Nitrates and Nitrites

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1. Sodium Nitrate

Sodium nitrate in the form of Chile saltpeter was the most important inorganic nitrogen fertilizer until about 1920; it is the only abundantly occurring mineral nitrate.

1.1. Properties [1]

Sodium nitrate [7631-99-4], Chile saltpeter, Chilean nitrate, $NaNO_3$, M_r 85.00, has an enthalpy of formation $\Delta H = -466.8$ kJ/mol [2], an enthalpy of fusion $\Delta H = +15.7$ kJ/mol [3] and mp 306.8 °C [3]. For pressure dependence of the melting point see [4]. At 25 °C, anhydrous sodium nitrate forms colorless trigonal crystals of space group D_{3d}^{6}; $\varrho_{298} = 2.261$ g/cm^3 [3]; $C_{p, 298} = 93.1$ J mol^{-1} K^{-1} [2]; refractive index at 589 nm $n_\omega = 1.587$, $n_\epsilon = 1.336$ [3]. This modification forms trigonal crystals of space group D_{3d}^{5} at a transition point of ca. 275 °C.

Sodium nitrate does not form hydrated solid phases (Fig. 1). The salt is hygroscopic and readily dissolves in water; at 25 °C, 92.1 g dissolves in 100 g of water [3]; enthalpy of solution
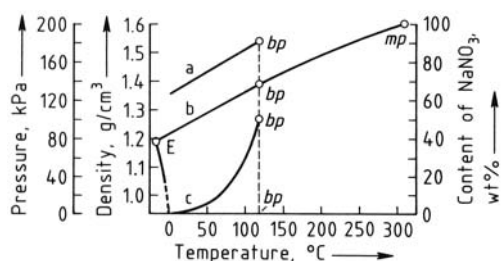
Figure 1. Properties of a saturated solution of sodium nitrate in water a) Density; b) Content of sodium nitrate; c) Vapor pressure bp = boiling point of saturated solution containing 68.5 wt% sodium nitrate at 101.3 kPa and 119 °C; E = cryohydric point: −17.5 ± 0.5 °C, 38.0% sodium nitrate

Table 1. Analyses of caliche samples (composition in wt%)

Salt	1	2	3	4	5
$NaNO_3$	34.2	34.4	43.3	28.5	53.5
KNO_3	1.6				17.3
Na_2SO_4	8.4	1.6	25.3	5.4	1.9
$CaSO_4$	6.3	1.6	30.9	2.7	0.5
$MgSO_4$	2.0	5.4		3.4	1.4
NaCl	32.0	4.0		17.2	21.3

at infinite dilution $\Delta H_{298} = + 20.5$ kJ/mol [3]. Sodium nitrate is soluble in liquid ammonia and forms $NaNO_3 \cdot 4NH_3$ below −42 °C. The solubility of sodium nitrate in anhydrous methanol is 2.8 wt% at 25 °C [5].

Sodium nitrate is an oxidant and releases oxygen on heating:

$$NaNO_3 \rightleftharpoons NaNO_2 + 1/2\,O_2 \quad \Delta H_{298} = +109\,\text{kJ/mol} \quad (1.1)$$

Molten sodium nitrate remains stable in air up to 500 °C; reaction (1.1) reaches equilibrium with the evolution of oxygen between 600 and 750 °C [6]. The product (sodium nitrite) decomposes (see Section 4.1). Alkali nitrates contain small amounts of nitrites at temperatures as low as 300 °C [7]. In aqueous solution, alkali nitrates have little oxidizing power; they are reduced to ammonia by nascent hydrogen.

1.2. Occurrence

Deposits of sodium nitrate (the mineral nitratine) occur chiefly in arid regions such as Peru, Mexico, Egypt, and South Africa. The only commercial deposits are, however, in Chile. The origin of these deposits has not been determined conclusively. A number of theories have been proposed since the early 1960s [8–10].

The Chilean deposits lie between latitudes 19° and 26° at ca. 800–1600 m above sea level. The uppermost bed is 20–40 cm thick and consists of unconsolidated weathering products containing only a little salt ("chuca"); the next bed, up to 3 m thick, is called "costra"; it is usually a coarse breccia cemented with clay and salts of the

saltpeter deposits. The "caliche" or salt bed proper lies beneath and has a thickness of 0.5–5.0 m. It is also brecciated and contains various salts (Table 1) and widely varying amounts of clay, sand, and gravel.

In addition to nitratine ($NaNO_3$) and generally a little niter (KNO_3), the rock often contains a wide variety of components: halite (NaCl), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), bloedite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), glauberite ($Na_2SO_4 \cdot CaSO_4$), polyhalite ($K_2SO_4 \cdot MgSO_4$ $2CaSO_4 \cdot 2H_2O$), and darapskite ($NaNO_3 \cdot$ $Na_2SO_4 \cdot H_2O$). In addition to the salts listed in Table 1, borates, iodates, other iodine compounds, and perchlorates may be present in amounts up to a few tenths of a percent.

Reserves may well support several more centuries of working. In Chile alone, reserves of commercial caliche containing 7 wt% sodium nitrate are estimated at 2.5×10^9 t. Reserves of lower quality are about ten times greater [11].

1.3. Production

1.3.1. Chile Saltpeter

The winning of sodium nitrate from caliche is very complicated. The raw material contains only 7–40 wt% sodium nitrate (corresponding to 2–7% N) and requires multistage processing to achieve an acceptable yield. The saltpeter industry in Chile produces ca. 600 000 t of sodium nitrate, 50 000 t of sodium sulfate, and more than 3000 t of iodine yearly [12]; it is one of the world's leading producers of iodine ($\rightarrow$ Iodine and Iodine Compounds, $\rightarrow$ Iodine and Iodine Compounds, Chap. 8.).

As early as 1810, low yields of impure saltpeter were produced by small boileries in Chile. The first improvement was the *Shanks hot-leaching process*, introduced in 1876 [13, 14]. Caliche

with a minimum sodium nitrate content of 13 wt% was extracted with mother liquor at ca. 110 °C; after crystallization of sodium chloride at < 5 °C, the product was obtained by crystallization at 22 °C. The yield was 65–80%, and the energy cost was high. The 200 or so plants employing the Shanks process ranged in capacity from 10 000 to 100 000 t/a of sodium nitrate. High energy costs made the Shanks process uncompetitive with synthetic saltpeter after World War I.

The *Guggenheim low-temperature leaching process* was developed in 1923 [8, 15]. By the beginning of the 1930s, two Guggenheim plants with sodium nitrate capacities of 500 000 and 600 000 t/a had been built. The Guggenheim process features relatively low leaching temperatures (40–45 °C), 90% yields, low energy consumption due to good heat utilization, rational methods of caliche mining, and very large plant units. The process can economically handle caliche containing as little as 7 wt% sodium nitrate. Old spoil heaps of spent earth can be processed along with residues from leaching the coarse caliche fraction containing > 7 wt% sodium nitrate.

The isolation of sodium nitrate is based on differences between the solubility curves of the salts contained in the caliche. For example, the solubility of sodium nitrate is four times greater than the solubility of sodium chloride in water at 45 °C (Fig. 2). Operating condit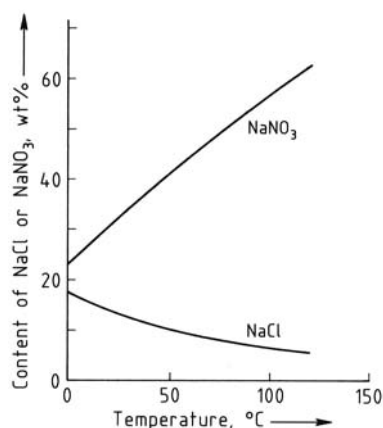ions must be avoided under which insoluble or sparingly soluble double salts containing sodium nitrate are stable. For example, if the Mg^{2+} and Ca^{2+} concentration in the recycle liquor is sufficiently high, darapskite ($NaNO_3 \cdot Na_2SO_4 \cdot H_2O$) forms the insoluble "protective compounds" blödite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and glauberite ($Na_2SO_4 \cdot CaSO_4$). Darapskite is a sparingly soluble component that accounts for 30% of the sodium nitrate in caliche and is stable below 55 °C.

The production of Chile saltpeter from caliche is summarized in Figure 3. The warm (40–45 °C) mother liquor recycled to leaching contains ca. 330 g/L of sodium nitrate. The leaching process is performed in a series of vats, each having a capacity of ca. 1000 t of crushed ore. The underflow of each vat is heated before passing to the next one since the dissolution of sodium nitrate is endothermic. Sodium nitrate therefore dissolves preferentially. The product solution obtained after leaching contains 450 g/L of sodium nitrate and is cooled to 5–10 °C in heat exchangers and with ammonia refrigerating equipment. The mother liquor obtained after centrifugation of crystallized sodium nitrate is heated to 40–45 °C with heat from the condensers in the ammonia chilling loop and then with cooling water from the diesel engines used to generate electric power. Crystalline sodium nitrate obtained after centrifugation contains 3.0–3.5% moisture; it is generally melted at ca. 340 °C and prilled. The granulated product contains only about 1% sodium chloride. Table 2 gives a detailed product analysis [17]. Large modern plants also produce coarse crystals of Chile saltpeter, which do not require further processing by melting.

To recover more than 80% of the sodium nitrate present in caliche, the "spent earth"

Figure 2. Solubility curves of sodium nitrate and sodium chloride in a saturated aqueous solution containing solid sodium nitrate and sodium chloride [16]

Table 2. Analysis of saltpeter products

Component	Granulated sodium nitrate,[*] wt%	Granulated potassium nitrate,[*] wt%	Synthetic saltpeter, wt%
$NaNO_3$	98.32	67.37	99.70
KNO_3		30.36	0.06
NaCl	0.67	0.97	0.09
$Na_2B_4O_7$	0.24	0.23	
$NaIO_3$	0.03	0.03	
Moisture	0.17	0.21	0.10
Undetermined	0.57	0.83	0.05

[*] From Chile saltpeter [17].
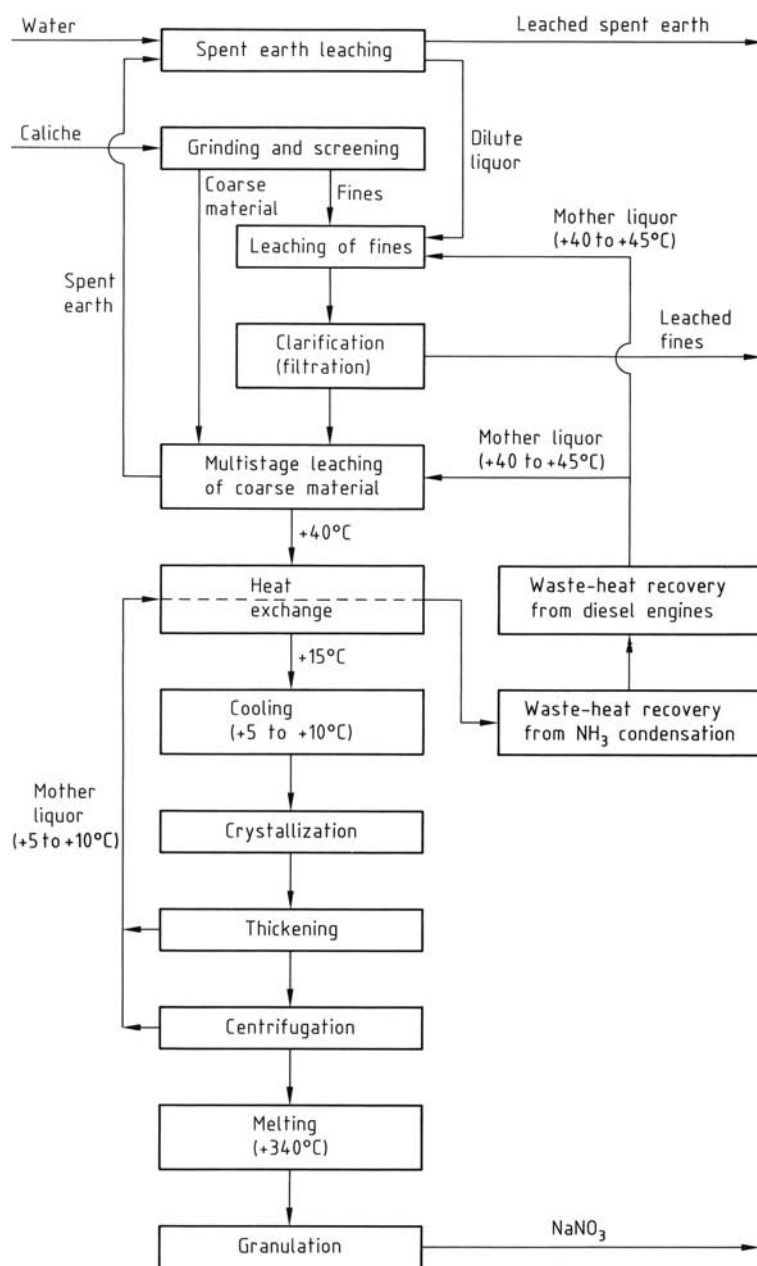
Figure 3. Guggenheim process for the production of Chile saltpeter

containing 1.0–1.5 wt% sodium nitrate must be leached with water. The resulting dilute liquor is either used for leaching fine caliche (Fig. 3) or placed in large open pans and evaporated by the sun and the hot dry winds of the salt desert; precipitated crystals are removed periodically.

Greater utilization of solar energy in the future will allow economical processing of caliche containing as little as 4% sodium nitrate.

Byproducts. Iodine recovery from the mother liquor begins when the sodium iodate

content reaches 6–9 g/L. The enriched solution is treated with sodium hydrogen sulfite to precipitate free iodine:

$$2\, NaIO_3 + 5\, NaHSO_3 \rightarrow I_2 + 3\, NaHSO_4 + 2\, Na_2SO_4 + H_2O \tag{1.2}$$
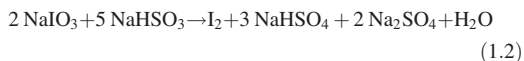
Iodine is separated by filtration and purified by sublimation. The side stream after iodine recovery is returned to the circulating mother liquor.

The recovery of Chile niter (KNO_3) as a byproduct is profitable if the caliche contains > 2–3 wt% potassium nitrate. This product also accumulates in the mother liquor. To reduce processing costs, the product is refined to a potassium nitrate content of only 30% (Table 2).

1.3.2. Synthetic Sodium Nitrate

The most important method for producing synthetic sodium nitrate is the reaction of tail gases from nitric acid plants with sodium hydroxide or sodium carbonate solution. This method is, however, intended for tail-gas clean-up (removal of nitrogen oxides) rather than for nitrate and nitrite production.

Tail-gas absorption initially yields some sodium nitrate and larger amounts of sodium nitrite. The reactions that produce nitrite alone

$$2\, NaOH + NO_2 + NO \rightarrow 2\, NaNO_2 + H_2O \tag{1.3}$$

$$Na_2CO_3 + NO_2 + NO \rightarrow 2\, NaNO_2 + CO_2 \tag{1.4}$$

proceed faster than the reactions that produce both nitrite and nitrate.

$$2\, NaOH + 2\, NO_2 \rightarrow NaNO_3 + NaNO_2 + H_2O \tag{1.5}$$

$$Na_2CO_3 + 2\, NO_2 \rightarrow NaNO_3 + NaNO_2 + CO_2 \tag{1.6}$$

The countercurrent absorption process takes place in 18–8 stainless steel columns connected in series. In sodium carbonate absorption, the columns are packed with ceramic rings; iron rings are used for sodium hydroxide absorption.

Fresh alkaline solution is circulated into the last column. The liquor is forwarded batchwise to successive columns and finally withdrawn with a content of ca. 500 g/L of sodium nitrate and sodium nitrite. The product liquor contains both nitrate and nitrite, even if nitrite removal is employed (see Chap. 4). Nitrite is decomposed

by inversion with nitric acid at 50 °C in a column made of 18–8 steel prior to nitrate recovery:

$$3\, NaNO_2 + 2\, HNO_3 \rightarrow 3\, NaNO_3 + 2\, NO + H_2O \tag{1.7}$$
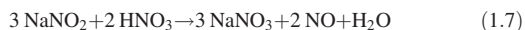
The highly concentrated nitrogen monoxide can be used to synthesize other compounds (e.g., hydroxylamine) or can be returned to the nitric acid plant.

The residual nitrogen monoxide is stripped from the inverted solution with steam or air at ca. 100 °C. The solution is then neutralized with sodium carbonate or sodium hydroxide, passed through a precoat filter, and concentrated batchwise in multistage iron evaporators. The first stage is operated at 100–120 °C ($p = 120$–150 kPa in the vapor space). The resulting solution should not crystallize and should still dissolve any salt deposits formed in the second stage. The second stage is operated under vacuum ($p = 10$–20 kPa) at 65–75 °C; the product is concentrated to form a slurry containing ca. 20% precipitated sodium nitrate. The crystals are separated in a centrifuge without cooling. Depending on the quality required, they are washed more or less intensively with cold water. Sodium nitrate from the centrifuge has a moisture content of 2–3 wt% and is dried to ca. 0.1 wt% moisture in drums heated with flue gas. The product is dried, cooled, and stored in bins.

The mother liquor from the centrifuge is recycled to the first evaporator stage along with the wash water. Discharge of the liquor is only necessary if the alkali used contains more chloride than permitted in sodium nitrate by quality standards. Accordingly, the process generally does not produce any wastewater.

1.4. Product Forms, Storage, and Transportation

Chile saltpeter is marketed as both a "granular" product (mainly used as a fertilizer) and a coarse crystalline product. Technical-grade synthetic sodium nitrate is a fine, crystalline white powder with a bulk density of about 1.36 kg/L. It is sold as an untreated product and also as a free-flowing product containing up to 0.1% alkyl aryl sulfonate as an anticaking agent [18]. Table 2 presents analyses of sodium nitrate.

Sodium nitrate can be transported in bulk form. The technical grade, especially the

untreated product, is generally shipped in polyethylene bags. As an oxidizing agent, sodium nitrate must not come in contact with readily oxidizable products during transport and storage.

1.5. Uses

Inorganic nitrates and nitrites overlap in their areas of application. Mixtures of the compounds are sometimes employed. More than half of the sodium nitrate produced worldwide (including Chile saltpeter) is used as a fertilizer for crops such as cotton, tobacco, and vegetables. In contrast to other nitrogen fertilizers, sodium nitrate does not overacidify the soil. In Europe and the United States, sodium nitrate is of minor importance compared to other fertilizers.

The major industrial use of sodium nitrate is in the explosives industry. It is employed along with ammonium nitrate in the production of water-containing slurry and gel explosives, whose consistency is stabilized with rubber additives. Sodium nitrate, like potassium nitrate, is added to ammonium nitrate melts (see Section 2.5). Sodium nitrate is also used in pyrotechnics, for example, in flare mixtures.

Large amounts of sodium nitrate are used in the glass and enamel industry as a refining agent for removing air bubbles from melts.

In metallurgy, molten salt mixtures containing sodium nitrate are employed as heat-transfer baths for quench hardening and tempering of steel, light alloys, and copper alloys. For the range 260–550 °C, $NaNO_3$–KNO_3 melts are used; melts containing ca. 45% sodium nitrite along with potassium nitrate and sodium nitrate can be used from 150 to 300 °C [19]. The heat of fusion of the salt mixture can be utilized to keep the temperature constant; the solidification point of the ternary system KNO_3–$NaNO_3$–$NaNO_2$ can be adjusted precisely by altering the proportion of components. Metal parts with oxide scales can be pretreated by briefly dipping them in molten $NaNO_3$–$NaOH$ so that they can be electrically descaled in a sodium sulfate solution without the use of acid (more environmentally friendly); similar methods employ potassium nitrate.

Molten mixtures of sodium nitrate, other alkali nitrates, and nitrites function as heat-transfer and heat-storage media in solar technology.

The maximum temperature for this application is ca. 600 °C. The thermophysical properties of such melts are described in [20–23].

Mixtures of sodium nitrate and borax also serve as an auxiliary in soldering and welding. Sodium nitrate is recommended as a corrosion-inhibiting additive in antifreezes and cooling brines. In the regeneration of spent sulfuric acid by distillation in cast-iron vessels, passivation with sodium nitrate is used to prevent corrosion.

Sodium nitrate is used to promote combustion; it is added to activated carbon when sulfur dioxide is oxidized to sulfur trioxide in exhaust-gas combustion devices and is also used to improve the combustibility of tobacco. Cleaning agents for plugged drain pipes are made from sodium nitrate, aluminum filings, and an alkali; hydrogen produced by the action of water is oxidized by sodium nitrate, and this reaction provides the heat needed for effective cleaning. Molten sodium nitrate serves as a reaction medium, for example, in the electrolytic production of chromium dioxide for magnetic tape. A melt of sodium nitrate and potassium nitrate provides a suitable medium for the thermal decomposition of dissolved ammonium nitrate to dinitrogen monoxide. The same melt can be used for the conversion of urea to cyanuric acid in a method devised by Stamicarbon. Pickling salt contains sodium nitrate.

Other applications of sodium nitrate include the production of dyes, pharmaceuticals, charcoal briquetts, and other nitrates.

1.6. Economic Aspects

The output of Chile saltpeter has decreased continually since the late 1920s (Table 3). Despite competition from synthetic sodium nitrate, output seems to have reached a stable level. In Chile, production capacity increased in 1984 [24], and another plant is planned [25]. The cost of producing Chile saltpeter is far less sensitive to rising energy prices than that of synthetic sodium nitrate, which requires ammonia and caustic soda as feedstocks. Most Chile saltpeter is exported; the most important consumers are Western Europe (120 000 t/a), especially Spain and The Netherlands, and the United States (100 000 t/a) [17].

Few production figures are available for synthetic sodium nitrate. Sodium nitrate has not been

Table 3. Production of Chile saltpeter (10^3 t)

Year	Production	Year	Production
1830	1	1940	1380
1850	30	1950	1660
1880	220	1960	930
1900	1650	1970	700
1910	2470	1975	800
1920	2530	1979	650
1928	3160	1984	710
1933	530	1987	590

manufactured in the United States since 1988. Further stagnation of sodium nitrate production is expected in the near future. This forecast could change if solar energy development is stepped up [26].

2. Potassium Nitrate

Potassium nitrate was manufactured in China with the aid of bacteria as early as the Middle Ages. Up to the beginning of the 20th century, its only important use was in the production of gunpowder.

2.1. Properties [27]

Potassium nitrate [*7757-79-1*], saltpeter, KNO_3, M_r 101.10, has an enthalpy of formation $\Delta H_{298} = -492.8$ kJ/mol [2], an enthalpy of fusion $\Delta H = +11.9$ kJ/mol [3], and *mp* 334 °C; for pressure dependence of the melting point, see [4]. At 25 °C, anhydrous potassium nitrate forms colorless rhombic crystals of space group $D_2^{16}{}_h$; $\varrho_{298} = 2.109$ g/cm^3; $C_{p, 298} = 96.36$ J mol^{-1} K^{-1} [2]; refractive index at 589 nm $n_\alpha = 1.335$, $n_\beta = 1.5056$, $n_\gamma = 1.5064$ [2]. This modification forms rhombic crystals of space group D_{3d}^5 at a transition point of ca. 127.7 °C (enthalpy of formation $\Delta H = +5.1$ kJ/mol) [28], [29]. High-pressure allotropes account for the caking tendency of potassium nitrate [30].

Potassium nitrate does not form solid phases containing water (Fig. 4). Its enthalpy of solution in water at infinite dilution is $\Delta H_{298} = +34.9$ kJ/mol [3]. Potassium nitrate is soluble in liquid ammonia; no ammoniates are known. The solubility of potassium nitrate in anhydrous methanol at 25 °C is 0.34 wt% [5].
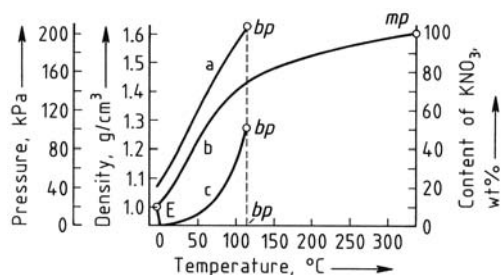

Figure 4. Properties of a saturated solution of potassium nitrate in water a) Density; b) Content of potassium nitrate; c) Vapor pressure *bp* = boiling point of saturated solution containing 77.0 wt% potassium nitrate at 101.3 kPa and 115.6 °C; E = cryohydric point: -2.85 °C, 9.66% potassium nitrate.

Like sodium nitrate, potassium nitrate liberates oxygen on heating. The endothermic reaction

$$KNO_3 \rightleftharpoons KNO_2 + 1/2\, O_2 \quad \Delta H_{298} = +124 \text{ kJ/mol} \qquad (2.1)$$

is reversible. In contact with air, pure molten potassium nitrate is stable up to about 530 °C; reaction (2.1) comes to equilibrium between 650 and 750 °C. Above 750 °C, the nitrite product decomposes with the formation of nitrogen oxides [6]. The KNO_3–$NaNO_3$ system forms a eutectic with 45% sodium nitrate, *mp* ca. 218 °C. Solid solutions exist above 175 °C with no miscibility gap; at room temperature the system has a miscibility gap from 0.5 to 99.9 wt% sodium nitrate. The composition of the aqueous solution saturated with both salts is described in [31].

2.2. Occurrence

Potassium nitrate (in the form of the mineral niter) occurs as efflorescences on soils. Deposits in China and the East Indies were economically important; in the first half of the 19th century, more than 10 000 t/a of potassium nitrate were produced by leaching such soils (current annual production is still several thousand tonnes). Before the large-scale manufacture of converted saltpeter began, East Indian saltpeter enjoyed a virtual monopoly.

Potassium nitrate is present in tobacco plants, from which it can be extracted with water and recovered to diminish nitrogen oxide evolution during smoking.

2.3. Production

For older processes, see [14, 27].

2.3.1. Bacterial Production of Saltpeter

Bacterial production of potassium nitrate was employed from the 17th to the 19th century in Europe. This was necessary to avoid having to import this raw material, which was indispensable for military purposes during wartime. Nitrogen-rich organic wastes, especially animal feces and urine, were placed in loose, air-permeable piles of earth together with lime and potash; the nitrogen compounds were converted to nitrates by bacterial nitrification. After several years, the mass was leached with water. Potash was added to the crude liquor to convert calcium and magnesium nitrates to potassium nitrate and sparingly soluble calcium and magnesium carbonates. The filtered liquor was evaporated to obtain saltpeter, which was purified by recrystallization.

2.3.2. Converted Saltpeter

From the mid-19th century until the 1950s, the conversion of Chile saltpeter with potassium chloride was the most important potassium nitrate production process (Fig. 5). Potassium chloride was supplied in large quantities after 1860 by the German potash industry.

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl \qquad (2.2)$$

The process is based on the slight increase in solubility of sodium chloride with temperature. The mother liquor from potassium nitrate crystallization in the preceding cycle (point C in Fig. 6) is heated and reacted with stoichiometric quantities of sodium nitrate and potassium chloride. Impure starting materials are generally used in this step. The reaction mixture (point A, Fig. 6) is concentrated at 100 °C with the addition of sodium carbonate; sodium chloride and impurities (e.g., $MgCO_3$) precipitate and are filtered out. The filtrate (point B, Fig. 6) is again diluted with the evaporation condensate (to prevent sodium salts from precipitating on cooling), clarified, cooled to 5 °C to precipitate potassium nitrate, and centrifuged. The mother liquor (point C, Fig. 6) is recycled. The potassium
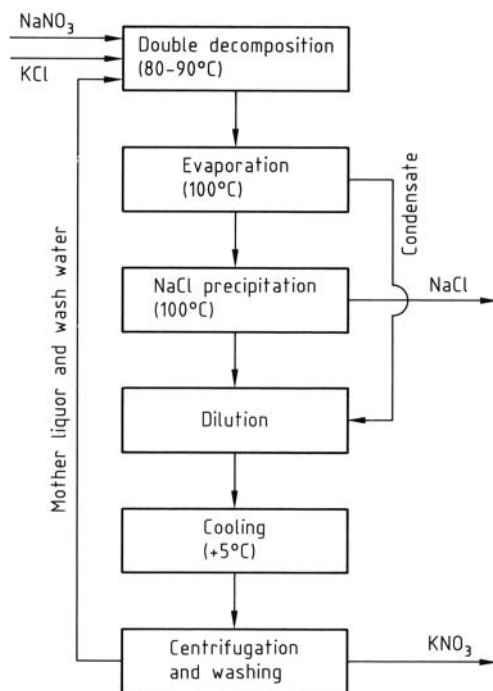

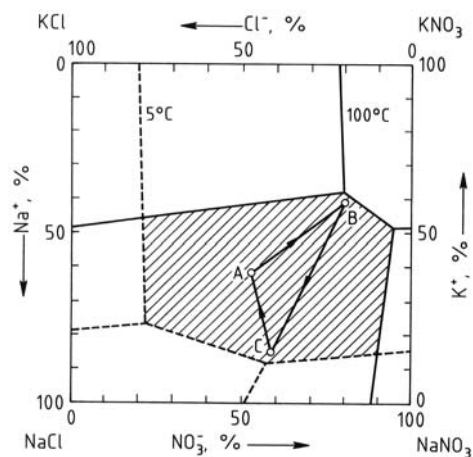**Figure 5.** Conversion of sodium nitrate to potassium nitrate

Figure 6. The $NaNO_3$–KNO_3–KCl–$NaCl$–H_2O system Jänecke's method [34] is used to plot the relative content of cations and anions in percent equivalents in the salt mixture corresponding to the saturated solution. Absolute concentrations or quantities of water are not shown. Values for 5 °C are according to [32], for 100 °C according to [33]. The lines labeled 5 and 100 °C represent the boundaries of fields in each of which one of the four salts occurs as the solid phase in the saturated solution. In the shaded region, sodium chloride precipitates from the saturated solution at 100 °C but potassium nitrate precipitates at 5 °C. (See text for explanation of the working triangle ABC.)

nitrate product is recrystallized for technical purposes. Because of high energy costs and other factors, the conversion process can no longer compete with the processes described in Sections 2.3.3; 2.3.4; 2.3.5; nevertheless, older plants continue to use it. Physical and chemical fundamentals are described in [32–35]; process design may be found in [36, 37].

2.3.3. Potassium Nitrate from Calcium Nitrate

A number of processes have been developed for obtaining potassium nitrate from calcium nitrate, which is a byproduct of other processes (e.g., digestion of rock phosphate with nitric acid).

With potassium sulfate as a starting product, the reaction

$$Ca(NO_3)_2 + K_2SO_4 + 2\,H_2O \rightarrow 2\,KNO_3 + CaSO_4 \cdot 2\,H_2O \tag{2.3}$$
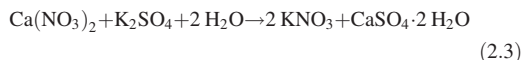
yields sparingly soluble gypsum, which is easily separated. This is the basis for the relatively simple Victor process [38], which was employed after 1951 in Germany for several decades to manufacture potassium nitrate [39]. Other methods employ potassium chloride as raw material but have no industrial importance [39].

In another proposed process, limestone is first reacted with nitric acid to form calcium nitrate. Potassium sulfate is then added to the resulting liquor at ca. 100 °C. The gypsum formed is removed and the reaction mixture is cooled. Potassium nitrate crystals are isolated with a purity of 99.5%, and the mother liquor is recycled to the beginning of the process [40].

A process based on the use of calcium nitrate and ion exchangers has also been proposed [41].

2.3.4. Potassium Nitrate from Ammonium Nitrate

Potassium nitrate is made from ammonium nitrate (available in high purity) and potassium chloride by double decomposition in aqueous solution:

$$NH_4NO_3 + KCl \rightarrow KNO_3 + NH_4Cl \tag{2.4}$$

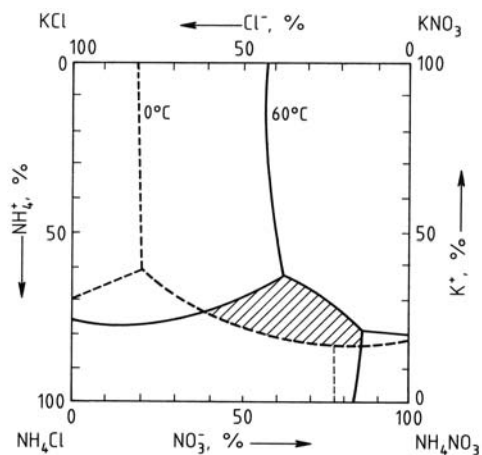The ammonium chloride byproduct is easily separated.

Figure 7. The NH_4NO_3–KNO_3–KCl–NH_4Cl–H_2O system (see Fig. 6 for the method of plotting) In the shaded region, ammonium chloride precipitates from the saturated solution at 60 °C but potassium nitrate precipitates at 0 °C. Absolute concentrations are not shown (see [41])

The solubility relationships (Fig. 7) in the system of reciprocal salt pairs described in reaction (2.4) [42] lead to a simple reaction design (Fig. 8) [43]. The starting reagents are added in alternate stages. Ammonium chloride precipitates at a higher temperature and from a higher concentration than potassium nitrate. Evaporation is therefore necessary prior to ammonium chloride crystallization, the condensate being recycled before potassium nitrate crystallization. Because the salt solution is aggressive, molybdenum-alloyed carbon steel is used for process equipment. Fertilizer-grade product containing 95 wt% potassium nitrate and 5 wt% ammonium nitrate is manufactured by this process [24], [44].

2.3.5. Potassium Nitrate from Potassium Chloride and Nitric Acid

Production without Chlorine Formation. In an aqueous medium containing 50% nitric acid, the reaction

$$HNO_3 + KCl \rightleftharpoons KNO_3 + HCl \tag{2.5}$$

proceeds without oxidation of chloride ion to chlorine and/or nitrosyl chloride only if the temperature is below 40 °C (or below 70 °C at 40% HNO_3). A number of process design options are available: removing hydrogen chloride by
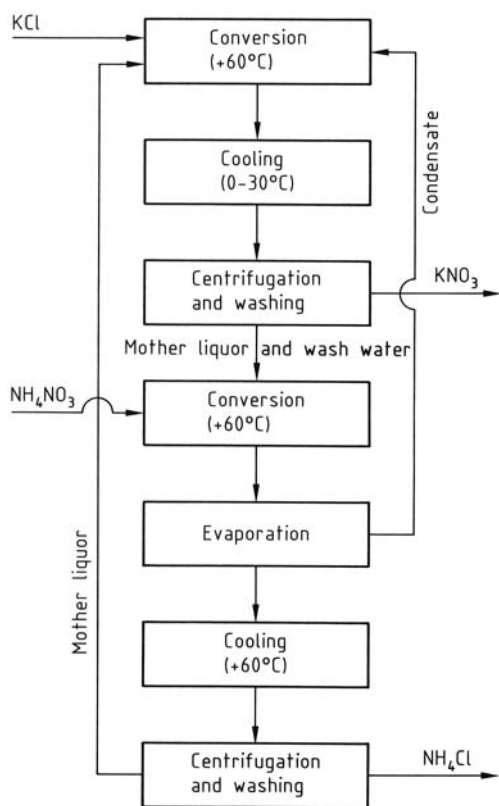
Figure 8. Potassium nitrate production from ammonium nitrate

absorption, decreasing potassium nitrate solubility by the addition of alcohol, or using cation exchangers. Only the Israel Mining Industry (IMI) process has been introduced on a large scale (Fig. 9) [45]. Solid potassium chloride is reacted with nitric acid at 5–10 °C (c) in the presence of an organic solvent (*n*-butanol or isopentanol). The solvent extracts the hydrogen chloride, and potassium nitrate is precipitated quantitatively from the aqueous phase. The advantage of the low digestion temperature is that hydrogen chloride is extracted from the organic solvent in preference to nitric acid; furthermore, the aqueous solution contains less potassium nitrate. The three phases present (potassium nitrate, aqueous phase, organic phase) are then separated. The potassium nitrate is centrifuged and washed with water (e). The aqueous phase is returned to the reactors (c). The purity of the product (> 95%) [46] is sufficient for use as

fertilizer; recrystallization is necessary for the technical grade. Hydrogen chloride is separated as a 22% aqueous solution from the alcohol (which is not miscible with water in all proportions) by countercurrent extraction with water in three mixer–settler units (f). After extraction, the alcohol, which contains nitric acid, is returned to the conversion reactor. Separation of hydrochloric acid from the solvent has been improved by use of a different solvent that extracts nitric acid preferentially and extracts virtually no hydrochloric acid [47]. Haifa Chemicals uses tributyl phosphate for this purpose. Another proposal for improving the process is to replace the alcohol by an organic acid and an amine [48]. Rigid poly(vinyl chloride) and titanium are used as construction materials, with graphite for distillation equipment. A substantial portion of investment is for solvent conditioning.

This process is employed in two potassium nitrate plants in Haifa. Potassium nitrate output in 1987 was 250 000 t, of which ca. 30 000 t was of technical purity and the remainder fertilizer grade [49]. The hydrochloric acid byproduct is utilized for the digestion of rock phosphate.

Production with Chlorine Formation. The South West Potash Corporation (SWP) process is employed on a large scale for the production of potassium nitrate and chlorine [44, 50]. The most important steps follow (Fig. 10) [14]:

1. Potassium chloride is reacted with 65% nitric acid in an autoclave at 75 °C and ca. 200 kPa to yield potassium nitrate, chlorine, and nitrosyl chloride.

$$4\,HNO_3 + 3\,KCl \rightarrow 3\,KNO_3 + Cl_2 + NOCl + 2\,H_2O \quad (2.6)$$
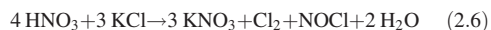
2. Nitrosyl chloride is oxidized with 80% nitric acid to yield chlorine and nitrogen dioxide.

$$NOCl + 2\,HNO_3 \rightarrow 1/2\,Cl_2 + 3\,NO_2 + H_2O \quad (2.7)$$
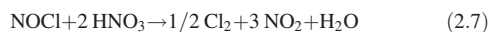
3. Nitrogen dioxide is oxidized with oxygen and absorbed in water to yield 65% nitric acid, which is recycled to the potassium chloride conversion step.
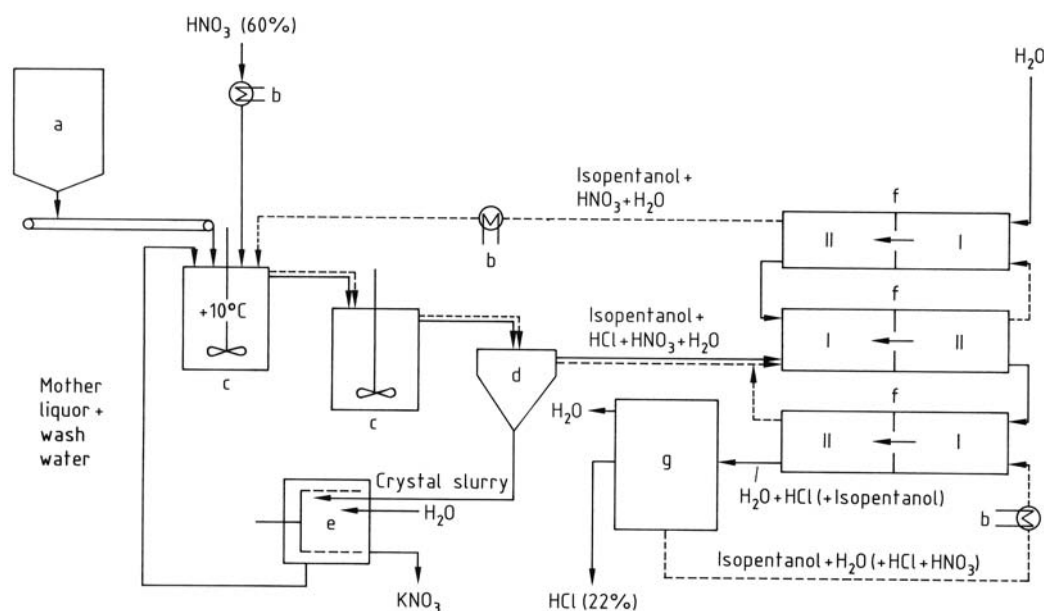
$$4\,NO_2 + O_2 + 2\,H_2O \rightarrow 4\,HNO_3 \quad (2.8)$$

Figure 9. Simplified flow sheet of the IMI process (based on literature data) a) Potassium chloride supply; b) Cooler; c) Reactor; d) Decanter; e) Centrifuge; f) Extractor (I = mixer, II = separator); g) Multistage evaporator (details not published) Dashed lines indicate streams containing mainly isopentanol.

(Alternatively, nitrogen dioxide can be withdrawn as end product.)

4. The solution of potassium nitrate and nitric acid is concentrated to > 80% nitric acid by crystallization of potassium nitrate in a vacuum crystallizer. Nitric acid can be obtained in 75% or 85% concentration because the azeotropic concentration in the HNO_3–H_2O system at 80 kPa increases to 82% nitric acid if the liquid phase contains 40% potassium nitrate and to 87% nitric acid at 50% potassium nitrate [51].

5. The potassium nitrate is centrifuged, dried, melted at 340–350 °C, and prilled.

Intense corrosion dictates the use of titanium reactors with acid-resistant linings, whereas tower internals are made of glass or Teflon.

At present, Cedar Chemical Corp. (Trans-Resources) has an annual capacity of 100 000–120 000 t of potassium nitrate in an SWP plant at Vicksburg, Mississippi; ca. 20 000 t/a of the output is technical grade. Chlorine, dinitrogen tetroxide, and 65% nitric acid are obtained as byproducts.

2.4. Product Forms, Storage, and Transportation

All technical-grade and most fertilizer-grade potassium nitrate is sold as a fine crystalline product with a bulk density of 1.1 kg/L. Technical grades may be untreated or treated with fatty amines or stearates to prevent caking [18]. Fertilizer-grade potassium nitrate is also sold as prills (bulk density 1.3 kg/L, obtained by atomizing a melt at 340 °C), because prills have better storage qualities and are easier to apply as fertilizer. Table 4 gives the analyses of typical grades. As a rule, the technical product is shipped in plastic or multi-ply paper bags. As an oxidant, potassium nitrate must not be stored or transported with easily oxidized products.

2.5. Uses

About 75% of potassium nitrate is manufactured with a purity of only 90% for use as a nonhygroscopic fertilizer. The absence of chlorine is advantageous for growers of tobacco, citrus fruits,
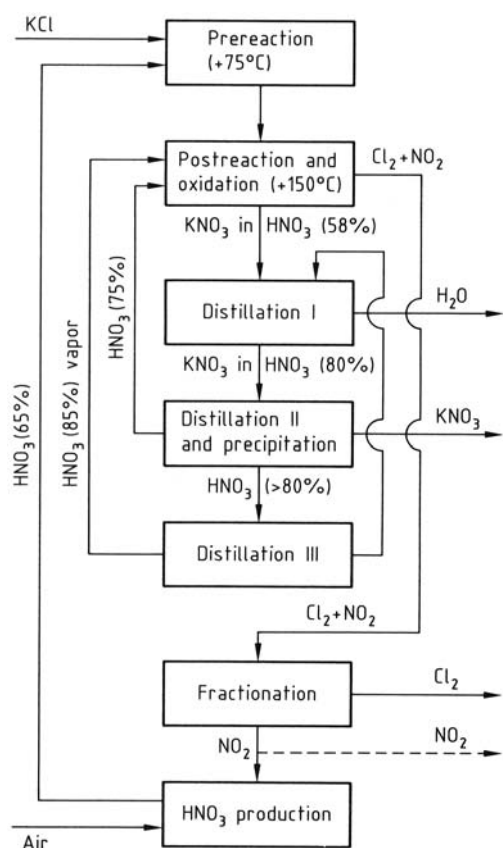
Figure 10. South West Potash Corporation process

Almost half of the technical-grade product is employed in metallurgy, mainly in heat-transfer baths in mixtures with other nitrates and nitrites (see Section 1.5). Potassium nitrate is also a component of soldering fluxes and welding electrodes. Large amounts are used in the glass, enamel, and ceramics industries. Glass devices and optical lenses can be improved by techniques based on Na^+–K^+ ion exchange (treatment of sodium-containing glasses in molten KNO_3).

About 10–20% of technical-grade potassium nitrate is consumed in the manufacture of explosives and pyrotechnics. Along with sodium nitrate and ammonium nitrate, potassium nitrate is an oxygen supplier in safety explosives. Because of its low hygroscopicity, potassium nitrate remains an important raw material for the production of matches and primer cords, as well as primer compositions with controlled burning rate for local heating. Another important use in the explosives industry is the addition of 2–10% potassium nitrate to ammonium nitrate to lower the melting point, which facilitates prilling and improves the stability of the resulting granules.

Small amounts of potassium nitrate are employed in food preservation, cheese processing, and for improving the quality of tobacco.

Because of its oxidizing properties, potassium nitrate can be used for desooting in combustion processes. It is also recommended as an agent for controlling noxious odors during the application of sewage sludge or manure (at the same time, it improves the fertilizing action of the waste).

and vegetables (especially for hothouse crops). Potassium nitrate can also be used in the production of clear liquid fertilizers and is an important constituent of multinutrient fertilizers.

Table 4. Composition (wt%) of potassium nitrate

	Technical grade		Fertilizer grade	
Component	Requirements for black powder[*]	Sample	Product I	Product II
KNO_3	min. 99.0	99.8	95.0	96.5
Cl^-	max. 0.03	0.015	0.2	1.8
NO_2^-	not specified		0.002	0.2
SO_4^{2-}	not specified	0.02	3.4	0.05
Na^+	max. 0.1	0.02	0.2	0.7
Ca^{2+} and Mg^{2+}	max. 0.07	0.03	1.0	0.1
Heavy metals	max. 0.1		0.02	0.02
Insolubles	max. 0.1	0.05	0.05	0.2
H_2O	max. 0.25	0.06	0.1	0.1

[*] Not all requirements are shown.

Potassium nitrate has been proposed as an oxidizing component in an acid-based gas generator system for the rapid inflation of air bags used to prevent injuries in motor vehicle accidents.

Potassium nitrate is also employed as an oxidant in chemical syntheses (e.g., alizarin synthesis).

2.6. Economic Aspects

Except for the small output from deposits still worked in India and the production of Chile saltpeter (which contains only 20–30% KNO_3, see Section 1.3.1), the only source of potassium nitrate for more than 100 years has been synthetic production. Although use of the technical-grade product can be expanded only slightly, a variety of processes have been developed to reduce the cost of manufacturing impure saltpeter and to increase its use as a fertilizer.

World production capacity in 1987 for synthetic potassium nitrate is about 425 000 t/a, 75% of which is fertilizer grade and only 25% technical grade (see Table 5). The largest producer is Trans-Resources with 340 000 t/a (Cedar Chemical and Haifa Chemicals, Israel) [52]. Israel is the largest exporter; its most important customers are the United States, Western Europe, and Latin America. By 1992, Haifa Chemicals will boost its capacity to 300 000 t/a [53]. The annual output of Chile saltpeter is 60 000– 75 000 t of potassium nitrate. Soquimich, the sole manufacturer in Chile, is the third largest potassium nitrate producer in the world [54].

Table 5. Potassium nitrate capacities in 1987 (10^3 t)

Country	Fertilizer grade	Technical grade
Israel	250	30
United States	80	20
FRG	0	30
Other West European countries	20	20
Eastern bloc	*	30
India	*	*
Chile (natural saltpeter)	60–75	0

*Capacity unknown.

3. Calcium Nitrate

3.1. Properties [55]

Calcium nitrate [10124-37-5], $Ca(NO_3)_2$, M_r 164.09, has an enthalpy of formation of $\Delta H_{298} = -937.4$ kJ/mol [2]. Anhydrous calcium nitrate crystallizes in the cubic system, space group T^6_h; $\varrho_{298} = 2.504$ g/cm^3 [3]; $C_{p,\,298} = 149.5$ J mol^{-1} K^{-1} [2]; refractive index $n = 1.595$ at 589 nm; mp 561 °C (incipient decomposition).

Anhydrous calcium nitrate is highly hygroscopic and readily soluble in water when heated (enthalpy of solution $\Delta H_{298} = -18.7$ kJ/mol at infinite dilution [56]); see also Figure 11 and Table 6. In addition to the anhydrous salt, three hydrates are known [57, 58]. The tetrahydrate [13477-34-4], $Ca(NO_3)_2 \cdot 4\ H_2O$, is the most important industrially: enthalpy of formation $\Delta H_{298} = +2130$ kJ/mol; monoclinic crystals of space group C^5_{2h}; $\varrho_{298} = 1.896$ g/cm^3; refractive index at 589 nm $n_\alpha = 1.465$, $n_\beta = 1.498$, $n_\gamma = 1.504$. The tetrahydrate dissolves in water with strong cooling (enthalpy of solution $\Delta H_{292} = +32.7$ kJ/mol at infinite dilution).

Calcium nitrate dissolves readily in liquid ammonia, methanol, and ethanol. A number of ammoniates are known.

Thermal decomposition of calcium nitrate

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + 1/2 O_2 \quad \Delta H = +369 \text{kJ/mol}$$

(3.1)
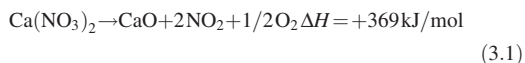
begins at 500 °C [6]. For the reaction mechanism, see [59].

Double Salts. Several weakly hygroscopic double salts are formed with ammonium nitrate [55]. The double salt $NH_4NO_3 \cdot 5Ca(NO_3)_2 \cdot 10H_2O$ has a high melting point (102 °C) and is important in the production of granular calcium nitrate. The double salt with urea, $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, is nonhygroscopic and can be employed as a fertilizer. The system $Ca(NO_3)_2$–KNO_3–H_2O includes the phase $Ca(NO_3)_2 \cdot 4KNO_3$ [60].

3.2. Occurrence

Only small amounts of $Ca(NO_3)_2 \cdot 4H_2O$ occur (nitrocalcite) as efflorescences in limestone caves, for example, in Kentucky.

Table 6. Data for the system Ca(NO_3)$_2$–H_2O (see also Fig. 11)

Transition point and temperature, °C		Content of Ca(NO_3)$_2$, wt%	Range	Stable hydrate formula	mp, °C
E[*]	−28.7	42.9			
			E–A	Ca(NO_3)$_2 \cdot 4H_2O$	42.7
A	+42.6	70.8			
			A–B	Ca(NO_3)$_2 \cdot 3H_2O$	51.1
B	+50.6	77.2			
			B–C	Ca(NO_3)$_2 \cdot 2H_2O$	
C	+51.6	78.1			
			above C	Ca(NO_3)$_2$	561
bp[**]	+151	79.0			

Water vapor pressure over saturated solution with solid Ca(NO_3)$_2 \cdot 4H_2O$

Temperature, °C	0	10	20	30	40
Pressure, kPa	0.36	0.69	1.25	1.99	2.63

[*] E = cryohydric point.
[**] Boiling point (101.3 kPa) of the saturated solution.

3.3. Production

Calcium nitrate became the first synthetic nitrogen fertilizer under the name Norge saltpeter. It was made by dissolving limestone in nitric acid and neutralizing the resulting liquor with powdered limestone or lime. This process is still in use, but ammonia is now employed for neutralization.

Calcium nitrate is also an important byproduct of nitric acid digestion of rock phosphates by the Odda process (→ Phosphate Fertilizers). It is either used directly for fertilizer production or converted to ammonium nitrate.

A calcium nitrate solution is also obtained when tail gases from nitric acid plants are absorbed in milk of lime. The initial nitrate–nitrite solution is converted to pure calcium nitrate solution by a reaction analogous to reaction (1.7).

3.3.1. Calcium Nitrate from Limestone and Nitric Acid

In this process, limestone is mixed with 50 –60% nitric acid (Fig. 12). Calcium nitrate is formed by the reaction

$$CaCO_3 + 2\,HNO_3 \rightleftharpoons Ca(NO_3)_2 + H_2O + CO_2 \qquad (3.2)$$
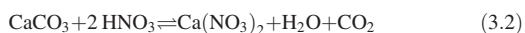
Water vapor and carbon dioxide are withdrawn from the process. Any remaining free
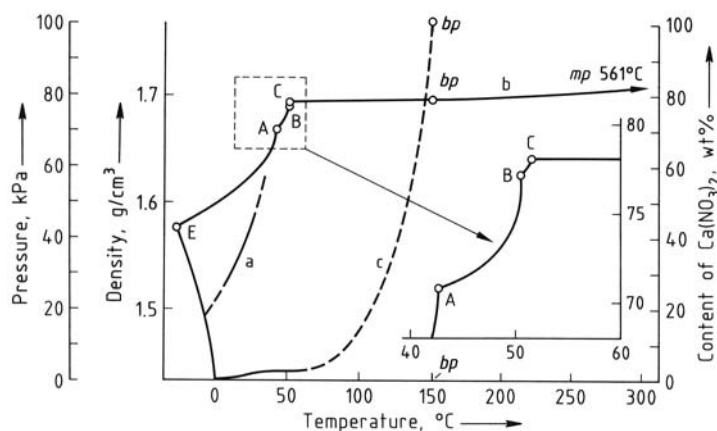
Figure 11. Properties of a saturated solution of calcium nitrate in water (see Table 6 for explanations) a) Density; b) Content of calcium nitrate; c) Vapor pressure
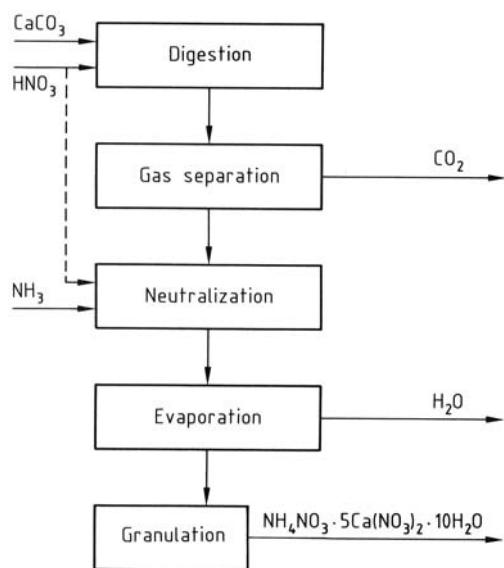
Figure 12. Production of calcium nitrate from limestone

nitric acid is then neutralized with ammonia to give ammonium nitrate; further ammonium nitrate can be added to adjust the content of this compound and to improve the storage qualities of the product. The calcium nitrate solution is then evaporated. Solid calcium nitrate can be subjected to any of the usual fertilizer processes (e.g., granulation, flocculation, or prilling).

The end product contains ca. 15.5 wt% nitrogen (0.9% ammonium N, 14.6% nitrate N). The main constituent (63%) is the easily crystallized phase $NH_4NO_3 \cdot 5Ca(NO_3)_2 \cdot 10H_2O$; also present are 12% $Ca(NO_3)_2 \cdot 2H_2O$ and 25% calcium nitrate.

### 3.3.2. Calcium Nitrate as a Byproduct of the Odda Process

The Odda process is based on the digestion of rock phosphate with nitric acid to give phosphoric acid and calcium nitrate (Fig. 13) [61, 62]:

$$Ca_3(PO_4)_2 + 6\,HNO_3 \rightarrow 2\,H_3PO_4 + 3\,Ca(NO_3)_2 \qquad (3.3)$$

The Ca^{2+} in the digester liquor is treated as a ballast. The $CaO : P_2O_5$ ratio serves as a measure of the ballast content and is decreased from 1.5 to 0.3 by removing the sand, with subsequent crystallization and removal of calcium nitrate.

The remaining liquor (nitrophosphoric acid) is neutralized with ammonia, evaporated, granulated, classified, and conditioned (coated).

Digestion of Rock Phosphate. The digestion of rock phosphate with nitric acid is an exothermic reaction and proceeds as follows at ca. 70 °C:

$$Ca_5[(PO_4)_3F] + 10\,HNO_3 \rightarrow 5\,Ca(NO_3)_2 + HF + 3\,H_3PO_4 \qquad (3.4)$$
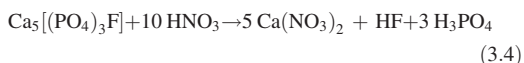
Usually 50–60% nitric acid is employed in an excess up to 20% over the stoichiometric amount, depending on the rock phosphate grade and process.

The digestion reaction is governed by three interrelated factors: digestion temperature, particle size, and residence time in the reactor. If the temperature is too high, nitric acid may decompose to form nitrogen oxides. If the temperature is too low and the particles are too large, a longer residence time is necessary.

Crystallization of Calcium Nitrate. The $CaO : P_2O_5$ ratio of the digester liquor is lowered by crystallizing and removing calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$ to enhance the water solubility of phosphorus pentoxide in the fertilizer. The quantity of calcium nitrate tetrahydrate obtained depends on the crystallization temperature, which is usually below 0 °C. The tetrahydrate crystals are washed with cold nitric acid and calcium nitrate–ammonium nitrate solution to recover as much of the phosphorus pentoxide content as possible. The crystals should contain less than 0.3 wt% residual phosphorus pentoxide. Experiments have shown that ca. 60 wt% nitric acid is suitable for washing. The acid is precooled to <10 °C, sometimes as low as −5 °C, to minimize the risk of redissolving the crystals.

Any acid remaining in the crystal filter cake would interfere with the subsequent conversion of calcium nitrate tetrahydrate. It is therefore eliminated by treatment with a solution of calcium nitrate and ammonium nitrate.

The tetrahydrate crystals are redissolved in ammonium nitrate solution. The cooling effect produced in this endothermic process and that resulting from the evaporation of ammonia are used to cool the crystallization liquor.
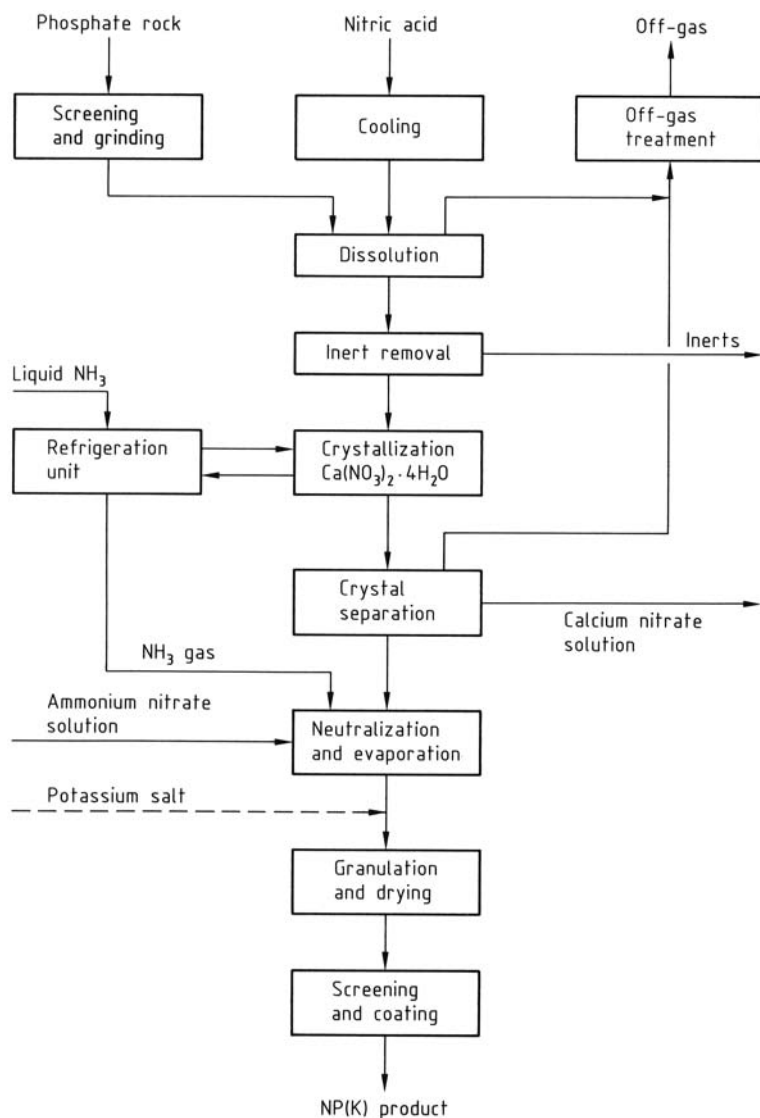
Figure 13. The Odda process

Either the calcium nitrate–ammonium nitrate solution is processed directly to fertilizers (see Section 3.3.1), or the calcium nitrate is treated with ammonium carbonate to yield ammonium nitrate.

Conversion of Calcium Nitrate. Figure 14 gives the flow sheet for calcium nitrate conversion. Ammonium carbonate is obtained by reacting ammonia and carbon dioxide in a 65%

ammonium nitrate solution in an absorption tower:

$$2\,NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3 \tag{3.5}$$
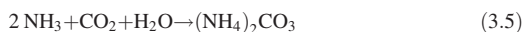
The reaction occurs in the liquid phase and the product contains < 38 wt% ammonium carbonate.

Calcium nitrate and ammonium carbonate are then reacted at ca. 50 °C in the conversion reactor:

Figure 14. Calcium nitrate conversion

$$(NH_4)_2CO_3 + Ca(NO_3)_2 \rightarrow CaCO_3 + 2\,NH_4NO_3 \qquad (3.6)$$

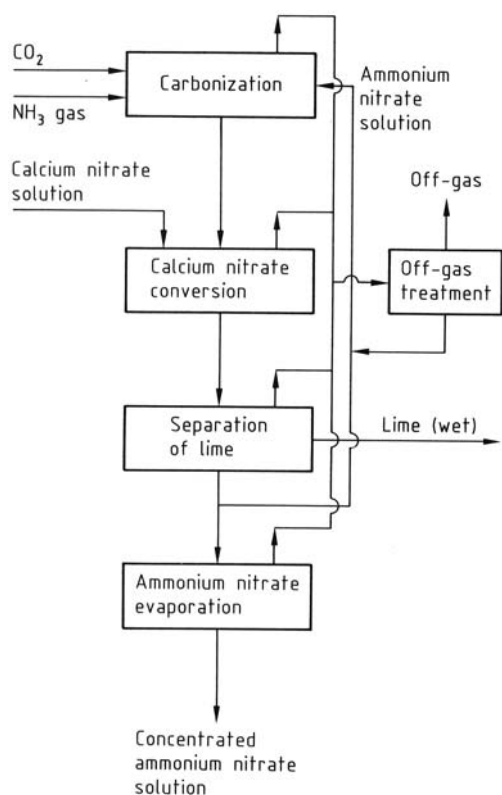The reactor operates with a small excess of ammonium carbonate. If the excess is too great, the precipitated lime becomes too fine and is difficult to process. With an excess of calcium nitrate, the precipitate becomes slimy and cannot be filtered. Another reason for avoiding an excess of calcium nitrate is to keep the calcium ammonium nitrate obtained by reacting lime with ammonium nitrate from becoming hygroscopic. Calcium ammonium nitrate, with lime as a filler, contains ca. 26 wt% nitrogen.

3.4. Product Forms, Storage, and Transportation

Calcium nitrate for fertilizer use is marketed as a noncaking grade that is usually treated with aryl alkyl sulfonates. Airtight bins are required for the storage of hygroscopic calcium nitrate. Coated or plastic bags are suitable for transportation. Like other nitrates, calcium nitrate must be kept away from oxidizable substances.

3.5. Uses

Calcium nitrate is employed as a nitrogen fertilizer either directly (see Section 3.3.1) or indirectly as calcium ammonium nitrate (see Section 3.3.2).

The combined use of calcium nitrate and urea in fertilizers has also been proposed [63, 64]. Other nitrates are obtained by reacting calcium nitrate with salts of other cations, preferably sulfates (see also Section 2.3.3).

Calcium nitrate is employed as a granulation aid for ground basic slag, ammonium and potassium sulfates, ammonium nitrate, and other fertilizer salts. Because of its high solubility, it is used as an oxidizing additive in water-containing explosives (along with ammonium nitrate).

Addition of calcium nitrate has been suggested as a way of improving the combustion qualities of heating oil and tobacco. It is also used in the preparation of cooling brines and in wastewater treatment (see Chap. 9). Because of its highly endothermic heat of solution, the tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$ can be used for cooling, for example in medical applications.

3.6. Economic Aspects

The use of calcium nitrate as a fertilizer is declining worldwide. In 1978, only 170 000 t of nitrogen was consumed in this form, most of it in Scandinavia (where the important producers are located), followed by Egypt. No statistics are available on the use of calcium nitrate in the industrial sector.

4. Sodium Nitrite

Sodium nitrite is the most industrially important salt of nitrous acid.

4.1. Properties [65]

Sodium nitrite [7632-00-0], $NaNO_2$, M_r 69.00, has an enthalpy of formation of
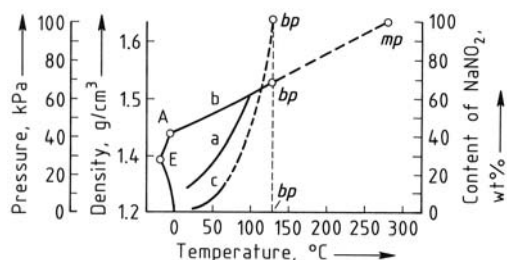
Figure 15. Properties of a saturated solution of sodium nitrite in water a) Density; b) Content of sodium nitrite; c) Vapor pressure bp = boiling point of saturated solution containing 68.7 wt% sodium nitrite at 101.3 kPa and 128 °C; A = transition point: −5.1 °C, 41.6% sodium nitrite; E = cryohydric point: −19.0 °C, 28.6% sodium nitrite

$\Delta H_{298} = -358 \pm 2$ kJ/mol. The β allotrope is stable at 25 °C and in the pure state forms colorless rhombic crystals of space group $C_2^{20}{}_v$; $\varrho_{298} = 2.168$ g/cm^3 [3]; $C_{p,298} = 63.64$ J mol^{-1} K^{-1}; refractive index at 589 nm $n_\alpha = 1.35$, $n_\beta = 1.46$, $n_\gamma = 1.65$. At 163 °C, this modification adapts a rhombic form of type $D_2^{25}{}_h$ (enthalpy of crystallization +1.2 kJ/mol) [66], mp 271 °C.

Sodium nitrite is hygroscopic (Fig. 15) [65]. The anhydrous salt has an enthalpy of solution of $\Delta H_{298} = +13.9$ kJ/mol at infinite dilution [3]. The hydrate NaNO$_2 \cdot 0.5$H$_2$O exists below −5 °C. Sodium nitrite is soluble in liquid ammonia; 2NaNO$_2 \cdot$ NH$_3$ forms below −64 °C. The solubility of sodium nitrite in 95% ethanol at 25 °C is ca. 1.4%.

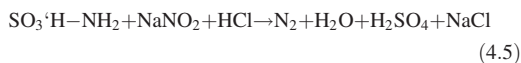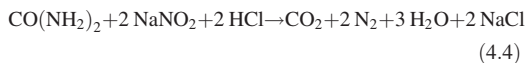Sodium nitrite oxidizes slowly in air. Above 330 °C it decomposes:

$$2\,NaNO_2 \rightarrow Na_2O + NO + NO_2 \tag{4.1}$$
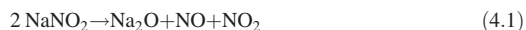
If the resulting nitrogen oxides are not removed, they react further with sodium nitrite:

$$NaNO_2 + NO_2 \rightleftharpoons NaNO_3 + NO \tag{4.2}$$

$$2\,NaNO_2 + 2\,NO \rightarrow 2\,NaNO_3 + N_2 \tag{4.3}$$

so that the end products of decomposition between 330 and 400 °C are sodium nitrate, sodium oxide, and nitrogen. Above 600 °C, the sodium nitrate product decomposes to oxygen and sodium nitrite (reaction 1.1), so that the end products at this temperature are sodium oxide, nitrogen, and oxygen [6].

Aqueous solutions of alkali nitrites reduce strong oxidizing agents (e.g., potassium permanganate solution), but in acidic solution they oxidize potassium iodide to iodine and Fe^{2+} to Fe^{3+}. They oxidize ammonium salts in weakly acidic solution to nitrogen above 50 °C. Urea and amidosulfonic acid are likewise oxidized to nitrogen:

$$CO(NH_2)_2 + 2\,NaNO_2 + 2\,HCl \rightarrow CO_2 + 2\,N_2 + 3\,H_2O + 2\,NaCl \tag{4.4}$$

$$SO_3\text{'}H-NH_2 + NaNO_2 + HCl \rightarrow N_2 + H_2O + H_2SO_4 + NaCl \tag{4.5}$$

In anhydrous melts at 210–220 °C, excess sodium nitrite oxidizes urea in an exothermic reaction that yields sodium carbonate and nitrogen:

$$CO(NH_2)_2 + 2\,NaNO_2 \rightarrow Na_2CO_3 + 2\,N_2 + 2\,H_2O \tag{4.6}$$

Equimolar quantities under the same conditions form sodium cyanate:

$$CO(NH_2)_2 + NaNO_2 \rightarrow NaCNO + N_2 + 2\,H_2O \tag{4.7}$$

The NaNO$_2$–NaNO$_3$ system forms a eutectic at 37.5 mol% sodium nitrate, mp 227 °C. Mixed crystals precipitate from the melt at all concentrations [67].

Nitrites do not occur in mineral form. Nitrite is formed as a metabolic product by microorganisms that oxidize organic nitrogen-containing substances; small amounts of nitrite are thus found in soil and groundwater.

4.2. Production

Until the beginning of the 20th century, sodium nitrite was produced by the reduction of sodium nitrate with lead, iron, zinc, manganese dioxide [which is oxidized to BaMnO$_4$ in the presence of Ba (OH)$_2$], coke, sulfur dioxide, and calcium carbide. Of these processes, the only one of industrial significance was the reduction of molten sodium nitrate with lead at ca. 400 °C. Other earlier processes are described in [14, 68].

Large-scale production of sodium nitrite is now based on the reaction of nitrogen oxides with sodium carbonate or sodium hydroxide solution.

The molar ratio of nitrogen oxides is called the "oxidation degree" (OD):

$$\frac{[NO_2]}{[NO]+[NO_2]}\cdot 100 = OD$$

At OD < 50%, the reaction is described by

$$2\,NaOH+NO_2+NO\rightarrow 2\,NaNO_2+H_2O \qquad (4.8)$$

Excess nitrogen monoxide does not react but is oxidized to nitrogen dioxide by ambient oxygen. At OD > 50% and a high partial pressure of oxygen, the following (slower) reactions also take place:

$$2\,NaOH+2\,NO_2\rightarrow NaNO_3+NaNO_2+H_2O \qquad (4.9)$$

$$2\,NaOH+3\,NO_2\rightarrow 2\,NaNO_3+NO+H_2O \qquad (4.10)$$

The reaction with sodium carbonate proceeds analogously. In practice, nitrate formation according to reactions (4.9) and (4.10) cannot be completely prevented even at OD < 50%.

To obtain nitrite solutions with a minimum nitrate content, the OD must be kept below 50% [69] and the pH above 8. In an acidic environment, nitrous acid is formed and decomposes to form nitric acid:

$$3\,HNO_2\rightarrow HNO_3+2\,NO+H_2O \qquad (4.11)$$
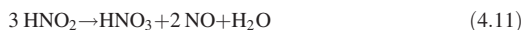
If a pure nitrite solution is desired, the gas leaving the absorption columns of the nitric acid plant must first be freed of entrained nitric acid. Because nitrogen dioxide is more thoroughly and rapidly absorbed in the columns than nitrogen monoxide, the gas mixture subjected to alkaline absorption has OD < 50% and contains 3–4 vol% oxygen. Alkaline absorption is described in Section 1.3.2 [70].

Nitrogen oxides produced by catalytic combustion of ammonia can also be used directly for the production of sodium nitrite. If the oxygen excess is kept small and an intermediate "acid washing" step is used, the OD can be kept lower than 50%.

4.3. Product Forms, Storage, and Transportation

Sodium nitrite is sold as the salt and in solution. The finely crystalline, slightly yellowish salt is marketed in untreated form and also after treatment with aryl alkyl sulfonates [18]. The salt contains ca. 99.0% sodium nitrite, 0.6% sodium nitrate, < 0.1% sodium chloride and sodium sulfate, and < 0.1% water.

Because of its hygroscopic nature and toxicity, sodium nitrite can be transported only in packaged form (plastic bags and metal tanks). It must be stored and shipped separately from oxidizable substances, ammonium salts, urea, food, and animal feeds. Sodium nitrite solution is marketed at a density of about 1.3 kg/L; it contains ca. 500 g/L sodium nitrite, 10–25 g/L sodium nitrate, and 5 g/L sodium hydrogen carbonate and has a pH of ca. 8. The solution can be stored in iron tanks.

4.4. Uses

Large amounts of sodium nitrite are consumed in the chemical and pharmaceutical industries for the production of nitroso and isonitroso compounds, diazotization reactions (especially for dyes), and the synthesis of pharmaceuticals (e.g., caffeine) and agricultural pesticides (e.g., pyramin).

Other applications of sodium nitrite are in metallurgy and corrosion prevention. It is used as an accelerator in phosphating, added to alkaline pickling solutions for aluminum, applied to steel as a descaling agent, added to drilling oils and abrasives, used for passivating metal surfaces and for creating protective coatings [e.g., of the type $Fe(NH_3)_x(NH_2)_3 \cdot yH_2O$] on carbon steels [71], and added as a corrosion inhibitor to lubricating oils and greases as well as to cooling water loops. Sodium nitrite serves as an oxidizing agent in the alkaline detinning of tinplate scrap [72] and a corrosion inhibitor in heat-transfer baths (see Section 1.5).

Sodium nitrite is used in lubricants for glass-forming equipment [73]. Like sodium nitrate and potassium nitrate, it is used as a heat-transfer medium.

Sodium nitrite is recommended as an additive in concrete and gypsum to improve strength and combat the corrosion of iron reinforcement.

In curing salts used in the food industry, sodium nitrite is still the most reliable agent for protecting against botulism, a dangerous bacterial contaminant of meats. High nitrite concentrations can, however, lead to the formation of

carcinogenic nitrosamines; legislative restrictions have, therefore, been imposed on the use of nitrite. Methods have been developed for achieving a satisfactory effect with minimal quantities [74]. The simultaneous addition of other substances (e.g., ascorbic acid) is reported to prevent the formation of nitrosamines [75, 76].

4.5. Economic Aspects

Sodium nitrite is produced as an important intermediate by the chemical industry in many countries, usually in conjunction with nitric acid production. Production statistics are not available.

5. Potassium Nitrite

5.1. Properties [77]

Potassium nitrite [7758-09-0], KNO_2, M_r 85.10, has an enthalpy of formation of $\Delta H_{298} = -375 \pm 5$ kJ/mol. The anhydrous product forms colorless monoclinic crystals of space group C_s^3, which are stable at 25 °C, $\varrho_{298} = 1.915$ g/cm^3 [3], mp 440 °C [3] (decomposition begins below the melting point).

Potassium nitrite is highly hygroscopic (Fig. 16) [78]; the enthalpy of solution of the anhydrous salt is $\Delta H_{298} = +13.4$ kJ/mol at infinite dilution [2]. The hydrate $KNO_2 \cdot 0.5H_2O$ exists below −8.9 °C.
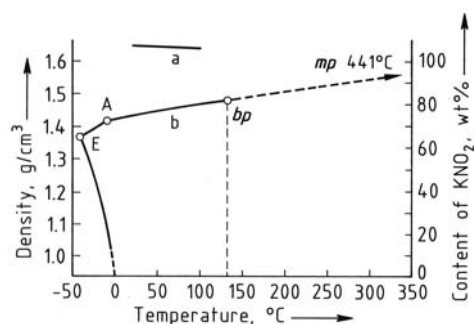

Figure 16. Properties of a saturated solution of potassium nitrite in water a) Density; b) Content of potassium nitrite
bp = boiling point of saturated solution containing 82.0 wt% potassium nitrite at 100.9 kPa and 132 °C; A = transition point: −8.9 °C, 71.9% potassium nitrite; E = cryohydric point: −40.2 °C, 64.9% potassium nitrite

Thermal decomposition of potassium nitrite yields nitrogen oxides and is analogous to that of sodium nitrite but begins at ca. 410 °C [6].

The system KNO_2–KNO_3 has a eutectic point at 316 °C and 22.5 mol% potassium nitrite [79]. In the quaternary system KNO_2–KNO_3–$NaNO_3$–$NaNO_2$, the composition with the lowest freezing point (142 °C) is 37.5 mol% potassium nitrite, 37.5 mol% sodium nitrate, and 25 mol% sodium nitrite [80, 23].

5.2. Production

Potassium nitrite can be obtained by reduction of potassium nitrate (similarly to sodium nitrite). A variety of other reactions between sodium nitrate and potassium salts have also been described [77]. Production of potassium nitrite by absorption of nitrogen oxides in potassium hydroxide or potassium carbonate solution is not employed on a large scale because of the high price of these alkalies. Furthermore, the fact that potassium nitrite is highly soluble in water makes the solid salt difficult to recover. The solubility relationships in the system KNO_2–KNO_3–H_2O are described in [81].

5.3. Uses

Potassium nitrite is used only in very small quantities, for example, as an oxidizing agent and as a corrosion inhibitor in washing with hot potash for removal of carbon dioxide from gas streams (e.g., synthesis gas). Potassium nitrite is more soluble than sodium nitrite and does not form sparingly soluble bicarbonate in carbon-dioxide-rich solutions.

6. Ammonium Nitrite

Ammonium nitrite is a very unstable compound that is virtually always handled in aqueous solution.

6.1. Properties

Ammonium nitrite [13446-48-5], NH_4NO_2, M_r 64.04 [3], has an enthalpy of formation of

$\Delta H_{298} = -260 \pm 5$ kJ/mol and forms cubic crystals, $\varrho_{298} = 1.69$ g/cm^3 [3]. The melting point is not well defined because of decomposition.

Ammonium nitrite is highly hygroscopic and readily soluble in water [78] (enthalpy of solution $\Delta H_{285} = +19.3$ kJ/mol at infinite dilution [3]). The saturated solution contains 42.5 wt% ammonium nitrite at the cryohydric point (-27.9 °C), 55.4% at 0 °C, and 65.0% at 20 °C. Hydrated solid phases are not known.

Solid ammonium nitrite is stable only in the pure, dry state. Exothermic decomposition begins at 60 °C and may occur explosively:

$$NH_4NO_2 \rightarrow N_2 + 2\,H_2O \quad \Delta H = -300 \text{ kJ/mol} \qquad (6.1)$$
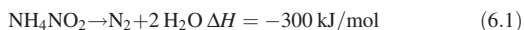
The saturated solution is stable only up to 30 °C; dilute solutions release nitrogen according to reaction (6.1) above 60 °C. Decomposition involves nitrous acid as an intermediate [82]; the stability of the aqueous solution is enhanced by the addition of ammonia, calcium hydroxide, or potassium iron(II) cyanide.

Dilute ammonium nitrite solutions can be inverted with nitric acid below 30 °C [83]:

$$3\,NH_4NO_2 + 2\,HNO_3 \rightarrow 3\,NH_4NO_3 + 2\,NO + H_2O \qquad (6.2)$$

Mixed crystals of ammonium nitrite and ammonium nitrate precipitate from an aqueous solution of NH_4NO_2–NH_4NO_3 containing $> 47\%$ ammonium nitrite at 20 °C [84]. The most highly concentrated solution in this system at 20 °C contains only 6% water, 48% ammonium nitrite, and 46% ammonium nitrate.
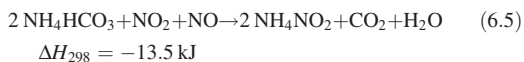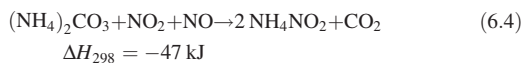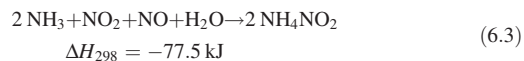
6.2. Production

Ammonium nitrite is produced and utilized industrially solely in the form of a weakly ammoniacal solution with pH > 7.5. When ammonium nitrite solution is prepared, the simultaneous formation of ammonium nitrate must be avoided because the two compounds cannot be separated from one another.

Ammonium nitrite is produced on an industrial scale from nitrogen oxides and ammonia or ammonium carbonate. The reaction is similar to that used for the formation of sodium nitrite. Because of the instability of ammonium nitrite (reaction 6.1), however, care must be taken to keep the pH between 8 and 9 and the temperature between 0 and + 5 °C.

The heat balance of ammonium nitrite formation depends strongly on the feed ammonium compound:

$$2\,NH_3 + NO_2 + NO + H_2O \rightarrow 2\,NH_4NO_2$$
$$\Delta H_{298} = -77.5 \text{ kJ} \qquad (6.3)$$

$$(NH_4)_2CO_3 + NO_2 + NO \rightarrow 2\,NH_4NO_2 + CO_2 \qquad (6.4)$$
$$\Delta H_{298} = -47 \text{ kJ}$$

$$2\,NH_4HCO_3 + NO_2 + NO \rightarrow 2\,NH_4NO_2 + CO_2 + H_2O \qquad (6.5)$$
$$\Delta H_{298} = -13.5 \text{ kJ}$$

Use of ammonium bicarbonate appears advantageous because no water is formed in the reaction to dilute the solution. However, since it has a low solubility the use of ammonium carbonate is generally preferred.

The process is usually carried out under an overpressure of 0.1–0.6 kPa [85]. The NO_2–NO gas mixture is first cooled to 0 °C to decrease the degree of oxidation (see Section 4.2) to 35–40% by condensation of dilute nitric acid, and then fed into absorption columns connected in series and packed with ceramic Raschig rings or fitted with sieve trays. The circulating solution is held at ca. 0 °C by coolers located at the bottoms of the columns and outside them. To prevent crystallization of ammonium bicarbonate, a metered amount of aqueous ammonia solution is added along with the ammonium carbonate. The final product solution has a pH of 8 and contains ca. 150–200 g/L ammonium nitrite, 20 g/L ammonium nitrate, 20 g/L ammonium carbonate, and 2–5 g/L ammonia. Ammonium nitrite mist is formed in the absorption step, a final gas scrub is therefore used to recover ammonium carbonate solution for reuse [86].

The ammonium nitrite yield relative to the nitrogen oxides inlet to ammoniacal absorption is less than 90%. Losses include nitrate formation, nitrite decomposition (reaction 6.1), and tail-gas and mist losses.

6.3. Uses

Ammonium nitrite can be used to passivate steam boiler equipment and chemical plants because it does not leave any nonvolatile residues behind.

It is also used as a blowing agent in the manufacture of hollow rubber articles. In the laboratory, very pure nitrites can be prepared from pure ammonium nitrite and the hydroxides of other cations.

7. Calcium Nitrite

7.1. Properties [87]

Calcium nitrite, [13780-06-8], $Ca(NO_2)_2$, M_r 132.09, has an enthalpy of formation of $\Delta H_{298} = -750 \pm 10$ kJ/mol, $\varrho_{273} = 2.26$ g/cm^3 [78], mp 398 °C (decomposition begins below melting point).

Anhydrous calcium nitrite is hygroscopic and dissolves readily in water (Fig. 17) [78]; the enthalpy of solution for 1 mol in 800 mol of water is $\Delta H_{293} = -8.5$ kJ/mol. The monohydrate crystallizes from solution below 129 °C to form silky hexagonal needles ($\varrho_{293} = 2.23$ g/cm^3).

Below 34.6 °C, the tetrahydrate $Ca(NO_2)_2 \cdot 4H_2O$ crystallizes in tetragonal form: $\varrho_{293} = 1.72$ g/cm^3, enthalpy of solution for 1 mol in 800 mol of water $\Delta H_{293} = +33.5$ kJ/mol.
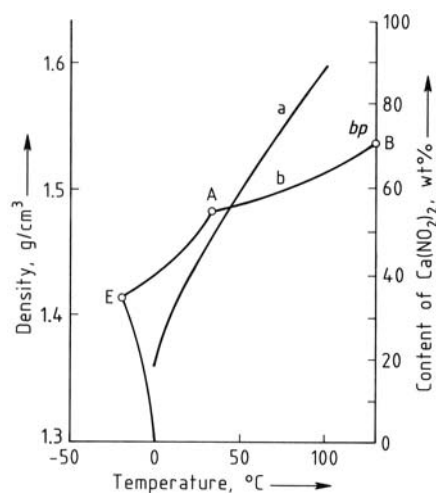

Figure 17. Properties of a saturated solution of calcium nitrite in water a) Density; b) Content of calcium nitrite bp = boiling point of saturated solution at 101.3 kPa and 133 °C with decomposition; A = first transition point: $Ca(NO_2)_2 \cdot 4H_2O + Ca(NO_2)_2 \cdot H_2O$ at + 34.6 °C and 55.1% $Ca(NO_2)_2$; B = second transition point: $Ca(NO_2)_2 \cdot H_2O + Ca(NO_2)_2$ at + 129 °C and 71% $Ca(NO_2)_2$; E = cryohydric point: ice + $Ca(NO_2)_2 \cdot 4H_2O$ at −20.0 °C and 34.2% $Ca(NO_2)_2$.

Calcium nitrite decomposes to calcium oxide and a mixture of nitrogen monoxide and nitrogen dioxide at temperatures as low as 250 °C [6]. The hydrates are decomposed by atmospheric carbon dioxide, with the formation of nitrogen oxides. A saturated solution of calcium nitrite boils at 133 °C (101.3 kPa) with decomposition.

7.2. Production

Calcium nitrite is formed when a mixture of gaseous nitrogen dioxide and nitrogen monoxide (OD < 50%) is absorbed in a suspension of calcium hydroxide. This process is used to clean up the final tail gases from low-pressure nitric acid plants when no demand exists for sodium nitrate or sodium nitrite. The spent absorption liquor contains calcium nitrite and generally some calcium nitrate. The nitrite can be recovered as the tetrahydrate $Ca(NO_2)_2 \cdot 4H_2O$ by concentration and cooling. This product has a lower solubility than calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$. The nitrite is not, however, recovered on a large scale; the calcium nitrite solution is usually inverted with nitric acid to obtain calcium nitrate.

7.3. Uses

No large-scale application exists for calcium nitrite. Calcium nitrite is reacted with the sulfates of other cations. The corresponding nitrite solutions are obtained after removal of the precipitated gypsum by filtration. Calcium nitrite mixed with calcium nitrate and calcium chloride is recommended as a noncorrosive salt for thawing ice on roads (along with $NaNO_2$). Calcium nitrite is proposed as a corrosion-inhibiting additive in concrete that also improves workability at low temperature.

8. Analysis of Nitrates and Nitrites

Nitrate Determination [88, 89]. For *volumetric determination*, nitrate is reacted in strongly alkaline solution with Devarda's alloy (50% Cu + 45% Al + 5% Zn) or in neutral solution with Arnd's alloy (65% Cu + 35% Mg) and thus converted to ammonia. The ammonia is distilled

into a receiver containing sulfuric acid and determined by acidimetric methods. Ammonium and nitrite are also detected and must, therefore, be determined separately. The method is not applicable in the presence of urea, urea–aldehyde condensates, cyanamide, or protein.

Gravimetrically, nitrate is determined as nitron nitrate after precipitation with nitron in acetic acid solution. Perchlorate, chlorate, nitrite, and other anions precipitate along with nitrate. The method cannot be used in the presence of urea–aldehyde condensates and protein.

At low concentrations (ppm range), nitrate is determined *photometrically* with 2,4-dimethylphenol, brucin, or sodium salicylate. Nitrite interferes and must be removed.

The *potentiometric method* with a nitrate ion-sensitive electrode is suitable for the determination of nitrate in single samples and for automated continuous monitoring (e.g., of wastewater) [90]. Perchlorate, iodide, chlorate, and bromide ions as well as high nitrite concentrations interfere with the method.

Nitrate can be determined in the presence of nitrite by *titrimetry* after reduction with iron(II) sulfate; the end point is indicated potentiometrically [91].

Prior to nitrate determination, nitrite can be destroyed in a weakly acidic medium with ammonium salts, urea, sodium azide, amidosulfonic acid, or hydroxylamine (cf. reactions 4.4 and 4.5).

Ion chromatography is an effective method for determining and separating nitrate [92]. The nitrate ion is detected either with a conductivity detector or a UV detector (excitation wavelength 254 nm). This technique has the advantages of high precision, rapidity, and independence of flow rate [93].

Nitrite Determination. High nitrite concentrations are determined by titration at ca. 35 °C with potassium permanganate in sulfuric acid solution. To avoid loss of nitrite, the solution is allowed to flow with stirring into acidified potassium permanganate solution until it becomes colorless [88]. Other ions that can be oxidized by potassium permanganate in sulfuric acid solution must be considered in evaluating the results.

Low contents of nitrite are determined photometrically with sulfanilamide and *N*-(1-naphthyl)ethylenediammonium dichloride as a red azo dye [94]. The reaction is specific for

nitrite and can be automated [95]. This method is recommended for series analyses (e.g., of water samples).

Determination of Cations. *Sodium* as the primary constituent can be determined gravimetrically by precipitation with uranyl magnesium acetate. This method can be employed even with a large excess of potassium [89]. Flame photometry and atomic absorption spectroscopy can be used for lower concentrations and in the trace range.

Potassium is precipitated as sparingly soluble potassium tetraphenyl borate and determined as such by weighing after treatment with sodium tetraphenyl borate in weakly alkaline or acidic solution [96–98]. Volumetric determination of potassium with sodium tetraphenyl borate and an electrometric end point indication is also important [98–100]. The chloroplatinate method is employed in the United States [89, 100].

Thermometry measures the heat (ca. −50 kJ/ mol) released when potassium is precipitated as the perchlorate [101]. Potassium is also determined by conductometric titration with sodium tetraphenyl borate [98].

The potassium content can be determined quickly in process analysis by flame photometry [89] and atomic absorption spectroscopy. In the plant, β or γ radiation of ^{40}K solid salts or a solution can be utilized for analysis, product inspection, and process control [102].

Ammonium is determined acidimetrically by distillation of ammonia from alkaline solution. Trace amounts can be determined by photometry after formation of indophenol or reaction with Nessler's reagent [94]. Potentiometric determination with an ammonia electrode is suitable for all concentration ranges [90].

Calcium and magnesium in nitrates and nitrites are determined volumetrically by titration with the demineralized disodium salt of ethylenediaminetetraacetic acid. Other divalent cations must first be masked or precipitated [103].

Determination of Impurities. *Water content* can be measured either by the Karl Fischer method or by determination of the weight loss at 105 °C [89].

High concentrations of *chloride* are determined volumetrically by titration with silver nitrate [89]; trace amounts are measured by titration with mercury(II) nitrate and diphenylcarbazone as indicator [100]. A photometric technique is based on the determination of iron (III) rhodanide formed after liberation of rhodanide ion from mercury(II) rhodanide by chloride ion [95]. Very low concentrations can be determined turbidimetrically as silver chloride at 420 nm. This has the advantage that toxic mercury is not involved in the analysis.

Chlorate can be determined iodometrically in strong hydrochloric acid solution. *Perchlorate* is determined gravimetrically as potassium perchlorate [89]. *Iodate* can be determined iodometrically in weakly acidic solution. (Nitrite ion must be destroyed before iodometric analyses are performed.)

Boric acid can be determined by acidimetric titration, either directly or after isolation as methyl borate in the presence of mannitol or glycerol [89].

9. Environmental Aspects

Nitrate Removal. Nitrates are undesirable in wastewater for two reasons: uncontrolled denitrification can interfere with the final clarification step in biological wastewater treatment plants, and high nitrate concentrations can cause contamination of drinking water.
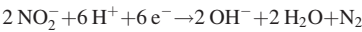
In 1970 the World Health Organization (WHO) issued guidelines recommending that the maximum limit for nitrate concentrations should be 50 mg/mL, this was later reduced to 45 mg/mL. The WHO also recommended a maximum acceptable concentration of 100 mg/L [105]. In the United States the EPA proposed regulations for drinking water on May 22, 1989 [106]. Public comment closed August 21, 1989, and the final rule was scheduled for December 1990. A maximum containment level for total nitrate and nitrite of 10 mg/L (as nitrogen) is proposed. As early as July 1980, the Council of the European Community issued a directive concerning the quality of water for human consumption [107]. The maximum permissible nitrate concentration was set at 50 mg/L, with a guide level of only 25 mg/L. Member countries agreed that drinking-water quality would meet this standard within five years (for the members Portugal, Spain, and Greece, who joined the EC later, the appointed five-year period started in 1988). To achieve this, some waterworks dilute their water with low-nitrate water; the trend to equip waterworks with nitrate removal facilities is also increasing. Because this equipment is very expensive, nitrate removal from wastewater before it reaches the treatment plant and reduction in nitrate loading of surface waters (agricultural) are desirable goals; see also → Fertilizers, 6. Environmental Aspects, Chap. 2.. Three methods have been described for the removal of nitrates from wastewater: reverse osmosis, anion exchange, and denitrification.

Reverse Osmosis. The principles of reverse osmosis are described elsewhere (→ Membranes and Membrane Separation Processes, 1. Principles, Section 3.3.). Pressure is used to force water through a membrane that is impermeable to any dissolved solutes or suspended solids. Despite its high cost, reverse osmosis is becoming more and more important in wastewater treatment; the cost depends on the nature of the inlet wastewater stream (pretreatment). If the wastewater has a high suspended solid content or the dissolved salts might crystallize, reverse osmosis can only be used to a limited extent because the membranes may become plugged. This technique results in the production of a concentrated nitrate solution, which is then dealt with by other methods.

Anion Exchange. Units based on anion-exchange resins [108] can only be used in special cases, because of their inadequate selectivity for nitrate versus chloride ions. The same is true for a process developed especially for the removal of nitrate from wastewater in cellulose nitrate production, which utilizes water-insoluble secondary amines in the chloride form as liquid ion exchangers [109]. In contact with wastewater, these substances exchange chloride for nitrate. In the next step, the amines exchange their nitrate ions for chloride ions from a potassium chloride solution to yield pure potassium nitrate as a byproduct. This technique, however, requires virtually chloride-free wastewater. A similar procedure has been described in which the amine is used in the sulfate form and ammonium nitrate is obtained as byproduct after stripping with ammonia gas [110].

Denitrification. Denitrification is currently the most important process for nitrate removal [111–114]. Nitrate is reduced to nitrogen by facultatively anaerobic bacteria (e.g., *Achromobacter*, *Denitrobacillus, Nitrococcus,* or *Spirillum*) under anaerobic conditions. These bacteria can use nitrate and nitrite as a source of oxygen.

$$2\,NO_3^- + 10\,H^+ + 10\,e^- \rightarrow 2\,OH^- + 4\,H_2O + N_2 \qquad (9.1)$$

$$2\,NO_2^- + 6\,H^+ + 6\,e^- \rightarrow 2\,OH^- + 2\,H_2O + N_2$$

To maintain metabolism, an adequate supply of carbohydrates must be present or added. The carbohydrates are oxidized to carbon dioxide and water.

Denitrification is the sole metabolic route for converting fixed nitrogen to the molecular form. The required anaerobic conditions are considered satisfied if the BOD_5 value (five-day biological oxygen demand) is more than 1.5 times the oxygen fixed in the nitrate.

Nitrite Removal. Nitrites must be removed from wastewater because they are toxic (see Chap. 10) and also because they interfere with the oxygen economy of natural waters and water treatment plants. Nitrite ions can be eliminated by oxidation to nitrate, by reduction to elemental nitrogen, or by denitrification (see Nitrate Removal).

Oxidation to Nitrate. Nitrite is reacted with, for example, sodium hypochlorite in a weakly acidic medium (pH 3–4):

$$NaNO_2 + NaOCl \rightarrow NaNO_3 + NaCl \qquad (9.2)$$

This process has the advantage of a high reaction rate with virtually 100% conversion. It can be used as a continuous method through relatively simple redox potential measurements and automation. It has the drawback, however, of increasing the sodium chloride content of water [115].

Another option is oxidation with hydrogen peroxide:

$$NaNO_2 + H_2O_2 \rightarrow NaNO_3 + H_2O \qquad (9.3)$$
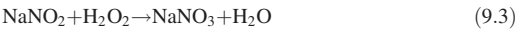
This reaction occurs at pH 3–3.5 and can be effected only in batch operation because a stepwise measurement and hydrogen peroxide

**Table 7.** Comparison of nitrite removal processes using hydrogen peroxide and sodium hypochlorite [110]

	Hydrogen peroxide	Sodium hypochlorite
Batch operation	yes	yes
Continuous operation	no	yes
pH	2.0–4.0	3.0–3.5
Concentration of oxidizing agent, wt%	35	12.5
Oxidizing agent required, kg/kg nitrite	2.25	13.5
Cost of oxidizing agent, DM/kg nitrite	3.85	6.48
Salt produced, kg/kg nitrite	0	2.5 NaCl
Loss of active agent on storage	no	yes

metering cycle must be used. The process has the advantages of low cost and no salting (Table 7) [115].

Nitrite is also oxidized to nitrate by *Nitrobacter* species under aerobic conditions:

$$NO_2^- + 1/2\,O_2 \rightarrow NO_3^-$$
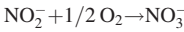
Reduction to Nitrogen. Nitrites can be reduced to nitrogen with amidosulfuric acid:

$$NaNO_2 + NH_2SO_2OH \rightarrow N_2 + NaHSO_4 + H_2O \qquad (9.4)$$
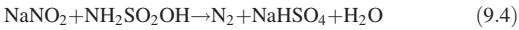
This reaction is of value for high nitrite levels and is carried out at ca. pH 4. Urea is also employed as reducing agent (reactions 4.4. and 4.5).

10. Toxicology and Occupational Health [116]

Nitrates and nitrites cause relaxation of smooth muscle cells [117, pp. 224–244], which can be so drastic that the contractile system is totally inhibited (protein phosphorylation). These compounds have a vasodilative action, allowing blood to pool in the veins so that the heart is not completely filled. The systolic blood pressure therefore drops, and the pulse rate increases. Dilation of blood vessels in the brain leads to headaches. Acute circulatory collapse and fainting are possible. Dilation of vessels in the retina leads to vision disorders.

Acute, severe poisoning is associated with a critical drop in blood pressure, vomiting, and cyanosis, and ends in death due to respiratory and circulatory failure. Methemoglobin produced by reaction of inorganic nitrite or amyl nitrite with hemoglobin is responsible for this

effect. Nitrates are converted to nitrites by microbes in the intestines. Methemoglobin prevents oxygen transport because its central heme group contains a Fe^{3+} ion which is incapable of binding oxygen. Only hemoglobin (Hb) with its central Fe^{2+} ion can bind oxygen reversibly:

$$Hb \cdot Fe^{2+} \cdot O_2 \rightleftharpoons Hb \cdot Fe^{3+} \cdot OH^-$$
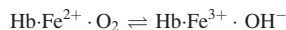
In the presence of nitrite, coupled oxidation occurs [117, p. 650]. Oxygen is transferred from the hemoglobin to nitrite with the formation of nitrate and methemoglobin (Fe^{3+}). In intact erythrocytes methemoglobin is reduced by enzymes (diaphorase, methemoglobin reductase).

Methemoglobin formation occurs more readily in premature and newborn babies than in adults. The intestinal flora of babies differs from that of adults and has a higher reducing capacity; nitrate is therefore more easily reduced to nitrite. In the fetus hemoglobin is more readily oxidized than in adults and the erythrocyte reductase system is not fully developed [118]. Vegetables fertilized with nitrate or tap water containing nitrate can cause methemoglobinemia in babies.

Severe intoxication is expected at an oral dosage level > 2 g. A single oral dose of 4 g of nitrite is lethal in humans [119]. In the event of poisoning, the stomach should be pumped and a physician notified [117, p. 250; [120, 121]].

Nitrosamines cause tumor formation in animals that depends on dosage and route of administration. Nitrosamines are classified as risk factors for tumor formation in humans.

In the stomach secondary and tertiary amines can react with nitrite to form nitrosamines. Secondary amines are formed during cooking (roasting, frying) of proteins and alcoholic fermentation, and are constituents of flavoring substances. Low nitrosamine concentrations are found in pickled meat, alcoholic beverages, and tobacco smoke. Tetracycline contains groups that can be nitrosylated. The drug aminophenazone has been withdrawn from the market on account of its nitrosamine content (*N*-nitrodimethylamine).

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