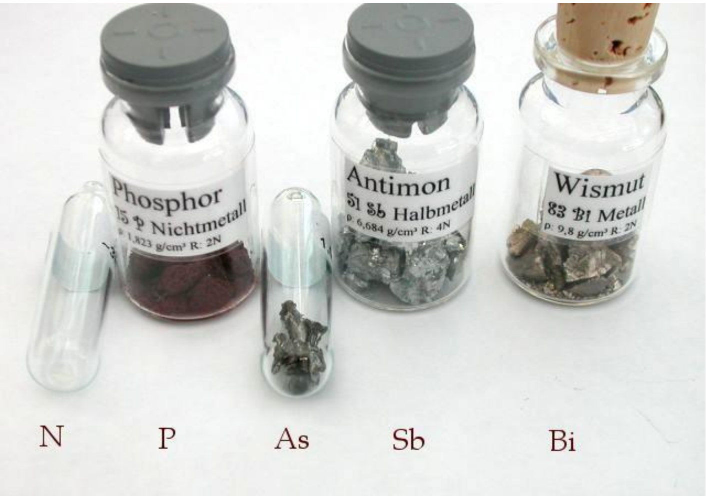
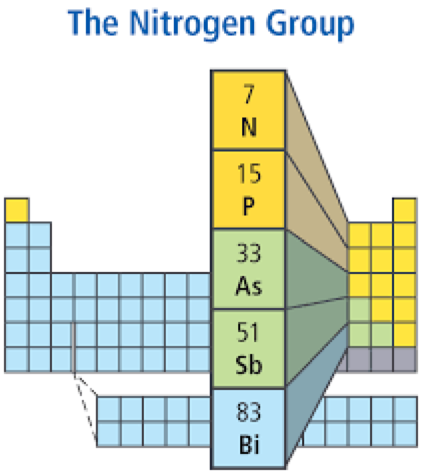
Group 15 (‘The Pnictogens’)





Bond Strength Trends

- Lone pair repulsion weakens N-N single bond.
- The optimum pπ-pπ orbital overlap is found for the N-triple bond.
- The N-triple bond strength (942 kJ/mol) is more than 50 % greater than 3 times the N-N bond strength (600 kJ/mol) → N_2 is a diatomic gas.
- The P-triple bond strength (480 kJ/mol) is about 30 % less than 3 times the P-P bond strength (630 kJ/mol) → P_4 (white phosphorous) is a single bonded tetrahedral molecule.

	D(kJ/mol)		D(kJ/mol)		D(kJ/mol)
C-C	346	N-N	160-200	P-P	210
C=C	602	N=N	400	P=P	(330)
C≡C	835	N≡N	942	P≡P	480

Nitrogen

- Nitrogen was discovered by the Scottish physician Daniel Rutherford in 1772. He removed oxygen and carbon dioxide from air and showed that the residual gas would not support combustion or living organisms. They called it “burnt" or" dephlogisticated air,” which meant air without oxygen.

- It is the fifth most abundant element in the universe and makes up about **78% of the earth's atmosphere**.

- Nitrogen is obtained from liquefied air by fractional distillation.

- The largest use of nitrogen is for the production of ammonia (NH_3).

- Nitrogen gas is largely inert and is used as a protective shield. Liquid nitrogen (**bp: – 196 °C**) is an inexpensive cryogenic liquid used for refrigeration, preservation of biological samples and for low-temperature scientific experimentation.

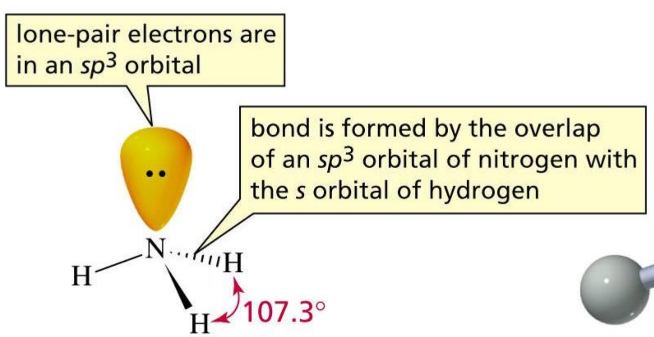
Liquid nitrogen tank of the BCH

Nitrogen

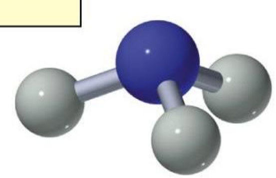
http://www.youtube.com/watch?v=MvatmPlKOYQ

Ammonia (NH_3)

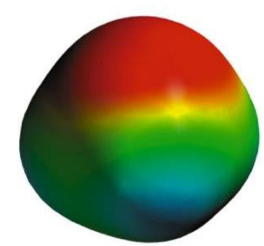
- NH_3 is a colorless gas with a strong odor.
- It is easy to liquefy (bp: **– 33 °C**) and the liquid can be used as a solvent for many salts.
- NH_3 is **well soluble in water**: 772 l of NH_3 can be dissolved in 1 l of water at 15 °C. The resulting solutions are basic.
- The hydrogen atoms can be replaced by metals → '**amides**' (e.g. $NaNH_2$) , '**imides**' (e.g. CaNH) and '**nitrides**' (e.g. Mg_3N_2).



NH_3
ammonia



ball-and-stick model of ammonia



electrostatic potential map for ammonia

Technical Production of NH_3: The Haber-Bosch Process

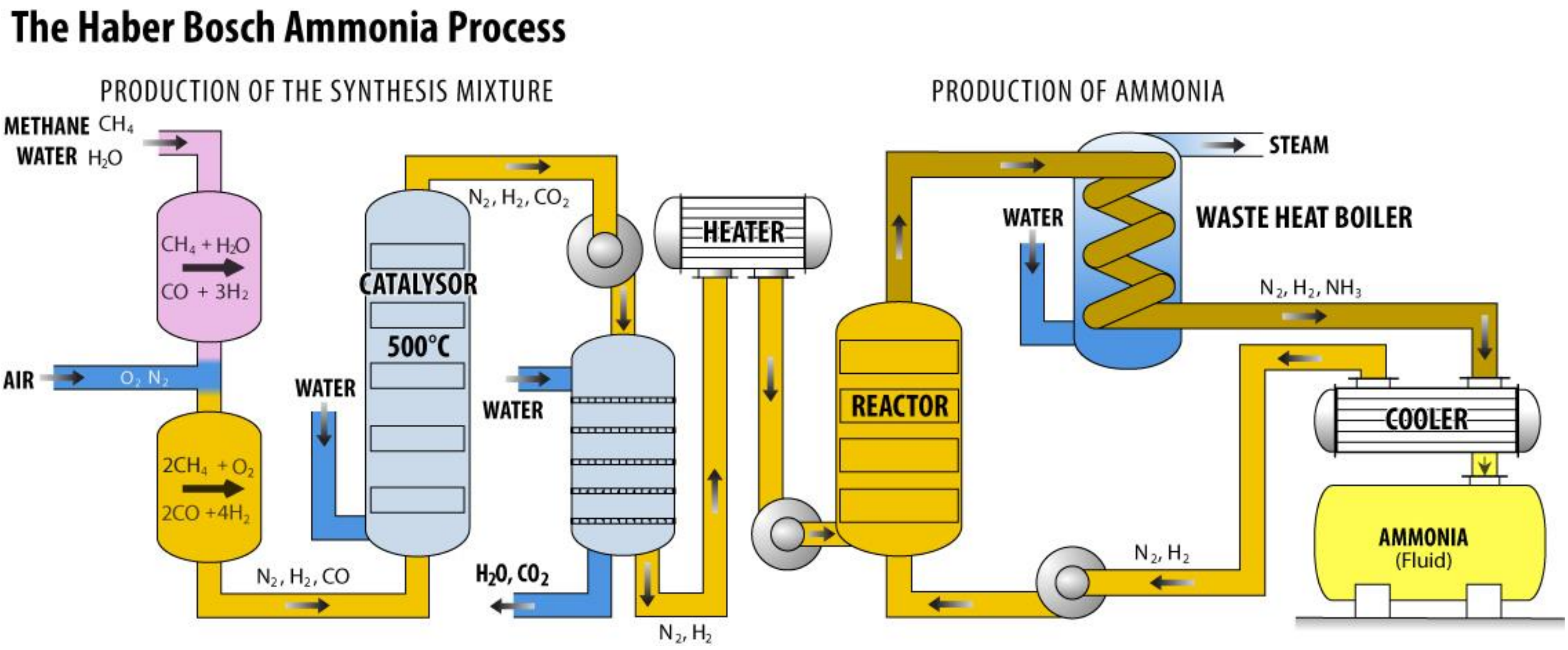
$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \qquad \Delta G° = -\,7.7\ \text{kcal/mol}$$

25 °C / 1 bar:	96 % NH_3
450 °C / 1 bar:	0.2 % NH_3
450 °C / 300 bar:	35 % NH_3

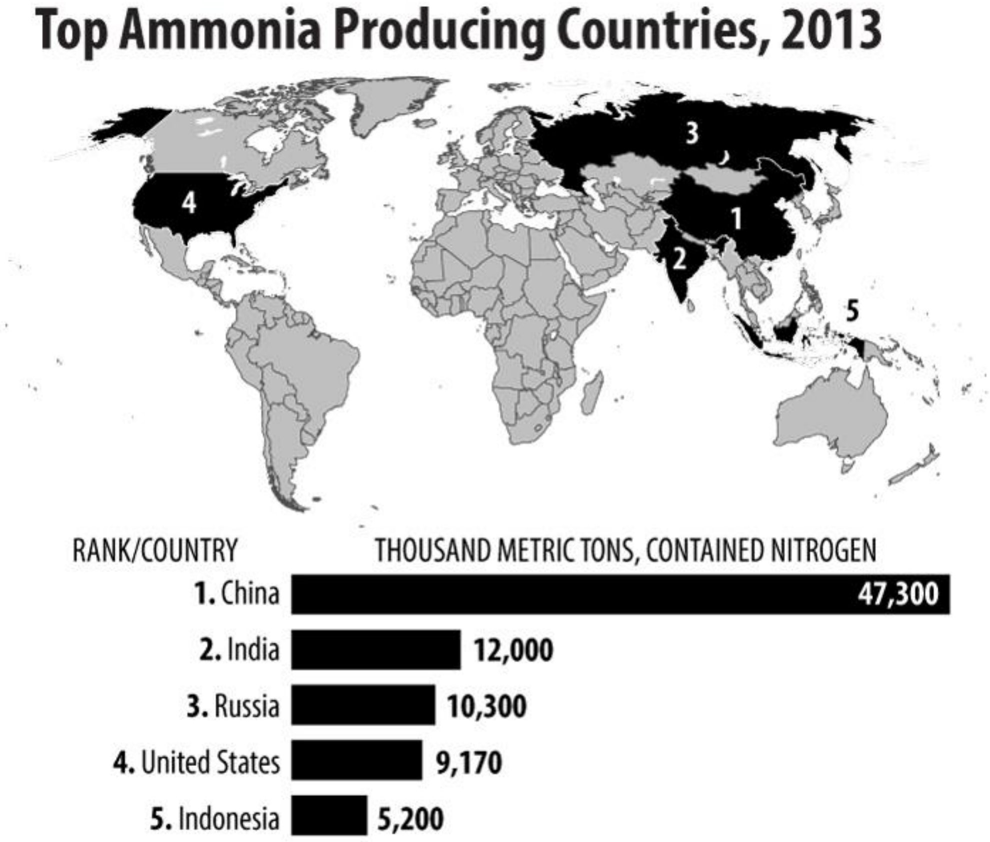
Fritz Haber
Nobel Prize in 1919

Carl Bosch
Nobel Prize in 1931

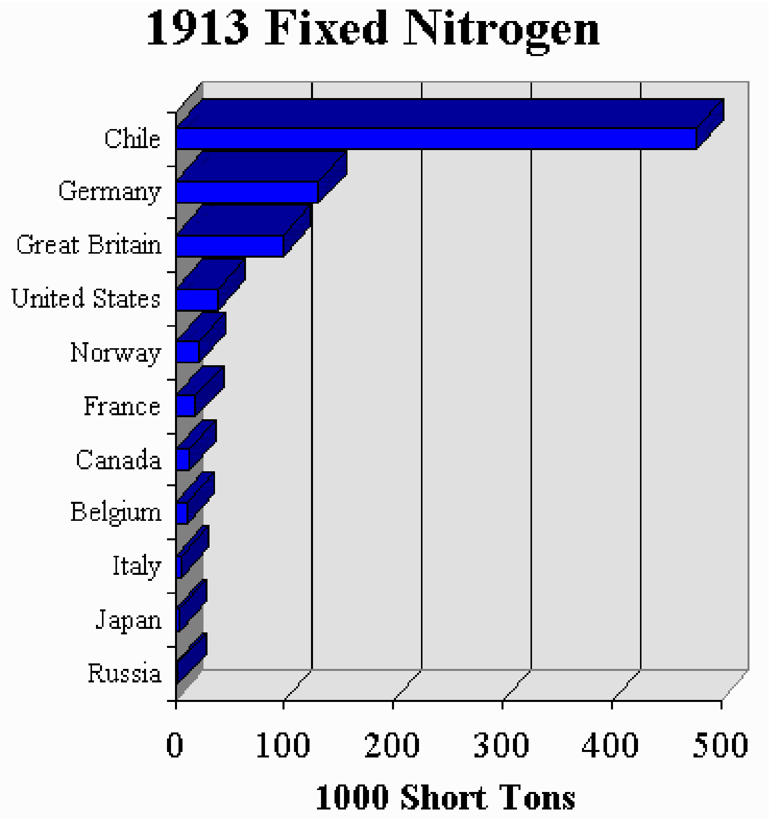
Technical Production of NH_3: The Haber-Bosch Process

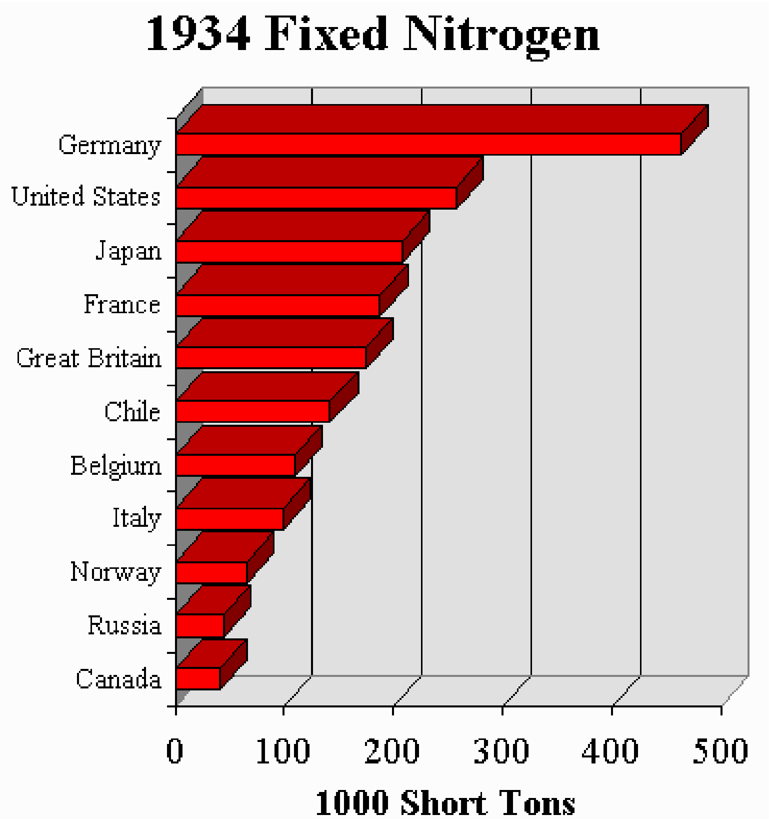


Technical Production of NH_3: The Haber-Bosch Process



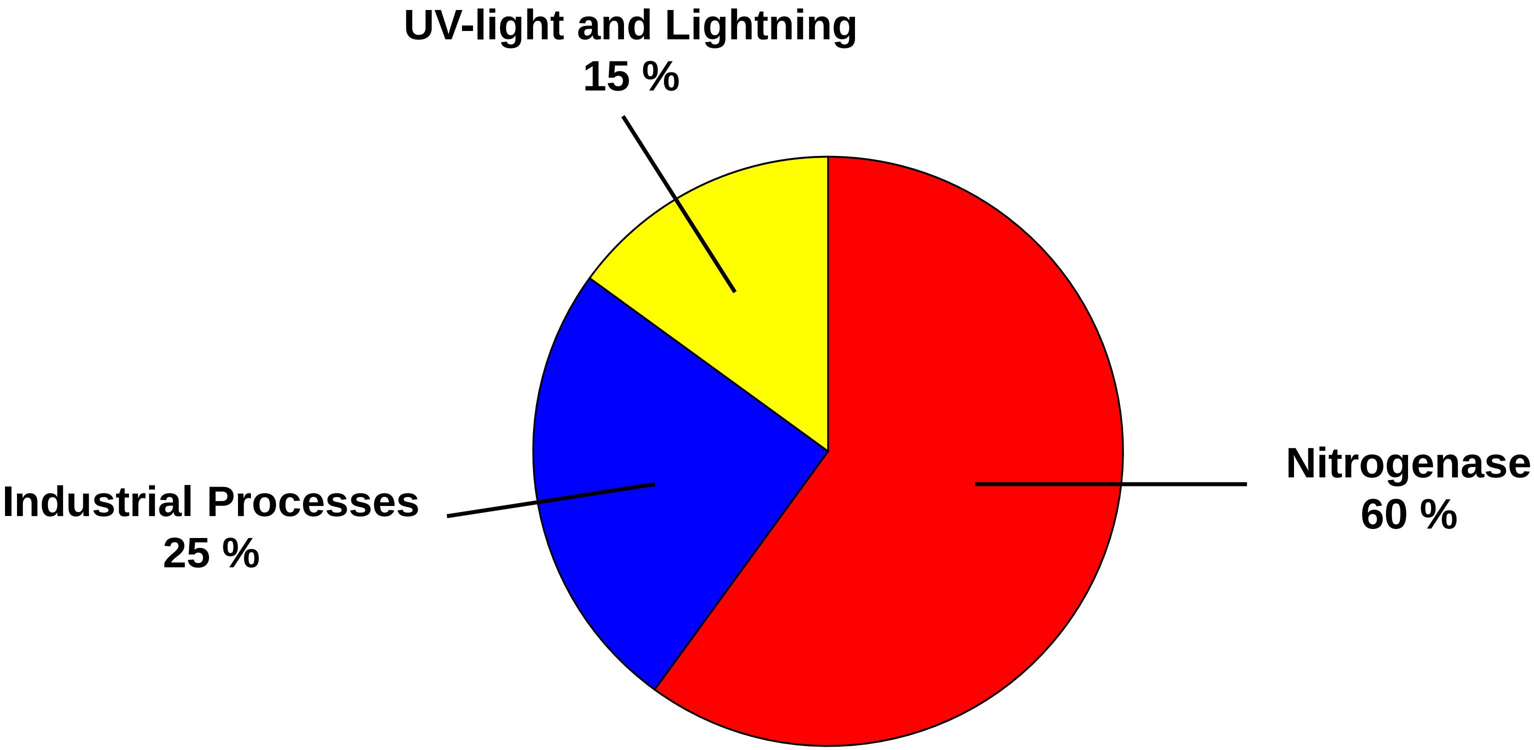
Historical Significance of the Haber-Bosch Process





Chile saltpeter ($NaNO_3$), accounted for more than 60% of the world's supply for most of the 19th century. Many historians and scientists think that Germany would have run out of nitrates by early 1916 if it had not been for German scientific discoveries and their industrial technology.

Nitrogen Fixation – A Comparison



Overall: approx. 280 Mt / year
80 % of the technical production goes into fertilizers

NH_3 and CO_2

Industrial ammonia production emits more CO_2 than any other chemical-making reaction. Chemists want to change that

Scientists around the world are working to reduce how much greenhouse gas the ammonia-making process emits

by *Leigh Krietsch Boerner, special to C&EN*

JUNE 15, 2019 | APPEARED IN **VOLUME 97, ISSUE 24**

Link to C&EN article

157.3 million:
Metric tons of NH_3 produced worldwide in 2010

451 million:
Metric tons of CO_2 emitted by NH_3 synthesis worldwide in 2010.

~1%:
Percentage of global CO_2 emissions that come from NH_3 synthesis.

Energy

H_2 Production

"CO_2 emissions from hydrogen production account for more than half of those from the entire ammonia production process."

"In total, from hydrocarbon feedstocks to NH_3 synthesis, every NH_3 molecule generated releases one molecule of CO_2 as a coproduct."

NH_3 and CO_2

The Siemens green ammonia test plant uses wind power to convert hydrogen and nitrogen to ammonia.

“The small plant, set up in shipping containers, takes electricity from a wind turbine, runs it through a hydrogen electrolysis unit, and then uses the resulting hydrogen to synthesize ammonia. … It’s a small-scale, proof-of-principle system.”

“Ammonia synthesis at a wind farm could help solve one of the biggest problems with renewable energy sources—they produce energy intermittently. … Similar to gasoline, ammonia can be shipped and stored, and it is easier to deal with than gaseous hydrogen, another possible carbon-free fuel”

The Ammonium Ion (NH_4^+)

Solutions of NH_4^+ salts are acidic:

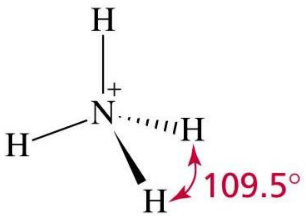
$$NH_4^+ (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + NH_3 (aq)$$

acidic solution

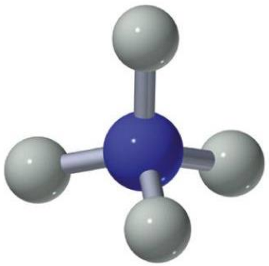
Salts can dissociate and evaporate on heating:

$$NH_4Cl (s) \rightleftharpoons NH_3 (g) + HCl (g)$$

'smelling salts'



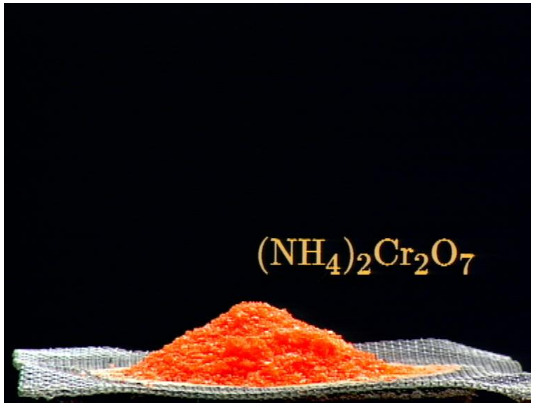
$^+NH_4$
ammonium ion



ball-and-stick model of the ammonium ion

electrostatic potential map for the ammonium ion

The Ammonium Dichromate Volcano

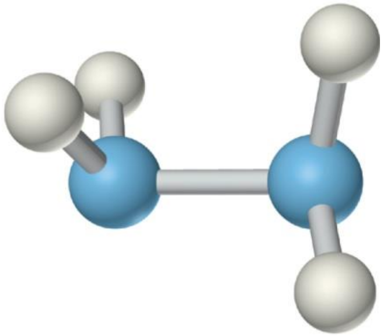


Ammonium dichromate volcano

$$(NH_4)_2Cr_2O_7\,(s) \xrightarrow{\text{heat}} N_2(g) + Cr_2O_3\,(s) + 4\,H_2O\,(l)$$

Hydrazine (N_2H_4)

- Hydrazine is a colorless liquid.
- The two NH_2 groups adopt a 'gauche' conformation.
- The N-N single bond is not very strong → upon heating, hydrazine decomposes in an explosion to NH_3 and N_2 (aqueous solutions can be handled without danger).
- A mixture of hydrazine and hydrogen peroxide can be used as a rocket fuel:



$$2\,H_2O_2\,(l) + N_2H_4\,(l) \longrightarrow N_2\,(g) + 4\,H_2O\,(g)$$

$$\Delta H_{rx} = -707\ \text{kJ/mol}$$

Hydrogen Azide (HN_3)

- Hydrogen azide is a poisonous, colorless liquid, which forms an acidic solution in water:

$$HN_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + N_3^-(aq)$$

- Hydrogen azide is **highly explosive**, producing a mixture of hydrogen and dinitrogen:

$$2\ HN_3(l) \longrightarrow H_2(g) + 3\ N_2(g)$$

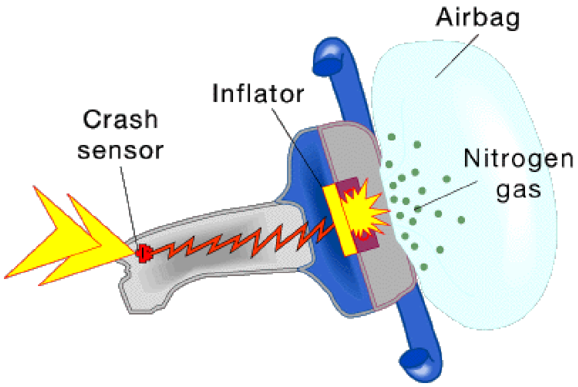
- The **salts are called 'azides'**. They are widely used in the explosive industry (e.g. $Pb(N_3)_2$ as a shock-sensitive detonator).

NaN_3

- NaN_3 decomposes rapidly when heated but is stable at room temperature.

- Applying an electrical spark initiates the rapid decomposition:

$$2\ NaN_3\ (s) \xrightarrow[\text{discharge}]{\text{electrical}} 2\ Na\ (s) + 3\ N_2\ (g)$$



Nitrogen Halides

- **NF_3** is the most stable of the nitrogen halides. It is prepared by the direct reaction of ammonia and fluorine:

$$4\ NH_3 + 3\ F_2 \longrightarrow 3\ NH_4F + NF_3$$

- **NCl_3** and **NBr_3** easily explode to give their constituent elements. Indeed, P. L. Dulong, who first prepared NCl_3 in 1811, lost an eye and three fingers while studying its chemical properties.

- Until recently NI_3 had only be prepared as the ammonia adduct **$2NI_3$ x NH_3**. The ammonia-free NI_3 **explodes at room temperature**.

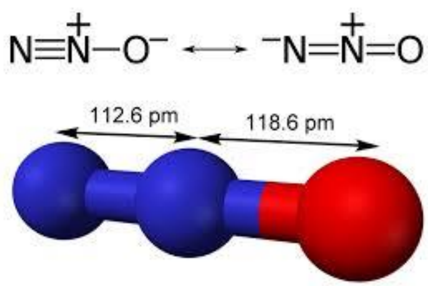
Nitrogen Triiodide (NI_3)

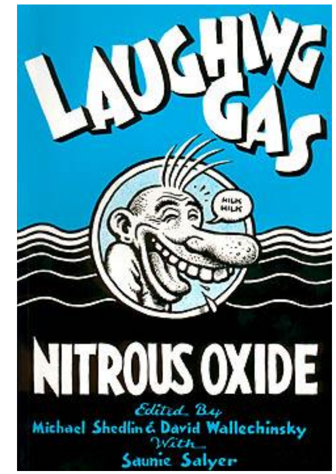
$2NI_3$ x NH_3 is a black powder produced when iodine crystals are added to a solution of concentrated aqueous ammonia. While the crystals of NI_3 are wet, they are stable, but when the substance dries off, the NI_3 is touch-sensitive, and decomposes explosively to produce nitrogen gas and iodine vapor.

$$2NI_3 \text{ x } NH_3 \longrightarrow 3\ I_2 + N_2 + 2\ NH_3$$

Dinitrogen Monoxide (N_2O) – 'Laughing Gas'

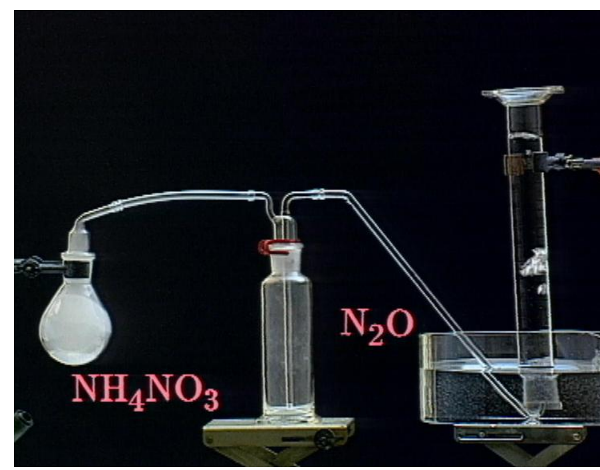
- N_2O is a non-toxic, odorless and tasteless gas.
- It has a linear geometry; **isoelectronic to CO_2** and N_3^-.





- When inhaled it produces insensibility to pain preceded by mild hysteria, sometimes laughter.
- N_2O can be prepared by *careful* thermal decomposition of ammonium nitrate:

$$NH_4NO_3 \overset{\Delta}{\rightleftharpoons} NH_3 + HNO_3 \xrightarrow{200\ °C} N_2O + 2\ H_2O$$



Dinitrogen Monoxide (N_2O)

Laughing gas party
1839

N_2O as anesthetic
1844

Whipping agent

Childbirth

Dinitrogen Monoxide (N_2O)

ATMOSPHERE

Nitrous Oxide: No Laughing Matter

Donald J. Wuebbles

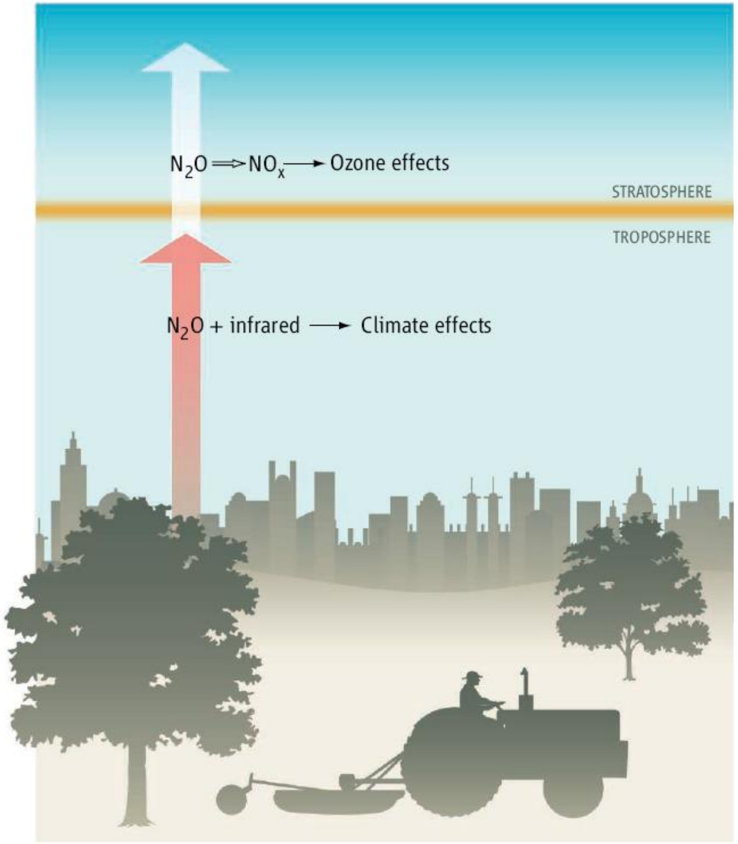
Rising atmospheric concentrations of nitrous oxide are contributing to global warming and stratospheric ozone destruction.

Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

By comparing the ozone depletion potential–weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

2 OCTOBER 2009 VOL 326 SCIENCE



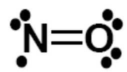
$$NO + O_3 \rightarrow NO_2 + O_2$$

$$O + NO_2 \rightarrow NO + O_2$$

$$\text{net: } O + O_3 \rightarrow 2O_2$$

Nitric Oxide (NO)

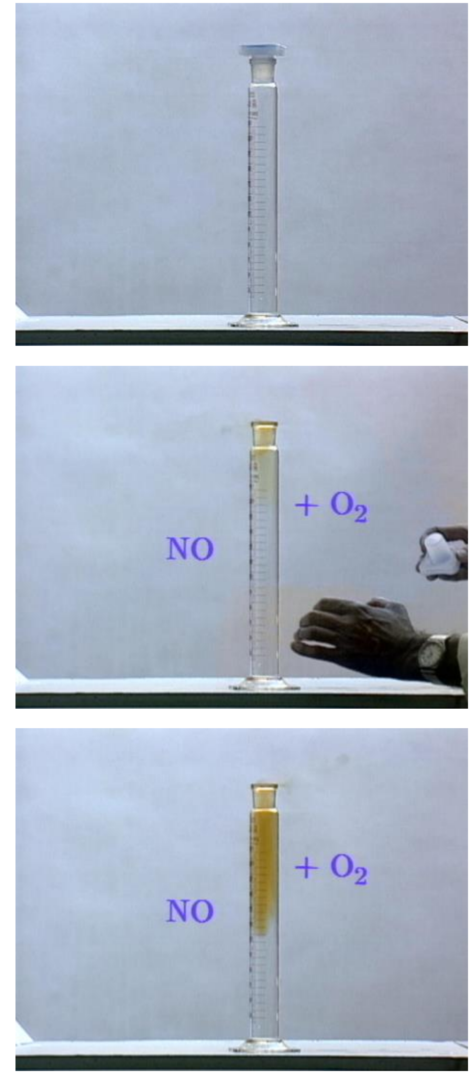
- NO has one unpaired electron (corresponds to CO plus one extra e^- in an antibonding orbital).



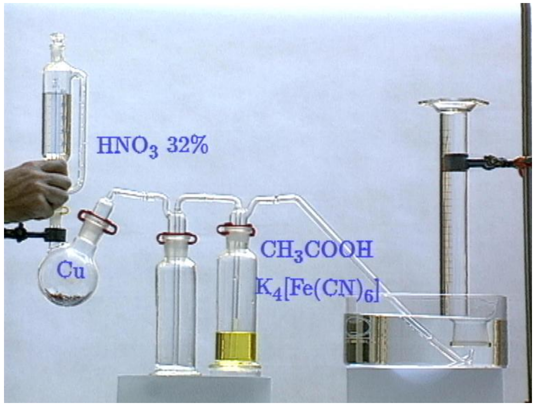
- NO has little tendency to dimerize to N_2O_2.
- Easily oxidized to NO^+ (nitrosyl cation); NO^+ is isoelectronic to CO and has an extensive metal chemistry.
- NO reacts rapidly with O_2:

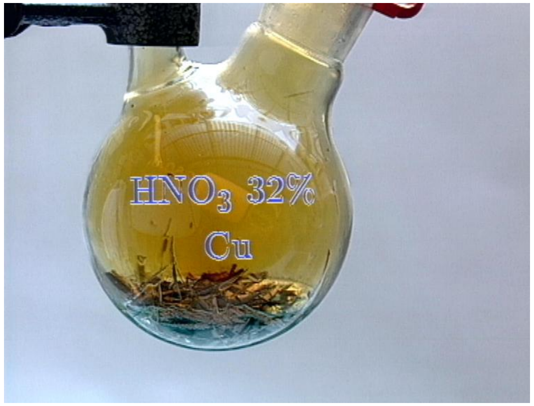
$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

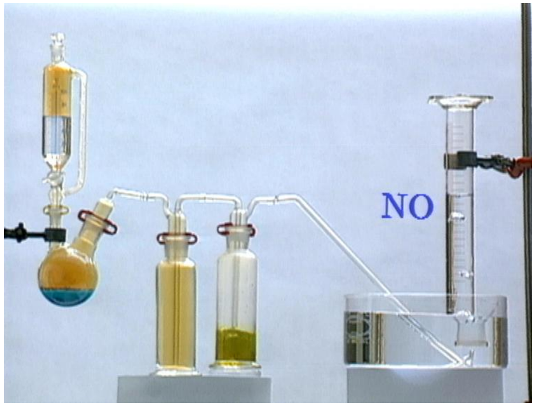
brown



Synthesis of NO





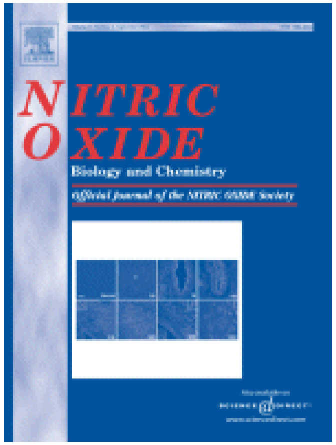


$$3\ Cu + 8\ HNO_3 \longrightarrow 2\ NO + 3\ Cu(NO_3)_2 + 4\ H_2O$$

Industrial production of NO is accomplished through catalytic combustion of ammonia, and in the laboratory it is produced through the reduction of nitric acid.

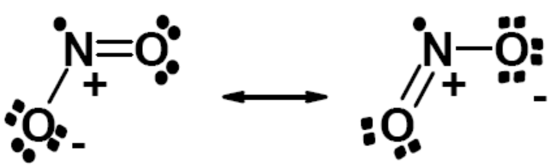
The Physiological Role of NO

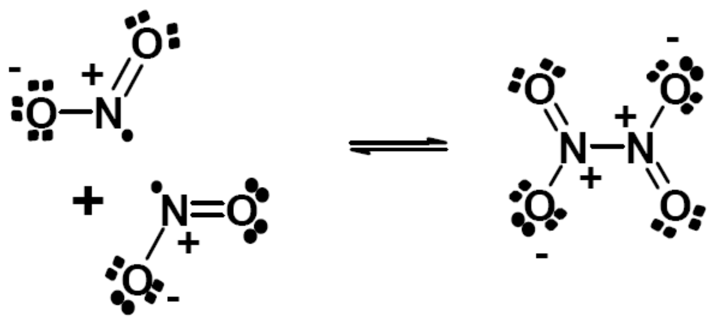
- **1979**: First described as a potent relaxant of peripheral vascular smooth muscle.
- **1992**: Molecule of the year of the journal *Science*.
- **1998**: Nobel Prize for Medicine.
- Used by the body as a signaling molecule.
- Serves different functions depending on body system. i.e. neurotransmitter, vasodilator, bactericide.
- ‘Nitro’ heart drugs like nitroglycerine and amyl nitrite lower the blood pressure by increasing the NO concentration.



NO_2 and N_2O_4

- **NO_2 is a radical** with a bond order of 1.5.
- NO_2 **dimerizes at low temperatures** but the N-N bond is weak.
- It is an important **atmospheric pollutant**.
- It is the oxidation product of NO.

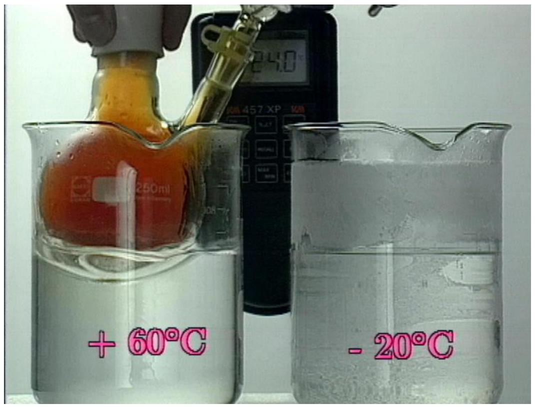


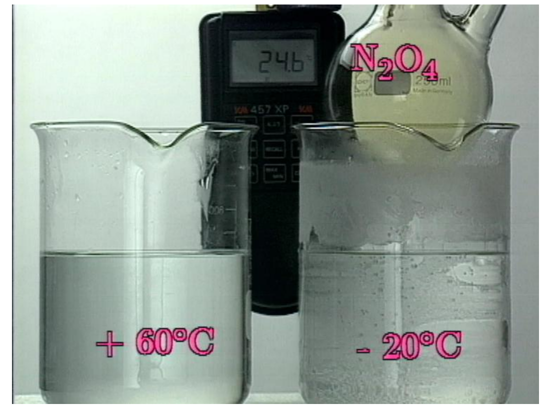


brown
paramagnetic

colourless
diamagnetic

The NO_2 – N_2O_4 Equilibrium

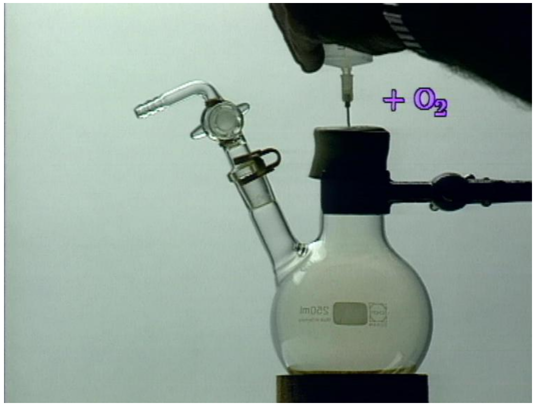


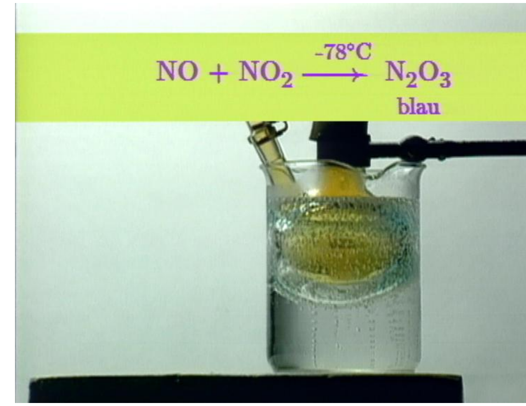


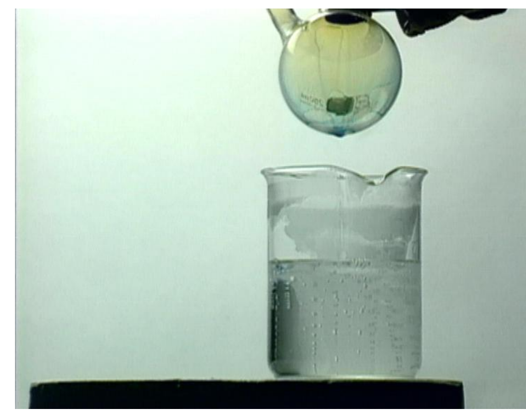
$$2\ NO_2 \rightleftharpoons N_2O_4 \qquad \Delta H° = -57.2\ \text{kJ/mol}$$

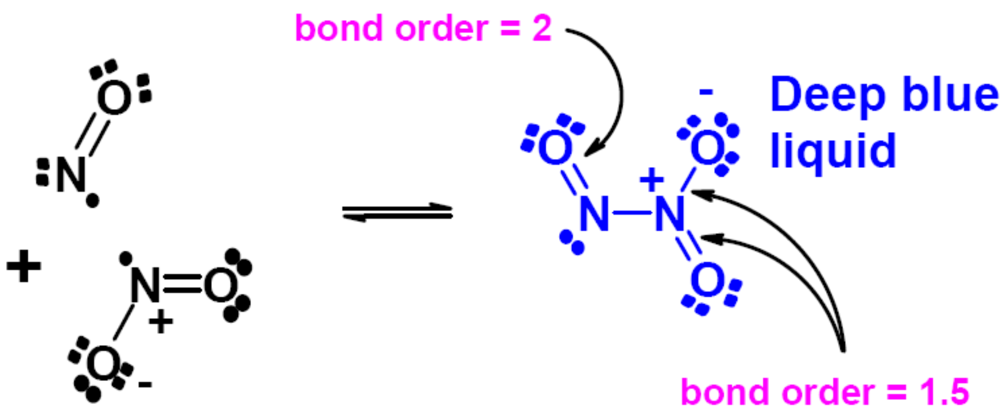
The change in color is due to the equilibrium between the brown, paramagnetic nitrogen dioxide and the colorless, diamagnetic dinitrogen tetroxide. At low temperatures, N_2O_4 predominates, with hardly any NO_2 present.

Dinitrogen Trioxide (N_2O_3)





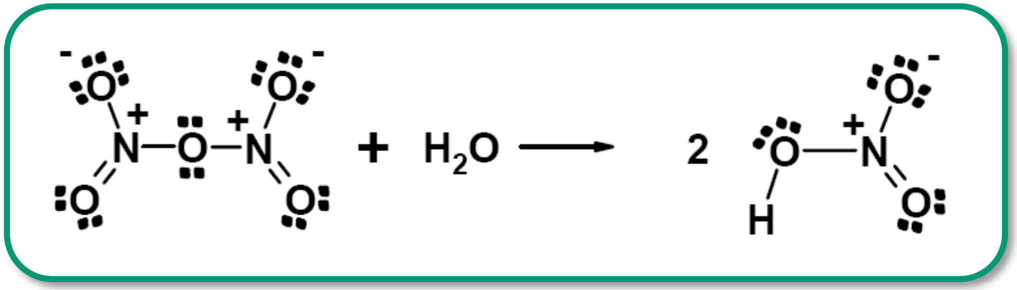


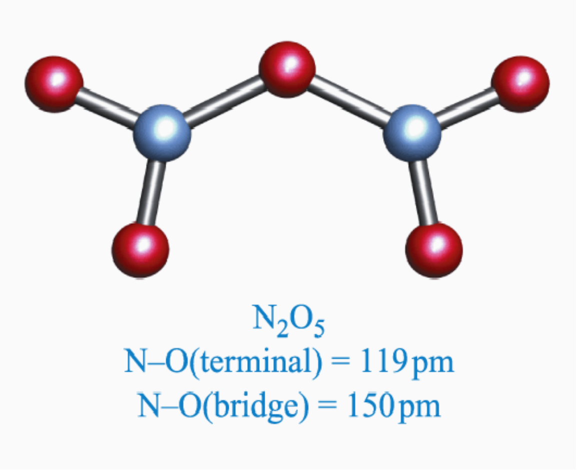


Formed as a blue liquid upon cooling of a mixture of the radicals NO and NO_2.

Dinitrogen Pentoxide (N_2O_5)

Anhydride of nitric acid





Environmental Problems of NO_x Gases

- NO and NO_2 are **collectively known as NO_x** and are familiar as one of the several components of automobile exhaust that create smog. In the hot combustion chambers of a car's engine, N_2 and O_2 react together to form NO. This process is normally unfavorable, but at high temperatures in the combustion chamber the reaction proceeds rapidly.

- Once released into the atmosphere, NO reacts to form NO_2, which is familiar as the brown hazy color of smog.

- NO_2 can then be split apart by ultra-violet radiation from the sun, to produce oxygen atoms. These then react with oxygen molecules to make ozone.

- NO_2 (along with SO_2) dissolves in the water droplets of clouds to give acids (HNO_3 and HNO_2). This corrosive mixture can then fall back to Earth as 'acid rain', which can be as acidic as lemon juice (pH 2.2-2.7).

Smog in Mexico City

Nitrogen Oxides – Summary

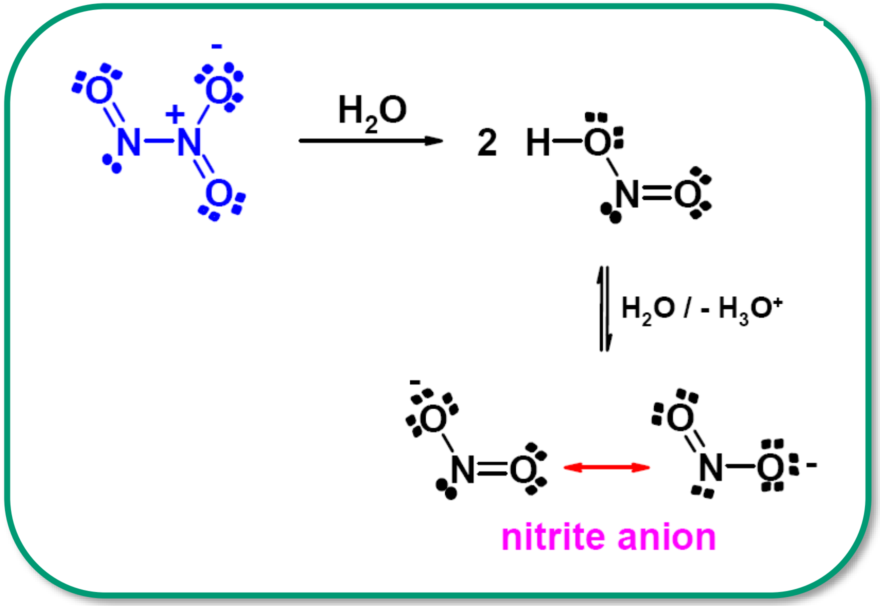
Oxidation State	+1	+2	+3	+4	+5
N-Oxides	N_2O	**NO** N_2O_2	N_2O_3	**NO_2** N_2O_4	N_2O_5

- The nitrogen oxides are – with the exception of N_2O_5 – metastable, endothermic compounds, which decompose upon heating to the elements.
- The oxides **NO** and **NO_2** have an unpaired electron but are radicals which are stable at room temperature. They are in equilibrium with the diamagnetic dimers.

Nitrous Acid (HNO_2)

- Nitrous acid, HNO_2, is formed upon dissolving N_2O_3 in water or upon addition of acids to nitrite salts.

- It has not been isolated as a pure compound. At room temperature, it readily decomposes to nitric acid and NO, the latter reacting further to yield brown fumes of NO_2:



$$3\ HNO_2 \longrightarrow HNO_3 + 2\ NO + H_2O$$

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

(→ Video)

Sodium Nitrite ($NaNO_2$)

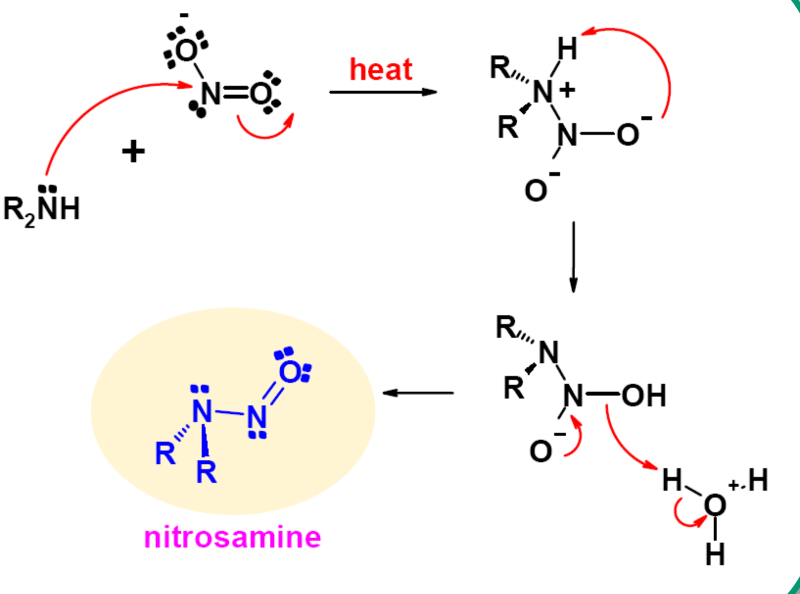
- $NaNO_2$ is used as a food preservative to inhibit bacterial growth. The nitrite ions (NO_2^-) in these meats inhibit the growth of a bacterium (*Clostridium botulinum*) which causes the fatal food poisoning known as *botulism*.

- It is also used because it fixes the bright red color of fresh meat, which would otherwise quickly fade to an unpalatable brown .

- But: cooking converts residual nitrite to nitrosamines – known carcinogens.

$$2\,H^+ (aq) + NO_2^- + Fe^{2+} \longrightarrow Fe^{3+} + NO + H_2O$$

intense red **(heme)Fe-NO**
binds as NO^+
isoelectronic with CO



Nitric Acid (HNO_3)

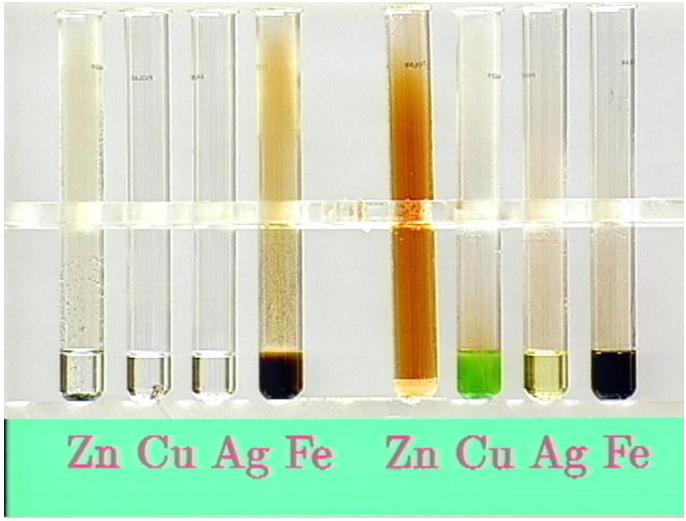
- HNO_3 is made on industrial scale by the Ostwald process.
- 100% pure, anhydrous nitric acid is a colorless anhydrous solid. What we call **'concentrated nitric acid'** is actually a solution of **68% by weight HNO_3** in water.
- HNO_3 is **strongly oxidizing**.
- **Aqua Regia** (approx 3 vols HCl to 1 vol HNO_3) attacks even the inert metals gold and platinum.

Nitric Acid and Metals

- Zinc metal reacts with 10% HNO_3.
- 10% HNO_3 does not dissolve copper.
- Silver does not react with 10% HNO_3.
- Iron reacts violently with diluted nitric acid.

- Zinc metal reacts with 65% nitric acid extraordinary strong.
- Copper is dissolved under formation of green copper(II) nitrate.
- Silver nitrate is produced with concentrated nitric acid.
- Iron does not react with 65% HNO_3 because of passivation.

10 % HNO_3 65 % HNO_3



The Ostwald Process

HNO_3 is made from ammonia by the *Ostwald Process* (developed in 1902 by the German chemist Wilhelm Ostwald, who got the Nobel prize in 1909). This process reacts together O_2 and NH_3 at 850°C and 5 atmospheres pressure, with the help of platinum and rhodium catalysts, to make NO. This is then oxidized to NO_2, which is then dissolved in water to make HNO_3.

Stage 1 primary oxidation

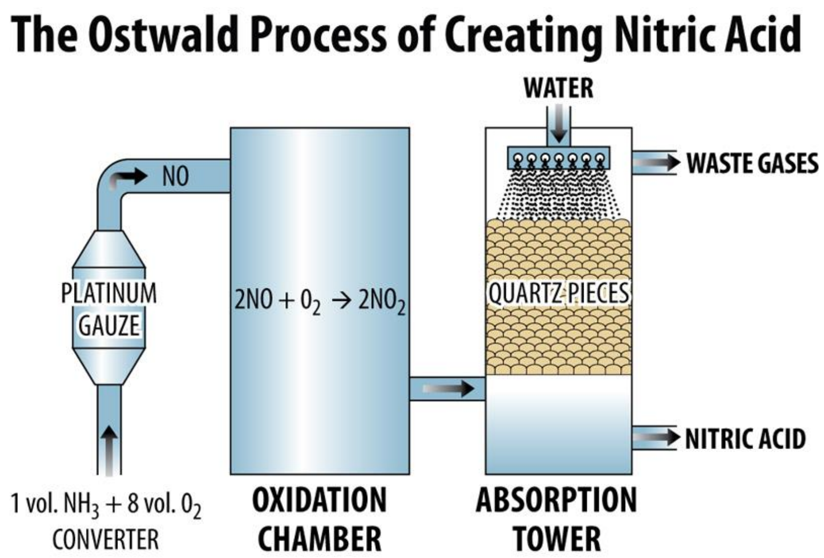
$$4\,NH_3\,(g) + 5\,O_2\,(g) \xrightarrow[\text{gauze}]{\text{Pt}} 4\,NO\,(g) + 6\,H_2O\,(g)$$

Stage 2 secondary oxidation

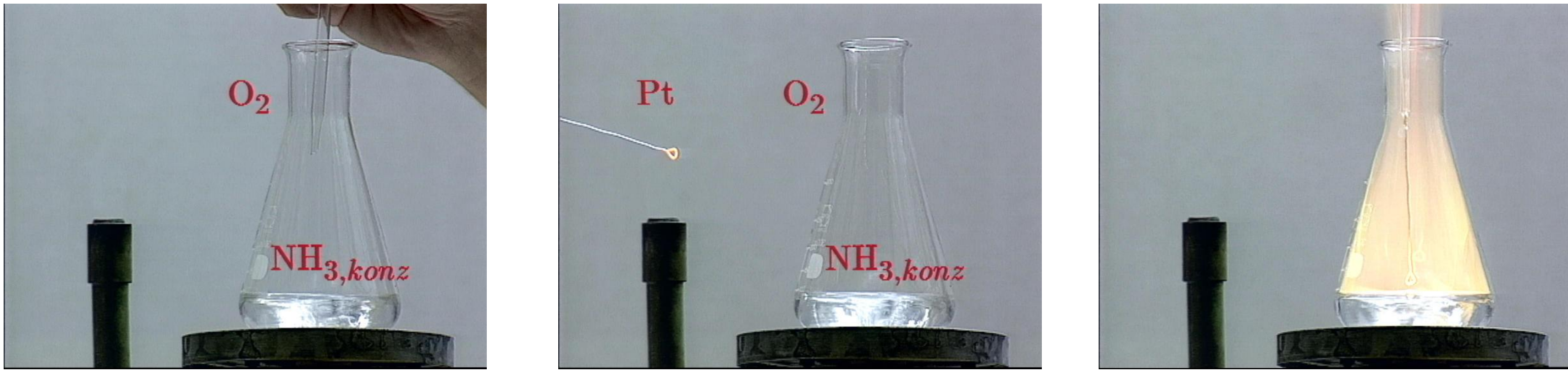
$$2\,NO\,(g) + O_2\,(g) \longrightarrow 2\,NO_2\,(g)$$

Stage 3 disproprtionation and hydration

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(l) + \underset{\text{recycle}}{NO\,(g)}$$



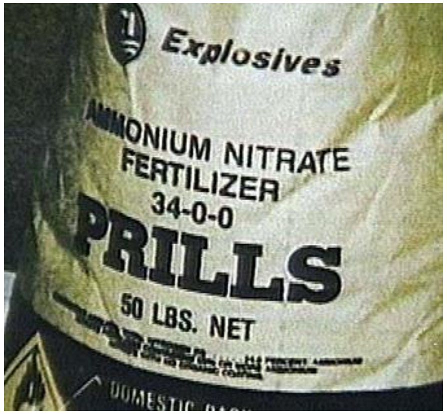
The Catalytic Oxidation of Ammonia



- An Erlenmeyer flask containing conc. ammonia solution is filled with oxygen. The glowing platinum loop is introduced into the NH_3 / O_2 atmosphere and a spontaneous self ignition occurs.
- Cr_2O_3 can also be used as the catalyst.

Ammonium Nitrate (NH_4NO_3)

- The biggest (80%) use of nitric acid is in making ammonium nitrate, NH_4NO_3.
- NH_4NO_3 is an ingredient in many gunpowder recipes, and is an important **explosive** in its own right, but is **mainly used as an agricultural fertilizer**.



NH_4NO_3 is one of the most commonly used fertilizers.

It works!
(half ton pumpkin)

Ammonium Nitrate (NH_4NO_3)

Ammonium nitrate explosion in Beirut 2020
(218 dead, ~ 300'000 homeless)

Ammonium nitrate explosion in Oppau in 1921
(561 dead, > 7000 homeless)

(→ Video)

Hydroxylamine (NH_2OH)

- Hydroxylamine is the hydroxy derivative of ammonia. It is a colorless solid.

- It slowly decomposes at room temperature – at 100 °C it explodes to give NH_3, N_2 and H_2O:

$$3\ NH_2OH \longrightarrow NH_3 + N_2 + 3\ H_2O$$

- More stable is the salt $[NH_3OH]Cl$ ('hydroxylamine hydrochloride').

Hydroxylamine was involved in recent accidents: An explosion at Concept Sciences, Pennsylvania, on February 19, 1999, which killed five people, injured at least 13, and destroyed a 45,000-ft2 structure.