Nitrate and nitrogen compounds

Nitrogen

from Latin: Nitrogenium

from Greek:

\(\text{νιτρον}\) (nitron) = salpeter,
\(\text{γενής}\) (genes) = forming

Nitrate / Nitric acid

- Nitrate and ammonia salts were already used by alchemists
- Ammonia: name derived from Temple of Jupiter, Ammon, Libya, where it was produced by distilling camel dung
- Nitric acid (HNO\(_3\)) was called *aqua fortis*
- A mixture of nitric acid with hydrochloric acid (HCl) was known as *aqua regina* (royal water, Königswasser) \(\rightarrow\) ability to dissolve gold
Nitrogen is considered to be discovered by the Scottish physician Daniel Rutherford in 1772 (called it: noxious air or fixed air)

Nitrogen also was studied at the same time by Carl Wilhelm Scheele, Henry Cavendish and Joseph Priestly (burnt air or phlogisticated air → phlogiston theory)

Antoine-Laurent de Lavoisier (father of modern chemistry) called it azote from Greek ἄζωτος (azotos = lifeless), as animals died in it and flames extincted → used in many languages (French, Russia)

Nitrate

Nitrates are salts and esters of the nitric acid

Nitrate anion

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{N} \\
\text{O} \\
\end{array}
\]

Ester of nitric acid

\[R-O-N=O\]
Nitrate

Applications

From a Taoist text tentatively dated to the mid-800s

Some have heated together sulfur, realgar, and saltpeter with honey; smoke and flames result, so that their hands and faces have been burnt, and even the whole house where they were working burned down.

- What was this for?

Nitrate

Applications

Gunpowder

- 15% charcoal, 10% sulfur, 75 % potassium nitrate
- Presumably discovered in the 9th century by Chinese alchemists searching for an elixir of immortality
- Gunpowder was the only propellant for cannons, guns and portable firearms before development of modern explosives
- Potassium nitrate became a strategic resource
Nitrate / Ammonia

Applications

Consumption of nitrogen compounds is dominated by fertilizers; also used for industrial applications

- nitrogen is a primary nutrient (together with phosphorus and potassium) → plant growth and increased yield
  - Ammonia (H\(_\text{N}_3\)) → fertilizers (97 % of N-fert. from ammonia), industrial uses, chemical feedstock
  - Nitric acid (HNO\(_3\)) → Osterwald process
  - Ammonium nitrate (NH\(_4\)NO\(_3\)) (concentrated N-fertilizer, explosives, synthetic fibers, foams)

Nitrate ore

The only commercially exploitable source of nitrate ore exists in Chile:

- Occurs in a 700 km long, narrow belt of the Atacama dessert
- Nitrate is concentrated in a layer called caliche
- Caliche rests on coba and under an overburden of costra and chuca
- Caliche is often a 1 m thick layer of white, brown or black color

Other minor deposits exist in: Egypt, Asia Minor, Columbia and California
Nitrate ore

Minerals in the chalice:

• Salpeter (KNO$_3$)
• Nitratine (NaNO$_3$)
• Bloedite (Na$_2$Mg [SO$_4$]$_4$ 4H$_2$O)
• Glauberite (CaNa$_2$ [SO$_4$]$_2$)
• Polyhalite (K$_2$Ca$_3$Mg [SO$_4$]$_4$ 2H$_2$O)
• Darapskite (Na$_2$[NO$_3$]SO$_4$ H$_2$O)
• Lautarite (Ca[I$_2$O$_3$])
• Dietzeite (Ca2[CrO$_4$]([I$_2$O$_3$]$_2$))

Nitrate ore

Composition of ore:

• 7 – 10 % NaNO$_3$
• 4 – 10 % NaCl
• 10 – 30 % Na$_3$SO$_4$
• 2 – 7 % Mg, Ca, K, Br and I
• 1 – 2 % H$_2$O
• 41 – 76 % gangue

⇒ unique mineral deposit as a result of arid climate since middle Miocene; concentrated saline material from sources including ocean spray and local volcanoes
Nitrate deposit

In the Atacama Desert (N-Chile)

War of the Pacific (Salpeterkrieg)

Borderlines before the war
War of the Pacific (Salpeterkrieg)

- 1825 Bolivia declared this area to be part of its territory though it was inhabited to 95% by Chileans
- 1860 large deposits of nitrate was found
- 1866 and 1874 agreed Chile and Bolivia on a border line along the 24th latitude; Chilean companies do not pay taxes for 25 years
- Nevertheless, the Bolivian gouvernement demanded special taxes to finance reconstruction after a severe earthquake in the coastal area
- 1879: Bolivia expropriated the Chilean companies and offered them for sale
- Chilean troupes occupied Antofagasta

War of the Pacific (Salpeterkrieg)

- 1873: Bolivia and Peru had made a secret treaty against Chile
- Chile declared war to Bolivia and Peru
- Chilean forces were superior
- 1880: Bolivia retreated
- 1883: Peace treaty between Chile and Peru → province Tarapacá was added to Chile
- 1884: Peace treaty between Chile and Bolivia → region of Antofagasta was added to Chile, Bolivia lost the direct access to the Pacific Ocean
- As a consequence, Chile possessed the nitrate deposits; mined by British and German companies
- Relationship between the three countries is still troubled today
Nitrate deposit

Nitrate production

- Production of natural nitrate became less important due to synthetic production
- Today nitrate is produced together with iodine and sulfate from caliche
- Iodine has replaced nitrates as the prime product
Nitrate deposit

Sidetrack to iodine

Natural resources of iodine

- Seawater (0.05 ppm) and certain marine organisms including seaweed (up to 0.45 weight-% on dry basis)
- Subsurface brines: gas field brines in young rocks; probably derived from seawater with max. iodine content of 150 ppm (Japan, Indonesia) or from older formations with iodine content up to 1'500 pp (USA)
- Caliche ore (Chile)
Sidetrack to iodine

World production:
1990 $\rightarrow$ 13'000 t
2007 $\rightarrow$ 28'000 t
Sidetrack to iodine

Use of iodine

- Antiseptic agent (iodine tincture, dish-washing detergent, sanitary and industrial disinfectant)
- Additive to table salt
- Radio-opaque agent for X-ray diagnoses
- Agent in photographic emulsion on film and as photographic developer
- Chemical catalyst
- Medication in a radiation emergency to block uptake of radioactive iodine isotopes by the thyroid gland

Synthetic ammonia production

Production of ammonia by the Haber-Bosch process

- Ammonia (NH₃) is produced from nitrogen and hydrogen
- Haber-Bosch process is the dominant process for production of ammonia
- High energy demand: 1.4% of global energy consumption is used separation of hydrogen for ammonia production
Haber-Bosch process

1. Formation of process gas: methane is reacted with steam over a catalyst of nickel oxide
   \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \]

2. Secondary reforming: takes place with the addition of air to convert the methane that did not react during steam reforming.
   \[ 2 \text{CH}_4 + \text{O}_2 \rightarrow 2 \text{CO} + 4 \text{H}_2 \]
   \[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

3. Oxidation of carbon monoxide to carbon dioxide
   \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

4. Removal of carbon dioxide

5. Synthesis of ammonia using a form of magnetite, as the catalyst
   \[ \text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g) \]
Synthetic ammonia production

Ideal parameters for the reaction are:

- Pressure: 250 – 350 bar
- Temperature: 550° C
- Proportion nitrogen : hydrogen = 1 : 3
- Use of a iron(II/III)-oxid Fe$_3$O$_4$ catalyst

Synthetic ammonia production

Importance and historical facts:

- Haber-Bosch process was patented in 1910
- Ammonia is a feedstock for fertilizer (e.g. reaction with CO2 to urea) or by the Osterwalder process to nitric acid
- Ammonium nitrate is a product from ammonia and nitric acid → production of explosives
- Development of the Haber-Bosch process to industrial application was forced in 1914 by the German Chief of General Staff as Germany was cut-off from the supply of natural nitrates
- Speculation: without this process, Germany would not have entered the war or would have had to surrender years earlier
Importance and historical facts:

- Nobel prices for the Haber-Bosch process
  1918: Fritz Haber
  1931: Carl Bosch (together with Friedrich Bergius)
  2007: Gerhard Ertl (for complete theoretical explanation of the process)

- Explosion of the ammonia plant in Oppau in 1921 is considered to be the most severe industrial catastrophe in Germany (561 people were killed)

- In the terrorist attack in Oklahoma city on April 19, 1995, a mixture of ammonium nitrate and fuel was used.

- 40% of nitrogen in a human body in industrialized countries has passed the Haber-Bosch process at least once

Eutrophication

Caspian Sea from orbit
Blooming of algae
Eutrophication

Eutrophication is a result of nutrient pollution (release of sewage, run-off carrying excess fertilizers):

- Excess plant growth (algal bloom)
- Algal bloom $\rightarrow$ high oxygen demand $\rightarrow$ algae die
- Decomposition of organic matter by microorganisms requires more oxygen
- Anoxic conditions: bacteria reduce nitrate to nitrite $\rightarrow$ toxic to fishes
- Formation of sapropel with $\text{H}_2\text{S}$, $\text{NH}_3$ and $\text{CH}_4$

End of the story!