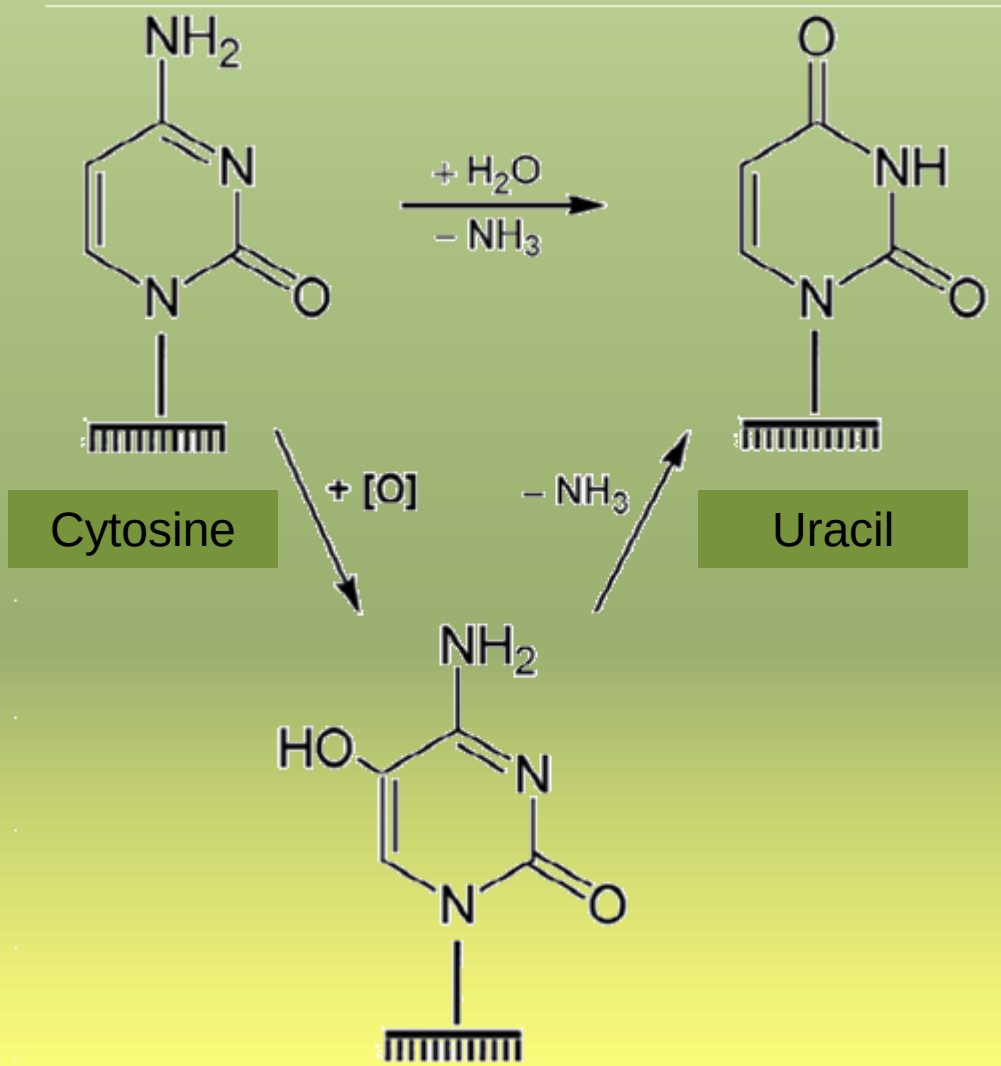
Nitrates act in the similar manner.



Adenine : Thymine



Inosine : Cytosine



5-hydroxy-cytosine

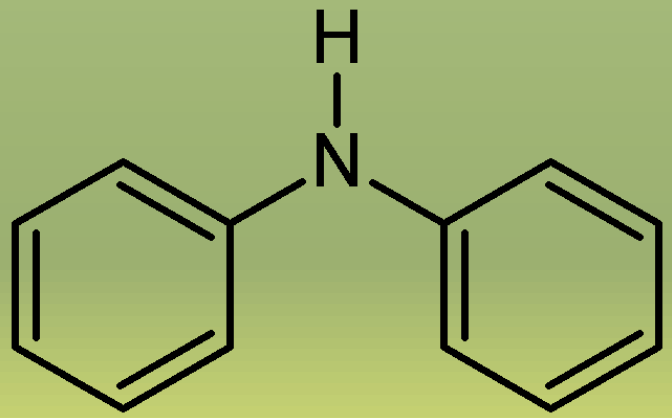
Organic nitrites (**R—O—N=O**) and organic nitrates (**R—O—NO_2**) are vasodepressors and can help to relieve ischemic heartache. Enzymes covert them to **NO**.

The most widely used ones is nitroglycerol.

$NaNO_2$ is not recommended now, since it can cause metheboglobin hypoxia.

Test reaction for nitrates NO_3^-

Diphenylamine solution **$(C_6H_5)_2NH$** in concentrated sulfuric acid gives deep blue color with nitrates because of the oxidation of diphenylamine by produced nitric acid.



Nitrites also give the same color with diphenylamine solution, but in the presence of a more dilute sulfuric acid.

Thank you for listening!!!