The decomposition of ammonium nitrate under fire conditions
— a review of ammonium nitrate thermolysis

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Emneord

Ammoniumnitrat

Temperatur

Brann og eksplosjoner

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Summary

Since the discovery of ammonium nitrate (AN) in the late 17th century, its behavior under heating has been of interest to the scientific community. Following its introduction as a commercially important chemical in fertilizers and explosive formulations, but also for the production of nitrous oxide (anesthetics), the safety field also became attentive to this as a consequence of the underlying explosion risks associated with handling, transport and storage of the material, especially when subjected to elevated temperatures.

Evidently, ammonium nitrate under fire exposure is now a well-established explosion hazard and has been responsible for some of the greatest industrial accidents to date. Accordingly, the investigative literature on AN thermolysis is immense, of which this review endeavors to present a comprehensive and contemporary compilation.

Morphology, decomposition pathways and the shock-sensitivity of AN are influenced by elevated temperatures and heating rates. However, researchers have never been able to induce explosion in pure AN under controlled conditions by heat alone. Here, other factors play an important part. Of these, confinement stands out as a crucial determinant – elevated pressure increases gas-solid phase interactions under decomposition, promoting exothermic behavior, even for pure AN. This is especially an important feature to consider if bulk amounts of AN is subjected to fire, as larger heaps are likely to self-confine.

Contaminants and combustible material are also well-known contributors to the explosion risks of AN. As more realistic and complex thermoanalytic and computational technologies have been developed, a greater understanding of the mechanisms behind the thermolysis of contaminated AN has emerged. For most contaminants, detrimental effects such as thermal run-aways and explosions seem to depend on a certain amount of initial heating and confinement.

Due to the prominent endothermic behavior of AN dissociation, however, AN is in most cases a relatively stable compound even when heated. This means, that strictly defined conditions are necessary for achievement of deflagration-to-detonation transitions or just deflagration alone. As the critical determinants for such transitions are yet to be established, heat exposure is still the most obvious, generic and critical cause of explosion in any fire related AN explosion.

Sammendrag

Siden oppdagelsen av ammoniumnitrat (AN) på slutten av 1600-tallet har effekten av dets oppvarming vært av vitenskapelig interesse. Da AN etter hvert ble et viktig kommersielt og industrielt kjemikalie som bestanddel i gjødsel- og eksplosivformuleringer, men også som utgangsstoff i produksjon av dinitrogenoksid, økte denne interessen betraktelig med hensyn til sikkerhet ved håndtering, oppbevaring og transport. Dette har vært en konsekvens av ANs underliggende eksplosjonsrisiko under brann og høye temperaturer, som har blitt eksemplifisert av noen av historiens største industriulykker. Det finnes derfor en stor mengde litteratur om ANs termolyse og egenskaper under brann. Denne litteraturstudien er en sammenfatning av resultater fra denne forskningen.

Under høye temperaturer påvirkes morfologien, dekomponeringsmønstrene og sjokk-følsomheten av AN. Selv etter et århundre med forskning på området har man likevel ikke vært i stand til å påvise eksplosjon i ren AN ved oppvarmning alene. Her spiller andre faktorer en viktig rolle og da spesielt inneslutning. Ved forhøyet trykk fremmes gass- og fastfaseinteraksjoner under ANs termolyse og eksoterme reaksjoner fremmes. Dette er en viktig egenskap å være oppmerksom på ved brann der store mengder AN er tilstede, da bulkmengder i visse tilfeller kan inneslutte seg selv under oppvarming.

Kontamineringer og brennbart materiale er også velkjente faktorer som øker eksplosjonsrisikoen i AN. Etter hvert som mer realistiske og komplekse termiske analyser og simuleringsmetoder har blitt introdusert til fagområdet, har man fått en bedre forståelse for mekanismene bak termolysen av kontaminert AN. For de fleste typer av kontamineringer ses det at de mest skadelige utfall som termiske kjedereaksjoner og eksplosjoner, er avhengig av en viss mengde oppvarming og/eller inneslutning.

På grunn av den anselige endoterme karakteren til AN dissosiasjon er det likevel en relativt stabil forbindelse, selv under oppvarming. Dette betyr at hensiktsmessige forhold er nødvendige for å oppnå deflagrasjon-til-detonasjonsoverganger. Da de eksakte determinantene og mekanismene for denne overgangen ennå ikke er etablert, er derfor temperaturpåvirkning fortsatt den mest selvinnlysende, generiske og primære eksplosjonsårsak i enhver brannrelatert AN-eksplosjon.

Content

Preface

The literature review presented in this report was carried out by the author in the context of the joint research initiative "Investigating the explosion risks of ammonium nitrate under fire exposure and its consequences" between FFI, The Norwegian Directorate for Civil Protection (DSB) and the industrial partners OY Forcit AB, Maxamcorp holding S.L., Orica Norway AS and Yara International ASA.

The project aim is to establish in-depth knowledge pertaining to the risks involved in transport and storage of AN products used in explosives manufacture, with emphasis on the initiation of explosion in AN and AN-based products when exposed to high temperatures. The work described herein reviews the available literature on the thermolysis of ammonium nitrate and its behavior under fire conditions. It is a deliverable of the projects' preliminary literature and state-of-the-art investigations.

The author would like to thank Assistant Professor Torben Højland at the University of Southern Denmark (SDU), Odense, Denmark and Dr. Tor Erik Kristensen at FFI for their valuable comments, suggestions and proofreading. Furthermore, the library service at FFI are acknowledged for their excellent support on retrieving even the most secluded document material.

Abbreviations

AN   Ammonium Nitrate

ANE   Ammonium Nitrate Emulsion

ANPP   Ammonium Nitrate Porous Prills

ANFO   Ammonium Nitrate-Fuel Oil

ANS   Ammonium Nitrate Solution

DFT   Density Functional Theory

DSC   Differential Scanning Calorimetry

FGAN   Fertilizer Grade Ammonium Nitrate

G-FGAN   Grained Fertilizer Grade Ammonium Nitrate

H_{crit} Critical height

STP   Standard Temperature and Pressure

TGA   Thermal Gravimetric Analysis

TGAN   Technical Grade Ammonium Nitrate

1 Introduction

The white and crystalline onium salt ammonium nitrate (NH_4NO_3) has been known to, and fascinated chemists, even since the early days of the phlogiston era. Its potential both as fertilizer and energetic material was quickly recognized.

The discovery of ammonium nitrate (AN) was most likely reported as early as 1659 by the German chemist Johann Rudolf Glauber (1604-1670). In the fourth part of his treatise Des Teutschlands Wolfahrt (Germany's Prosperity, 1656-1661)[*], he describes the formation of a "liquid and volatile salt" when mixing *aqua fortis* and *spirit of sal-armoniack,* now known as nitric acid (HNO_3) and aqueous ammonia (NH_4OH), respectively.[1] Also today, AN is produced by the neutralization of nitric acid with ammonia.[2]

Glauber mentioned little more about this "liquid salt" in his following publications, until the publication of the 7th part of his Pharmacopoeia Spagyrica in 1667, where he describes how ammonium salts can be made by the means of mixing spirit of urine with different acids.[3] In the accompanied second and third appendix, released in 1668, a "most secret sal-armoniack" is, however, mentioned for the first time.[4] Further described in the third appendix as a "fiery alkahest" and in pompous wordings such as "Eagle Wings" and "Lucifer", Glauber was certain that this compound was a most holy compound and a God-given gift to man.

The procedure for making regular sal-armoniack (NH_4Cl) was already well known at that time of the publication of the Pharmacopoeia, and in its appendices, Glauber furthermore revealed that a "secret sal-armoniack" could be made from the combination of spirit of urine (aqueous ammonia, NH_4OH) with oil of vitriol (sulfuric acid, H_2SO_4), i.e. ammonium sulfate (NH_4SO_4). The procedure for producing the most secret of the sal-armoniacks, nevertheless, remained undisclosed. As Glauber was recognized for his ability to produce "spirits" of high purity and quality, including nitric acid and liquid ammonia, it seems likely that this specific ammonium salt, the "fiery alkahest", described in the last pages of the third appendix of Pharmacopoeia, is indeed AN.

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[*] Des Teutschlands Wolfart was published in a series of 6 volumes between 1656 and 1661 following the Thirty Years' War. Here, Glauber describes and encourages the use of chemical processes and compounds from natural resources which he believes will be of importance to make Germany self-sufficient in both peace and war time.

AN is the most commercially important ammonium compound both in term of production volume and usage, largely due to its role as an ingredient in a range of fertilizers (24 % of world consumption of nitrogen fertilizers is AN).[2] During the last century AN has also emerged as a primary ingredient in commercial explosives by virtue of its oxidizing properties. In 2015, 600,000 tons of industrial explosives were consumed worldwide whereof 90 % comprising AN-based explosives. Of these, more than 80 % were bulk explosives produced on site.[5]

AN is considered to be a stable substance at room temperature and atmospheric pressure.[2,6] However, under certain conditions such as changes in temperature, pressure, morphology, bulk density and contamination, the sensitivity and explosion risk of AN increase considerably. Even though explosive events with AN during storage and transport are rare, they are not exceptional. In fact, some of the largest industry- and transport-related accidents to date have involved AN. Most of these have been the consequence of uncontrollable fires.[7-9] Babrauskas recently published a compilation of accidents involving AN and fire.[8] The overview highlighted the complex and somewhat unpredictable behavior of AN during fire incidents; of 57 cases reported, 17 culminated in explosion disasters. Still, due to the relatively large amounts of which AN is stored and transported, the consequences of these accidents, when they do take place, are often significant. Therefore, several inquiries into the thermolysis and explosive behavior of AN under fire exposure have been performed throughout the last century. Surprisingly, when considering the existing and extensive literature concerning the thermal behavior and properties of AN, only a handful of reviews exist.[10-14] These either lack comprehensiveness or limit their focus to combustion and potential use in novel propellant technologies. This review is thus an endeavor to present an extensive and contemporary compilation of research on AN thermolysis with focus on the consequence of fire exposure.

2   General properties of pure ammonium nitrate

2.1   Physical and chemical properties

AN is a white, crystalline and highly water-soluble salt with no stable hydrate forms. Due to its great hygroscopicity and water solubility, naturally occurring AN can only be encountered in some of the driest places on earth such as the Atacama Desert in Chile.[15] The distinct hygroscopicity has always been problematic for its use in both fertilizers and explosives formulations, as moisture-absorbing powders tend to agglomerate and cake. This again hampers the originally intended properties. Even as the current manufacturing processes and specialized coatings counteract a large proportion of these issues, it remains a concern during storage.[16-17]

AN is considered a stable compound under standard ambient temperature and pressure.[2,6] It does not burn at atmospheric pressure, but instead decomposes when temperatures surpass the boiling point. Still, detectable amounts of intact AN molecules have been confirmed in the vapor above the solid phase.[18-19] Contradictive to earlier theories of complete dissociation of the vapor, this is suggested to be a consequence of sublimation rather than recombination of the dissociation products in the gas phase.[18,20] An overview of AN's main properties can be found in Table 2.1.

Table 2.1   Overview of the general properties of AN.[2]

Properties of ammonium nitrate			
Formula:	NH_4NO_3	**Melting point:**	169.6 °C
Mw:	80.043 g/mol	**Boiling point:**	~ 210 °C
Color:	Colorless/white	**Crystal density:**	1.725 at 25 °C
Water solubility:	190 g/100 mL at 20 °C	**Oxygen content:**	60%
$\Delta_fH°$:	-365.6 kJ/mol	**Oxygen balance:**	20%

2.1.1   Morphology

In the solid state, AN possesses a distinct polymorphism and five stable crystalline phases are known (Table 2.2).[21-22]

Table 2.2   Overview of the crystalline phases of AN and their properties.[2,22-24]

System	Temp. range [°C]	Crystal system	Density [g/cm^3]
I (ε)	125.2–169.6	Cubic	1.594 at 130°C
II (δ)	84.2–125.2	Tetragonal	1.666 at 93°C
III (γ)	32.3–84.2	Rhombic	1.661 at 40°C
IV (β)	-16.9–32.3	Rhombic	1.725 at 25°C
V (α)	< -16.9	Tetragonal	1.710 at -25 °C

As solid phase transfers involve either shrinkage or expansion of the crystals, the changes can have considerable effect on physical and thermodynamic properties such as solubility, specific volume, heat capacity and even mode of decomposition.[22-23,25]

From a practical perspective, the IV-III transition at 32 °C is of particular relevance for solid AN products, as this transition leads to changes in the crystal packing as granular products breaks down into dust or fine particles.[16] This also introduces the well-known and undesirable problem of caking. When concerning safety, the changes in the crystal packing is also of some pertinence, as prills that have experienced thermal cycling are known to be more shock-sensitive.[26]

2.1.2   Density and grades

Several grades of AN are commercially available. The available qualities can in general be divided into laboratory, fertilizer (FGAN) and technical (TGAN) grade, respectively (Figure 2.1).

Laboratory grade AN is usually crystalline and is typically divided further into different purity grades for specific applications. Both FGAN and TGAN are usually manufactured as solid spheres, known as prills. Grains and granules are less common. The prills are produced by spraying droplets of molten AN solution into a prilling tower. Descending droplets are then formed as they are cooled and solidified by an upward flow of air.[2] The resulting density of the prill is dependent on the residual moisture of the molten AN, air temperature and flow rate.

FGAN products are produced as high density (> 860 kg/m^3), non-absorbent prills with low porosity, which is advantageous for agricultural use. These dense prills are manufactured using molten AN solutions greater than 99.6 % and a short prilling tower (20–30 m).[6] Depending on the desired properties of the finished product, the prills can also be treated with different coatings such as activated clay.
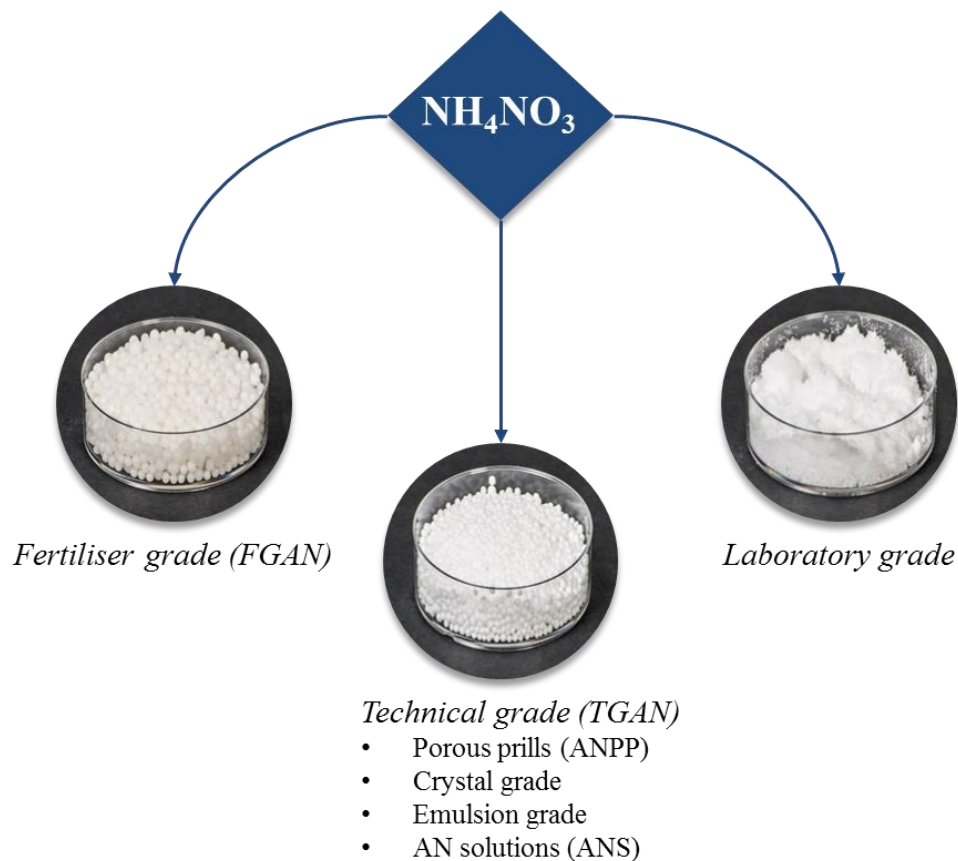
Figure 2.1   Overview of AN grades and qualities. Based on available qualities from Yara intl. ASA and Sigma-Aldrich®.

TGAN or industrial grade AN is of high purity (> 99 %) and conventionally used for explosives formulations in the form of low density (< 800 kg/m^3), porous prills (ANPP). Like dense prills, ANPP is also manufactured by spraying droplets of hot AN solution down a prilling tower. In this case, however, both the water content in the AN melt and the prilling tower is higher (3–4 % and 33–60 m, respectively). This yields smaller prills with much higher porosity, a desired

property in most AN-based explosives.[6] The prilling process for ANPP is usually followed by an additional drying- and coating step where a trace amount of an amine-based anti-caking coating agent is applied to enhance flowability and handling characteristics.[16]

TGAN is also available as emulsion grade and crystal grade. Emulsion grade TGAN is specifically made for the production of AN emulsion (ANE), which is a water-in-oil emulsion, mainly comprising aqueous AN solution, fuel oil and emulsifiers. While the emulsion grade TGAN is a non-porous prill with no added water-insoluble coatings, the crystal grade is a product of especially high purity (> 99.5 %), more commonly used in the production of nitrous oxide (N_2O) for medical and electronical use.

Finally, AN solutions are usually also found as part of the TGAN family. These are merely high- purity solutions of AN (90 % in water), used in the manufacturing of ANE products.

3 Effect of temperature on ammonium nitrate decomposition

3.1 Thermal decomposition of pure ammonium nitrate at atmospheric pressure

Following the early discoveries of Glauber, several other renowned chemists, such as Claude-Louis Berthollet (1748-1822) and Sir Humphry Davy (1778-1829), would later report their first detailed observations on AN decomposition.[27-29] Still, the first comprehensive study on AN thermolysis was performed almost two centuries after its discovery, by the famous French chemist Marcellin Berthelot (1827-1907). Over a 15-year period, starting with his first publication on the topic in 1869 and finally compiling his work in *Sur la Force des Matiéres Explosifs d'Après la Thermochimie* in 1883, Berthelot presented seven equations he theoretically found to be obtainable by heating the pure salt (Table 3.1).[30-31] Some of them were believed to be of explosive nature, despite the essentially insensitive nature of AN.

Reaction 1 and 2 (Table 3.1) are now well-established as two thermochemically coupled reactions, which are dominant between the melting and boiling point of AN.[2,6] Reaction 1 is the endothermic dissociation of AN into nitric acid and ammonia and becomes detectable around the melting point of AN.[22,32] Relative humidity and particle size as well as pressure and heating rate, are factors which influence the degree of dissociation.[33-34] Reaction 2 is a mildly exothermic decomposition pathway yielding nitrous oxide and water, but is not sufficiently exothermic to produce heat in excess of that absorbed by adjacent quantities of decomposing AN. Consequently, the behavior of unconfined AN on heating shows little tendency of self-acceleration or continued reaction after the source of heat is removed.[35-36]

It is not until the temperatures approach the boiling point of AN that alternative and more exothermic reaction pathways can take place (Eq. 3–6), particularly in the gas phase.[18] At this point, the exothermic output can become great enough to overcome the amount needed for self-acceleration.

Table 3.1   Overview of the seven decomposition reactions of AN thermolysis as suggested by Berthelot.[30] Conditions are indicated where reported.

#	Reaction equation	$\Delta H_r^{\Theta *}$ [kJ/mol]	Conditions
1	$NH_4NO_3 \rightleftharpoons HNO_3 + NH_3$	+184	Commences around melting point.[6,22,30,32,35]
2	$NH_4NO_3 \rightarrow N_2O + 2H_2O$	-36	Thermochemically coupled to eq.1 under careful heating between ~180–300 °C. Dominates above 210 °C.[6,12,30,32,35]
3	$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O$	-119	Explosive decomposition at temperatures above boiling point, under confinement or when initiated with a strong detonator.[24,37]
4	$2NH_4NO_3 \rightarrow 2NO + N_2 + 4H_2O$	-28	Side reaction taking place under incomplete detonation.[24,32]
5	$4NH_4NO_3 \rightarrow 3N_2 + 2NO_2 + 8H_2O$	-103	Elimination of nitrogen and nitrogen oxide. Side reaction at temperatures above boiling point.[24,32]
6	$3NH_4NO_3 \rightarrow 2N_2 + N_2O_3 + 6H_2O$	-90	Will only take place as a side reaction combined with other decomposition reactions. N_2O_3 exists in the dissociated state only as NO and NO_2.[24]
7	$5NH_4NO_3 \rightarrow 2HNO_3 + 4N_2 + 9H_2O$	-124	Only at certain conditions using noble metal catalyst.[24,38]

*Calculated standard reaction enthalpies (25 °C, 1 atm)

Nevertheless, molten, decomposing AN tends to seek towards a thermoneutral steady-state decomposition temperature at approximately 292 °C at 1 atm.[35-36]   This heat-limiting mechanism is partly attributed to the heat removal of the copious white fumes one usually encounters when AN decomposes and is dependent on the external pressure.[36] Similar behavior and steady-state temperatures have even been observed for the thermolysis of AN containing certain contaminants.[39]

It is a general perception that none of the seven reactions above will occur as a single reaction, but that they rather take place simultaneously and are interlinked.[30,40-41] Thus, eq. 3–7 still remain hypothetical as the exact reactions pathways under the necessary conditions are still unknown.[42] According to Berthelot, the different modes of reactions, or rather the predominance

of some of them, would depend on their relative speed and on the temperatures of which the decompositions takes place.[30-31]

 Yet, these temperatures are not necessarily fixed. In fact, for eq. 1 and 2, it has been found that these decomposition temperatures are subordinate to the rate of warming as the heating rate influences the mode of AN decomposition.[33,42-48] At higher heating rates, heterogeneous surface decomposition of AN is dominant and the endothermal dissociation of AN initially prevails, while slow heating rates lead to homogenous bulk decomposition where decomposition yielding nitrous oxide and water dominates (Figure 3.1).[33]
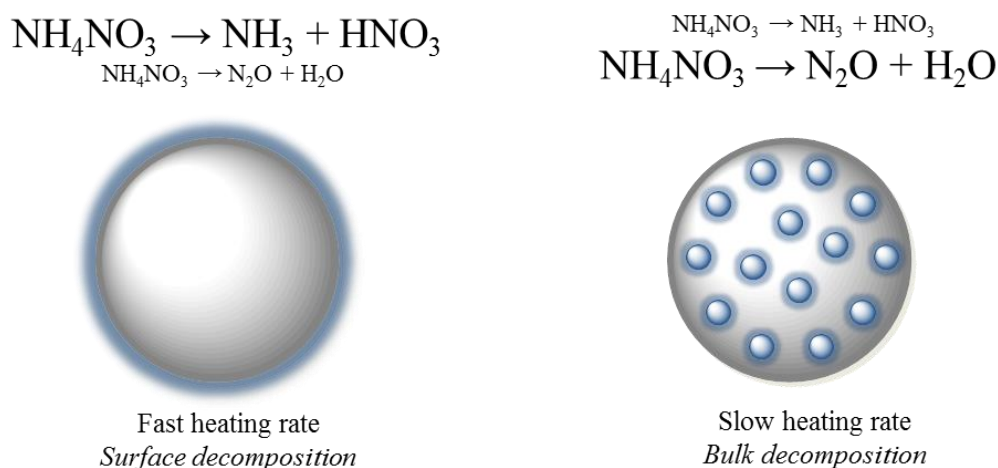
$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$
$$NH_4NO_3 \rightarrow N_2O + H_2O$$

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$
$$NH_4NO_3 \rightarrow N_2O + H_2O$$

Fast heating rate
Surface decomposition

Slow heating rate
Bulk decomposition

Figure 3.1   The consequence of different heating rates on mode of decomposition and reaction
predomination in an AN prill. Blue colouring indicates decomposition.

In 1922, Saunders performed a comprehensive study on the thermolysis of AN and its resulting gas products.[32] By this time, the nature of AN decomposition around its melting point was already well-known, due to the wide use of Sir Humphrey Davy's method when producing nitrous oxide from AN for anesthetic and analgesic (or even recreational) purposes.[27] Here, AN crystals are heated gently between 169–250 °C and the resulting gasses are subsequently passed through water vapor and pure nitrous oxide can then be collected. Similar methods are still employed today for small scale production. On an industrial scale, these have been more or less replaced by the more energy efficient Hoechst method. Introduced in the 1970, this method exploits the catalytic activity of chlorides and nitric acid on AN, which are added to an aqueous

solution of the salt. Decomposition can now take place at much lower temperatures around 100–160 °C.[49]

Even in Sir Davy's time, it was known, that if AN was heated too strongly during preparation of nitrous oxide, red fumes would evolve and violent reactions could take place.[50-51] Such a swift transfer from an endothermic process to an exothermic event, also noted by Berthelot in several of his reaction equations, underlines the complexity of AN thermolysis at elevated temperatures.

At 200 °C, Saunders found that pure AN decomposes only slowly, liberating 0.4 mL gas per gram AN per hour. He further observed that following its dissociation to nitric acid and ammonia, a gas containing 98 % of nitrous oxide was evolved as long as the temperature was kept below 250 °C.[†] Free nitrogen, which is now alleged to be a product of gas phase reactions,[52-54] was always present in quantities of nearly 2 % up to 260 °C.[32] This amount has been shown to be considerably exceeded at higher temperatures.[22,32,45,55-56] This is probably due to a shift between temperature-dependent decomposition mechanisms, as fast, radical decompositions are introduced at temperatures above 300 °C.[55,57] Other minor products such as nitrogen dioxide (NO_2) and nitrogen monoxide (NO), but also the dissociation products of AN, have later been identified in the decomposition gases, depending on the design of the experiment and conditions.[18,22,42,44-45,53-54,56,58-61]

The decomposition process and products were found to be unaltered in the temperature range of 210–260 °C.[32] However, when exceeding this, the gas formation started to evolve in rushes. Saunders even experienced two slight explosions when surpassing 260 °C, like others before him. When reaching the temperatures of boiling AN, increasingly violent reactions can indeed take place. Today, it is appreciated that the early reported explosions were more likely to be powerful deflagrations of the resulting gas products, rather than detonations.[62]

During deflagrating behavior, the amount of measured nitrogen oxides was found to increase substantially, leading to the following suggested decomposition pathway based on the measured gas products[32] :

$$8NH_4NO_3 \rightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O, \Delta H_r^{\Theta} = -64kJ/mol \quad [8]$$
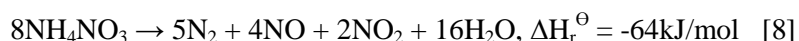
[†] Gaseous water was not collected and measured in Saunders' experiments.

According to Berthelot theories, this result would be the consequence of a combination and interlinkage of some of his stated equations (Table 3.1). A combination of eq. 4 and 5 is well-fitting in this case.

The apparent shift in decomposition behavior at these temperatures, especially when surpassing the steady-state temperature at 292 °C, can be partly explained by the earlier mentioned alteration in decomposition mechanism, but also as a consequence of other physical conditions such as confinement. This will be further elaborated in Section 4.

3.2   Proposed mechanisms of ammonium nitrate thermolysis

Due to the great amount of investigations on AN throughout the last century, it is now well-established that the thermal decomposition of AN is highly dependent on pressure, sample/bulk weight, confinement and heating rate.[2,6] From a thermodynamic perspective, AN can be considered as a metastable compound, as the decomposition to products of lower energy is prevented by an activation barrier. This is a key property in the ease of which AN is sensitized, as a range of different compounds readily reduces the thermostability of AN by lowering this barrier. To be able to reduce the accidental risks associated with such metastable compounds, a full understanding of the chemical reaction mechanism of which the explosive events are induced is essential. Yet, these are often intricate and of great complexity.

Even though no single mechanism can explain all the aspects of AN decomposition, there are certain general agreements on the decomposition of pure, unconfined AN.[43,45,54,57,59,63-65] The key step following the dissociation of AN into nitric acid and ammonia is the decomposition of nitric acid, yielding species which react with ammonia (Figure 3.2). Indeed, isotope studies revealed quite early that the nitrogens in the major decomposition product, nitrous oxide, must originate exclusively by N-N-bond formation between a nitrogen from NH_4^+ and NO_3^-, respectively.[66-67]

$$HNO_3 \rightarrow NO_2^+ + H_2O$$

$$NO_2^+ + NH_3 \rightleftharpoons NH_3NO_2^+ \rightarrow N_2O + H_2O$$

$$\sim 200\text{--}300\ ^\circ C$$
$$E_a = 118\ \text{kJ/mol}$$

Ionic decomposition

$$169.9\ ^\circ C$$
Melting

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

$$\geq 169.9\ ^\circ C$$

Dissociation

$$HNO_3 \rightarrow {}^\bullet OH + NO_2$$

$$NH_3 + {}^\bullet OH \rightarrow {}^\bullet NH_2 + H_2O$$

$${}^\bullet NH_2 + NO_2 \rightarrow [NH_2NO_2] \rightarrow N_2O + H_2O$$

$$> 300\ ^\circ C$$
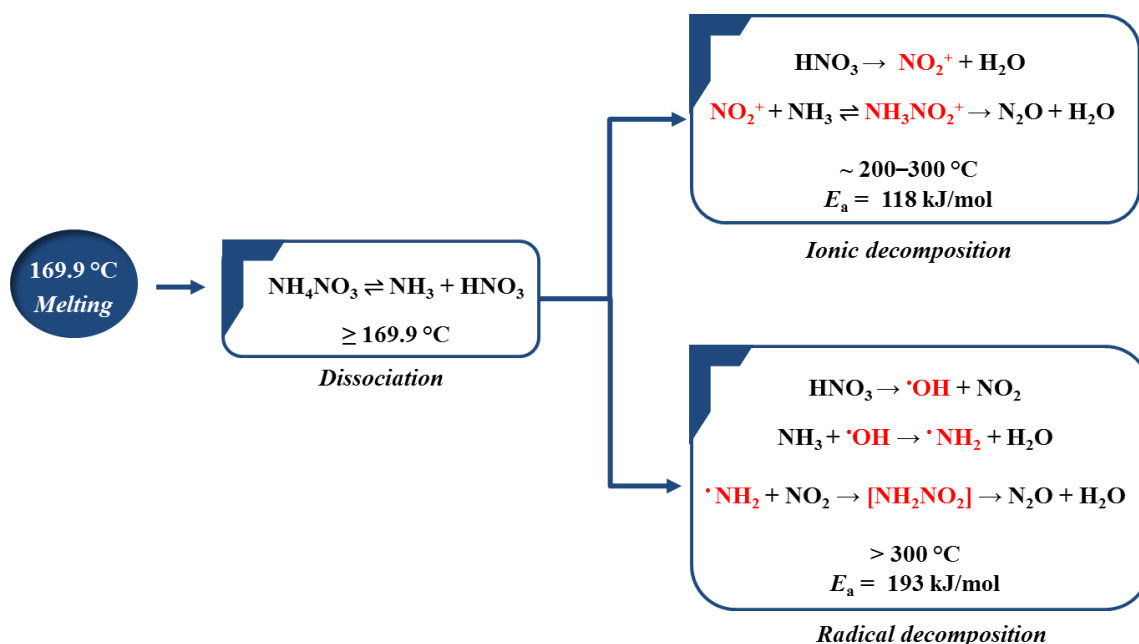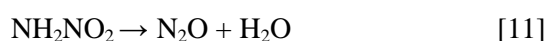$$E_a = 193\ \text{kJ/mol}$$

Radical decomposition

Figure 3.2   Proposed thermal decomposition mechanisms of ammonium nitrate at atmospheric pressure and increasing temperatures as suggested by Brower et al.[57] Respective temperature ranges and activation energies are indicated.

This is suggested to be a product of two possible pathways; an *ionic* reaction which occurs at *low* temperature with relatively *low* speed,[54,57] while a second, *radical* reaction occurs at *high* temperature and *high* speeds(Figure 3.2).[57] In addition, the thermal decomposition of AN follows 1st order kinetics.[7,68]

The first step of AN thermolysis commences around the melting point where it can dissociate into ammonia and nitric acid. In the temperature range of 200–300 °C, this is followed by an ionic decomposition where ammonia is oxidized by the decomposition products of nitric acid producing the intermediate $NH_3NO_2^+$ (Figure 3.2). The ionic decomposition only takes place in the condensed phase, while the radical can occur in both condensed and gas phase.[57]

Additional contemporary studies have added details to the ionic mechanism. Based on both experimental work and *ab initio* calculations, research suggests a mechanism where NH_4^+ and NO_3^- are involved in pathways forming the labile intermediate NH_2NO_2,[45,59,63-64,69] which is also found in the radical decomposition mechanism. Still, this is not a completely new thesis. The involvement of NH_2NO_2 in AN decomposition was already pointed out in a note by Abrams and

Davis[70] who reviewed the results of even earlier experiments published by Pelouze in the late 19th century.[71] Furthermore, Izato *et al.* found NH_2NO_2 as the most energetically favorable intermediate in their recent, computational study.[63] The same study also linked the crucial catalytic role of nitric acid in AN thermolysis to the formation of $NH_3NO_2^+$ followed by NH_2NO_2, as seen in equation 9-11.[32,40,56,72-73]

$$NH_4^+ + HNO_3 \rightarrow NH_3NO_2^+ + H_2O \qquad [9]$$

$$NH_3NO_2^+ + NO_3^- \rightarrow NH_2NO_2 + HNO_3 \quad [10]$$

$$NH_2NO_2 \rightarrow N_2O + H_2O \qquad\qquad [11]$$

As the temperature increases and surpasses 300 °C, radical trapping experiments have shown that the ionic decomposition mechanism is surpassed by a more rapid, radical reaction.[57] It is further suggested that the dissociation of AN is followed by a homolysis of the O-N bond in nitric acid into nitric dioxide and a hydroxyl radical (Figure 3.2). When this rate-determining homolysis is encountered, a high-speed radical chain reaction via the intermediate NH_2NO_2 can take place.[57]

A theoretical study by Cagnina *et al.* investigated the radical gas-phase decomposition in great detail using density functional theory (DFT) calculations.[65] The homolytic breakage of the N-O bond in nitric acid was identified as a rate-determining step also yielding NH_2NO_2 as the most stable intermediate. The total process was identified as a globally exothermic multi-step mechanism, involving unstable radicals. Yet, the rate-determining homolysis holds a quite high energy barrier (~ 225 kJ/mol) which must be overcome for the exothermic process to dominate. Thus, such a process can only occur under specific conditions such as continuous external high temperature stimuli, confinement or in presence of incompatible substances.[65]

3.3   The effect of temperature on density

To the extent of the author's knowledge, it has not been possible to establish experiments or methods where pure, unconfined AN has reached detonation by heating alone. This is, however, fully possible by shock initiation.[24,26,37,62] The initiation of AN by detonation transfer is, like for most explosives, closely linked to particle size and density, but also temperature. As described in section 2.1.1, temperature influences the morphology and density of AN directly.[2,6] As a

consequence, both heating and thermocycling of AN is associated with increased shock sensitivity (Figure 3.3).[26,74]
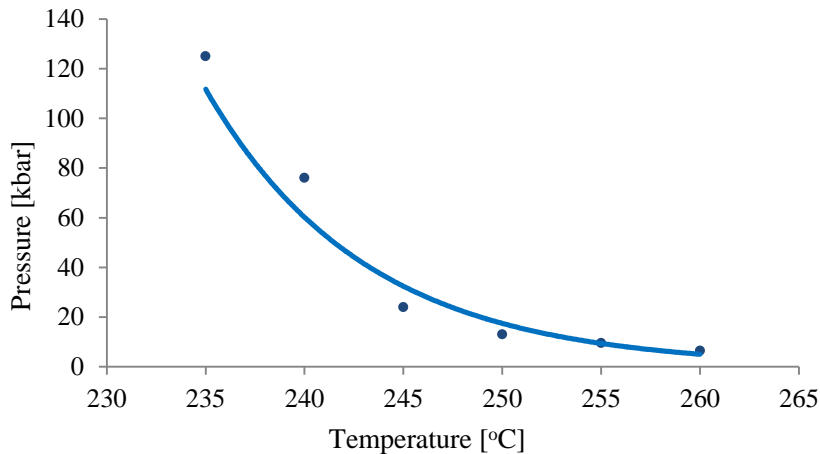

Figure 3.3   Relationship between temperature and critical shock pressure for initiation of molten AN using pentolite as initiator. Plotted from results attained by A. King.[62]

When AN is heated to temperatures above its boiling point, the sensitivity increases accordingly, as the gas evolution is able to aerate and thus lower the density to a much greater extent. As a consequence, the shock sensitivity of molten AN increases exponentially from 220 to 260 °C (Figure 3.3) which is partly caused by an increase in available hot-spots. This promotes shock wave propagation.[75] The physical alterations can ultimately reach critical diameters close to nitroglycerin dynamites, if sufficiently confined.[37,62]

4 The effect of confinement on ammonium nitrate decomposition

4.1 Steady-state decomposition and its dependence on pressure

The ability of elevated temperatures to promote exothermic decomposition pathways in AN has already been discussed. However, at atmospheric pressure, these are not sufficiently exothermic to turn the overall decomposition of AN from endothermic to exothermic. In fact, the decomposition of AN has been found to be net endothermic at pressures up to 3 MPa even at temperatures exceeding 400 °C.[18] Consequently, fire experiments with pure AN in large and bulk scale[‡] or even AN-fuel oil mixtures (ANFO), tend to show low heat penetration and controlled decomposition.[8,10,24,37,62,76-81]

As described previously, when AN is heated at atmospheric pressure, two concurrent reactions predominate: an endothermic dissociation (eq. 1) and an exothermic decomposition (eq. 2).

$$NH_4NO_3 \rightleftharpoons HNO_3 + NH_3, \ \Delta H_r^{\ominus} = + 184 \ \text{kJ/mol} \quad [1]$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O, \ \Delta H_r^{\ominus} = - 36 \ \text{kJ/mol} \quad [2]$$

Despite the exothermic contribution from the decomposition, when unconfined, all the available heat from the decomposition will be absorbed by the endothermic dissociation. Thus, the temperature of decomposing AN will be limited by its own dissociation.

In 1954 Hainer and Feick at Arthur D. Little, Inc. reported that as a consequence of this, molten, decomposing AN tends to seek towards a definite and predictable limiting temperature which can be expressed as function of the external pressure and of the heat supplied to, or removed from the molten mass by its surroundings (Eq.12).[35-36] This relationship has been verified in the temperature range of 200–350 °C under adiabatic, vented conditions and has shown to give reasonable predictions over a pressure range of 0.02–2 atm.[35]

[‡] The denoted experiments have been performed on large scale ranging from 5–500 kg and in bulk quantities ranging from 500 kg–20 tons.

Using available dissociation pressure versus temperature curves for adiabatic systems, the self-limiting temperature for decomposing AN can then be expressed as a function of the external applied pressure of the system (Eq.13) giving a self-limiting temperature of 293 °C at 1 atm.[82-83]

$$P = \left[1 + \frac{3}{2}\left(\frac{\Delta H_1}{Q - \Delta H_2}\right)\right]p \quad [12]$$

$$logP = \frac{-4.71 \cdot 10^3}{T} + 11.20 \quad [13]$$

P = total pressure or ambient pressure on the reacting mass in mm; Q = total heat of the system in kcal/mol; p = dissociation pressure of AN at the temperature in question in mmHg; ΔH_1 and ΔH_2 are reaction enthalpies for the dissociation and decomposition in kcal, respectively, at the temperature in question; T = the limiting absolute temperature.

As seen from equation 12, as long as Q is less than ΔH_2, the heated mass will cool off until the reaction arrests. Alternatively, if the mass is supplied with sufficient heat to account for both the endothermal dissociation and the heat loss, the temperature of the system can continue to rise until the limiting temperature T is reached.

If the formed gasses cannot escape and the applied pressure thus increases, the system will seek towards a new, higher limiting temperature. At this point, exothermic side reactions producing products such as nitrogen monoxide, nitrogen dioxide and nitrogen have become more dominant while the increased pressure suppresses the endothermic dissociation, ultimately changing the course and behavior of AN thermolysis. If the temperature and pressure become sufficiently high, the rate of decomposition can reach the critical ranges for explosions.[83]

Only few suggested figures on such hazardous decomposition rates exist, however.[77,83] This is unfortunate, as these could be useful in estimations of both the minimum temperatures and pressures for such behavior using the early findings of Hainer and Feick.

4.2 Consequences of elevated pressure on ammonium nitrate thermolysis

When AN decomposes, reactions can take place in the gaseous phase, condensed phase or interphase, depending on the conditions.[14,18,44-45,84-85] Consequently, the outcome and mode of AN decomposition can change drastically with changes in the gas- and condensed phase interactions. Elevated pressure has a significant influence on this.[14,18,22,44-45,80,84-87]

At low pressure, the gases formed during decomposition readily diffuse away and engage in little further reaction with the condensed phase. But, as the pressure rises, the diffusion rate of the gas products from the decomposing mass of AN is reduced and the concentration of these gases around the hot zone of the condensed phase increases accordingly (Figure 4.1).[18,85]

Thus, the extent of the heterogeneous gas-condensed phase chemistry escalates, leading to alternative decomposition reactions and exothermic events such as self-sustained decomposition or even ignition.[45,84] For unconfined AN, spontaneous ignition of the gas phase has been observed above 500 °C.[24] At elevated pressure, this temperature is likely to be considerably reduced, as an increase in pressure decreases minimum ignition energy.[88-89]
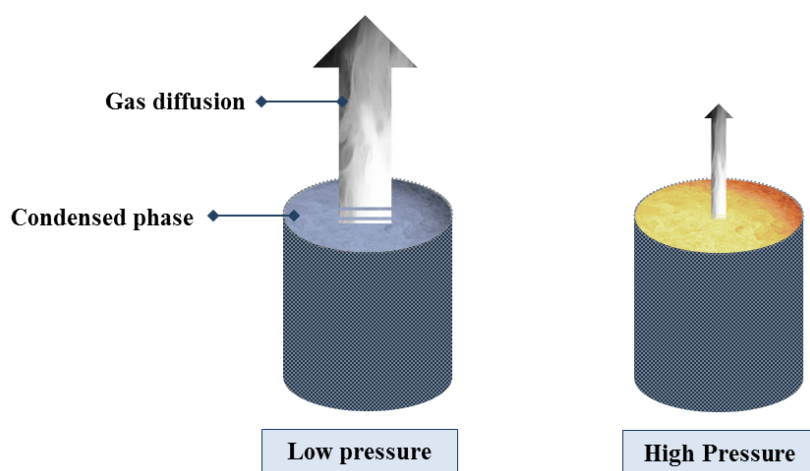

Figure 4.1   Effect of pressure on gas diffusion during decomposition and combustion of AN. Low pressure promotes high diffusion of gases and little further interaction with the condensed phase. Elevated pressure leads to reduced diffusion and greater gas-condensed phase; interactions which can promote exothermic decomposition and ignition.

The effect of confinement on AN thermolysis is clearly illustrated by Figure 4.2 showing two differential scanning calorimetry (DSC) experiments on AN performed with an open pan and a sealed glass capillary, respectively. While the decomposition onset at 243 °C is an endothermic process in the open experiment, the closed experiment not only shows a later decomposition onset at 285 °C, but also an apparent exothermic nature.[7]
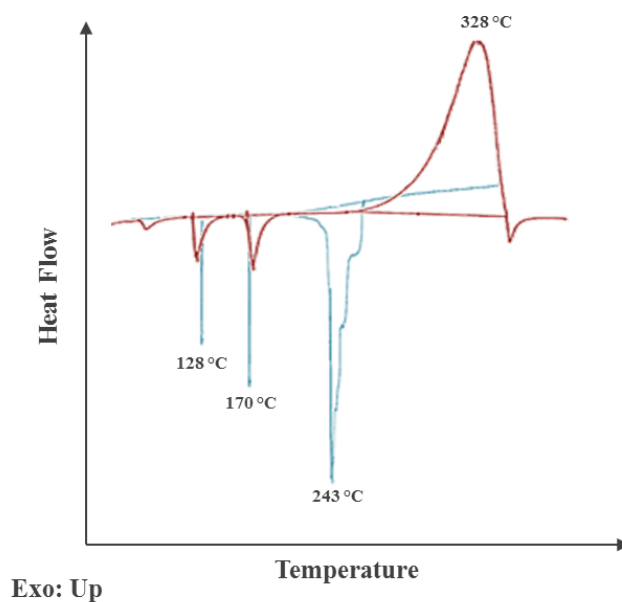
Figure 4.2   Illustration of DSC experiments on AN under open (blue) and closed (red) conditions, respectively. The entropy is characterized by exo (up) and endo (down). The following effects are observed: morphological changes (128 °C), melting (170 °C), net-endothermal decomposition of AN (234 °C, open experiment (1798 J/g)), net-exotherm decomposition (328 °C, closed experiment, (1185 J/g)). The graph from the closed experiment is adapted from Oxley et al.[7] while the open was performed using a TA instruments Q1000 with a standard aluminium crucible.

It has been shown, that this shift from endothermic to exothermic decomposition at elevated pressures, is accompanied by a drop in the concentration of ammonia and nitrogen dioxide in the gas phase.[18,90] These are probably connected, as the highly exothermic oxidation of ammonia by nitrogen dioxide (Eq.13) may take place in the gas-phase at elevated temperatures and pressures.[18,52,91]

$$2NH_3 + NO_2 \rightarrow N_2O + N_2 + 3H_2O, \ \Delta H_r^{\ominus} = -585 \text{ kJ/mol} \quad [13]$$
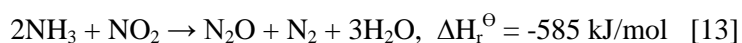
Seemingly, to achieve an overall exothermic decomposition of pure AN below its melting point, a certain amount of confinement is required. There is a clear overall trend when consulting the literature on heating experiments, both on analytical scales to scales of several tons.[10,24,37,62,76-80,92]

4.3   Combustion of ammonium nitrate

Even if the overall decomposition becomes exothermic and self-sustained, this does not mean that AN is capable of combustion under such conditions. For this to be feasible, the overall decomposition in the thermal decomposition zone must be of a sufficient exothermicity to be able to spread to the unreacted sample.[44] The threshold limit to obtain this in neat AN has been reported to be above 40 MPa when ignited.[80] Here, the gas and condensed phase interactions are adequate to promote further combustion. Therefore, if the exothermic activity in the condensed phase is sufficient, the thermal decomposition spreads constantly as burnable gases in the gas phase which ignites and then feed the flames in the combustion zone. The condensed phase reactions are in fact found to have the greatest effect on the combustion characteristics of AN, when sufficiently confined.[14,85]

The interactions of the gas- and condensed phases during combustion at different pressures, contributes to the complexity of the outcome of heating AN under confinement. In the absence of these secondary reactions between the gas- and condensed phases, the reaction temperatures are not likely to exceed steady-state temperatures.[35,57] The pressures necessary to promote deflagration in neat AN are much higher than e.g. AN mixed with combustible materials.[80] Due to the additional reaction heat provided, the required pressure for combustion of AN when part of such mixtures can be reduced significantly, often more than 10 folds.[80]

Studies on open experiments heating up to 3 kg AN above its boiling point and subsequently adding combustible materials such as fuel oil, metal powders, molten metal, paper and polyethylene, have also been reported.[37,62,79] None of these experiments have disclosed any signs of explosions and it has been suggested that in open systems, even when adding contaminants, boiling AN will not spontaneously explode.[79]

The Bureau of Mines reported a extensive series of experiments designed to simulate the burning of AN in deep beds where high pressure may exist by virtue of the inertia of the bed. Samples of up to 5 kg of AN prills were topped with an inert material in 3 inch wide steel pipes of varying height (6–21 feet) and ignited in the bottom with an ammonium perchlorate-based ignitor. Self-sustained decomposition was initially obtained in most experiments. Still, no explosions were reached even at pressures close to 70 MPa.[37] For most samples, the decomposition either died out or decomposed controllably. Thus, even though combustion and

exothermic events can take place at these pressures, especially upon the addition of combustible material, a transfer to detonation is not necessarily the final result. This was also found to be valid in the van Dolah study; tubes containing AN mixed with polyethylene only propagated into run-away and explosion if passing a critical pressure of 7–8 MPa.[37]

The pressure-increase observed in the large deep bed experiments of van Dolah underlines the direct consequence of the bulk size which is the ability of self-confinement. In relations to this, a close link with the bed height of test samples and the ability of AN to detonate under heating has in fact been reported.[80] Ermolaev *et al.* performed open heating experiments on mixtures of crushed AN and 16 % charcoal (m = 8 g, d = 0.84 g/cm^3) in a bomb calorimeter, but explosions only seemed to take place when surpassing a critical height.[80] By measuring pressure over time, it was found that when the sample surpassed a height of 320 mm for a tube with a diameter of 16 mm, the burning transforms from the initial smooth behavior of combustion to a sharp peak with amplitude of several hundred MPa, indicating a low-speed detonation.[80] Unfortunately, equivalent experiments have yet to be reported for pure AN. Due to its incapability to sustain burning, even at elevated pressure, such experimental set-ups would have to be carried out in dimensions, which are unrealistic for most laboratories and test areas. Such scale-up predicaments still prevail in the area of chemical hazard assessments.

5 The effect of contaminants on ammonium nitrate decomposition

It is well established that contaminants hold pronounced effects on the thermal decomposition properties of AN, even in very small quantities. Addition of contaminants can lead to alternative and highly exothermic pathways, which are able to turn the normally net-endothermic decomposition of AN into an exothermic event. However, due to the extent of the endothermic nature of the first dissociation step in AN decomposition (~176 kJ/mol), this still withholds a great impact on the thermal outcome, even with such contaminants present.

The presence of contaminants obscures the decomposition of AN even further, and can involve a number of consecutive and simultaneous reactions and phase equilibria. The effects of contaminants on AN decomposition is important to consider when evaluating the possible hazardous outcome in fires where AN can be subjected to them.

5.1 Acids, bases and water

The influence of AN's own dissociation products on decomposition rate was already recognized and linked to their acid and base properties in the 19th century, as the decomposition of AN was found to be dependent not only on the mass of AN, but also the proportion of free acid present.[40] Similar observations have also been published in several ensuing studies.[32,56,68,73]

An increase in nitric acid concentration catalyzes the thermolysis of AN.[54,72-73,83,93] This is an important quality, as the concentration of nitric acid in AN can increase when heated or even during storage, if exposed to moisture.[17,32,73,93] Even as early as 1830, Emmet linked this to the greater diffusion of ammonia from the AN residue following dissociation.[94] The presence of water seems to be essential for this catalytic effect, probably by virtue of the ionization of nitric acid, which is necessary to initiate dissociation.[67,72,93,95-96] Still, the catalytic effect of nitric acid is believed to not only rely on its protonating abilities.[53,61,97]

While water promotes dissociation of AN, its effect on the decomposition of AN is not as straightforward. Several independent studies have shown that while completely dry AN does not decompose, but rather sublimes, even up to 300 °C, certain amounts of water inhibit the decomposition of AN.[54,67,93,95-96] Bennet investigated these opposing effects at 180 °C and found

that the positive catalytic effect on the decomposition rate of AN only takes place in a very narrow area of moisture contents between 0.03–1%.[96] Thus, while small amounts of water is necessary to initiate the decomposition process, even up to 300 °C, the presence of moisture will at a certain point have a inhibitory effect.

Other acidic species than nitric acid have also shown to promote similar accelerating effects on AN thermolysis.[7,68] Sun *et al.* studied the effect of sulfuric and hydrochloric acid and found that the same decomposition products were produced as for pure AN, however, with an apparent shift in the dominant product as nitrous oxide is substituted for nitrogen.[68] Moreover, the activation energy of AN thermolysis was significantly reduced. The catalytic effect of acids is believed to be ionic of nature, as their effect diminishes when reaching temperatures where the radical mechanism is suggested to take place.[7,68] Nevertheless, additional individual or synergetic effects of resulting anionic species following deprotonation or solvation of any acid must also be taken into account.

Contrary to acids, increased concentration of ammonia in an AN melt will initially inhibit thermolysis.[40,54,61,73,98] Decomposition arrests even at temperatures 50–60 °C above the normal decomposition temperature.[98] Similar behavior has been observed with other basic compound.[7,48,96,99-100] Hence, in general, the addition of acids will promote AN thermolysis while bases will impede it.

For ammonia, the inhibiting behavior can only be observed before the temperatures exceed 300 °C. At this point, ammonia not only fails to inhibit the decomposition process, but simply accelerates it. In fact, ammonia is only able to inhibit thermal decomposition at temperatures and partial pressures which are capable of inhibiting the dissociation of AN.[98] Thus, if the dissociation pressure of ammonia upon AN exceeds its partial pressure in the gaseous phase, then the presence of ammonia will instead favor highly exothermic reactions with AN itself.

5.2   Halides

The prevalent effect of even small amounts of chloride salts on AN thermolysis has been appreciated since the earliest reported investigations on AN incompatibles, but also in quite recent studies.[7,32,53-54,69,73,83,93,99,101-106] The catalytic effect of such compounds on AN decomposition is quite prominent even at concentrations as low as 0.1 %.[92] In addition to the

greater exothermal output, the initial temperature of decomposition can decrease as much as 80 degrees while the decomposition rates can increase to three orders of magnitude greater than that of pure AN.[69,83,101] The catalytic activity of chloride ions does, however, require an induction period before a transfer from endothermic to exothermic decomposition can be observed.[32,83,103] This induction period, which time span can last from minutes to several hours depending on the temperature and added amount of chloride, has been showed to be obviated by acidity and lengthened indefinitely by alkalinity at temperatures up to 175 °C.[7,53,101]

Saunders' study from 1922 on AN thermal decomposition also entailed investigations on the effect of, at that time, common impurities in AN. AN could contain impurities such as hydrochloric acid (HCl), boric acid (B(OH)$_3$) and sodium nitrate (NaNO$_3$) as the nitric acid used in the synthesis of AN contained impurities from Chile salpetre, the main precursors for nitric acid production until the introduction of the Ostwald method.[24]

Saunders added 0.1–2 % sodium or ammonium chloride to the samples and observed increased decomposition temperatures and accelerated gas evolution, including small amounts of chlorine gas. A shift in the decomposition pathways also became evident, as a higher production of nitrogen compared to that of pure AN was measured. Indeed, the increased production of nitrogen has now been attributed to equation 3 which releases more than three times the heat compared to that of pure AN.[106]

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O, \Delta H_r^{\ominus} = -119 \text{ kJ/mol} \quad [3]$$
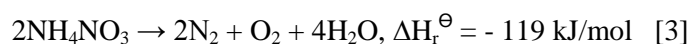
With the addition of 2 wt% chloride salts, Saunders found that the nitrogen yield was similar to the amounts measured when deflagration was observed, but achieved at even lower temperatures (Table 5.1).[32]

Other studies have also reported such increases in nitrogen yields and linked it to an increase of acidity in the sample as the chloride reacts with AN and produces hydrochloric acid (HCl).[69,101-102,106] By performing simultaneous thermal and gas analysis on AN and potassium chloride mixtures (9:1) in both open and sealed systems, Izato *et al.* found that potassium chloride (KCl) reacts with nitric acid in the gas phase producing hydrochloric acid. Hydrochloric acid may then react further with AN while yielding chlorine-radicals which subsequently support radical chain reactions.[106]

Table 5.1   Relative amounts N$_2$ in the resulting gas following AN thermolysis at different temperatures and with addition of NaCl. Adapted from Saunders.[32]

Temperature [°C]	Conditions	N$_2$ yield [%]
210–260	Pure	< 2
> 260	Pure. Heated to deflagration.	~ 46
~210	NaCl (0.1–2 %)	~ 30–50

Many other propositions have forwarded in order to explain the effect and mechanism of chlorides on AN decomposition, including acidification, radical, ionic and red-ox pathways and even involvement of intermediates such as chloramines.[7,14,53,65,68,93,101-102,104,107-108] However, there still seems to be no general agreement on the exact mechanism by which chloride ions cause destabilization of AN.

Conversely, a certain amount of confinement has been confirmed as essential for a net exothermic decomposition, also for AN-KCl mixtures.[106] Even though open DSC experiments show a lowered on-set decomposition temperature of the AN-KCl mixture, the net reaction does not turn exothermic. As a contrast, in experiments where sealed pans are used, a sharp exothermic peak can be observed. In this case, the heat of reaction was found to be almost 1.5 kJ/mol greater than that of pure AN. It was found that the open pan does not retain the nitric acid to the same extent as the closed, which prevents the gas from reacting with the potassium chloride in the solid sample.

Even though chlorides have the most pronounced destabilizing effect on AN, other halides also influences the thermostability in a similar manner.[7] By performing DSC studies in closed tubes with AN and halide salt (5 wt%) mixtures, Oxley observed that except for fluoride, the halides had a destabilizing effect on the thermal stability of AN. In confined samples, chloride lowered the exothermic maximum temperature the most, reducing it by almost 70 °C compared to that of pure AN.[7] As a contrast, fluoride salts show stabilizing effects by reducing the onset temperature. Similar observations have also been reported by other research groups.[53,96,109] Still, when decomposition does commence, the total exothermal output is still greater in AN contaminated with fluoride salts.[7]

For the three halides Cl, Br and I, the relative destabilizing effect seems to correlate with the acidity of their corresponding acids and the destabilizing effect increases as the corresponding acid weakens.[7] On the contrary, fluoride is an exemption to this as it in fact shows stabilizing properties even if hydrofluoric acid (HF) is the weakest of the acid halides. This inconsistency can probably be explained by the basicity of the fluoride ion, as the other halide ions are more or less neutral.

5.3   Metal ions

Several metal salts are also found to sensitize AN by reducing its thermal stability. Even though there are metal salts that execute detrimental effects on the thermal decomposition of AN, a large number of such salts have, however, been shown to actually have little to no effect (Table 5.2).[7,53,96] Evidentially, the influence on AN stability greatly depends on the specific metal ion involved.[7] Secondly, the properties of the anion of the salts are also of great importance as the anion may also contribute as a destabilizing contaminant. The sulfide ion in iron sulfides is a known example.[110-112]

Table 5.2   *Overview of nitrate and oxide metal salts investigated by Oxley et al.[100] when added to AN (5 wt%). The maximum temperature measured at 10 % decomposition with DSC($T_{10\%}$) is compared to that of neat AN. An increase in $T_{10\%}$ indicates stabilizing salts and are shown in green (> 0–5 % increase in $T_{10\%}$) and blue (≥ 5 % increase in $T_{10\%}$), while a decrease in $T_{10\%}$ indicates a destabilizing salts and are shown in orange (< 0–5 % decrease in $T_{10\%}$) and red (≤ 5 % decrease in $T_{10\%}$).*

Metal	Nitrates	Oxides
Alkali	Na, K	N.A.*
Alkaline earth	Mg, Ca, Ba	Mg, Ca, Ba
Transition	Cr, Fe, Mn, Co, Ni, Cu, Zn, Ag, Cd	Cr, Fe, Mn, Co, Ni, Cu, Zn, Cd
Basic	Al, Pb	Al, Pb

*Not applicable

One of the most important properties of the metal salts, including its solubility in molten AN, have been found to rely not only on the redox potential of the metal ion, but also its charge to mass ratio.[100] When added as nitrate salts, where nitrate acts as an inert counter ion, metal cations with high charge to mass ratio such as Cr^{3+}, Al^{3+} and Fe^{3+} hold a much stronger

destabilizing effect on AN. This is likely to be related to the increase in acidity.[100] This is further supported by the fact that their corresponding alkaline oxides show no or even stabilizing effects instead (Table 5.2).[7,53,100]

Chromium(III) oxide (Cr_2O_3), an amphoteric compound, on the other hand, strongly catalyzes the decomposition of AN. In fact, both Rosser and Guiochon found that chromium compounds soluble in liquid AN such as $Cr^{2+/3+}$-salts and dichromate salts would catalyze its decomposition even in amounts as low as 0.01 wt% yielding nitric acid, nitrogen and water.[53,113] The threshold limits for such exothermal decomposition of AN have been investigated for the ions Cr^{3+}, Mn^{3+}, Co^{2+} and Cu^{2+}.[114-115] The threshold limit of Cr^{3+} from chromium nitrate ($Cr(NO_3)_3$) was identified as 0.03 mol% compared to 0.7 mol% for nitrate salts of Mn^{3+}, Co^{2+} and Cu^{2+}. At greater concentrations, the particular catalytic effect of chromium can efficiently accelerate the decomposition to explosive rates.[114]

The mechanism of metal-ion promoted thermolysis is believed to be complex and relies on the type of metal involved.[53,116] Contrary to chloride-catalyzed decomposition, an induction period has not been reported with metal ions.

5.4   Combustible material

Being an oxidizing material, AN can promote combustion of fuels. Thus, the addition of combustible material to AN will ultimately form highly flammable and possibly explosive mixtures. Several alterations in the decomposition process can be observed such as an increase in burning rate, lowering of the exothermic maximum and the ignition temperature, promotion of self-driven decomposition and reduction of the threshold pressure at which convective burning arises.[80] Furthermore, the addition of combustible material in AN does not only create flammable mixture, but is also associated with greater shock sensitivity.[24] In fact, specialized formulations of AN and combustible materials are of the most commonly applied civil explosives today.[117]

The ability of AN to promote combustion was already recognized to some extent in the earliest investigations of its properties.[30-31] Nevertheless, it was not commonly appreciated as a safety issue until the great disaster at the docks of Texas City, US, on April 16, 1947. Here, the ship SS Grandcamp, carrying more than 2,100 tons of grained FGAN (G-FGAN), caught fire early in

the morning and later exploded at 9:12 a.m. following several fire-fighting attempts.[118] Unaware that AN itself supplies oxygen to a fire, the ship master ordered the ship hatches to be closed in an endeavor to suffocate the fire. Instead, this would contribute with an additional, now known, safety risk: confinement. A second ship that also carried AN, the SS High Flyer, was ignited by burning debris from the first explosion and culminated itself in a second explosion 16 hours later. The accident killed at least 581 people and injured more than 5000.[118] The FGAN carried by the vessels consisted of grained AN coated with ~ 0.75 % wax and conditioned with about ~ 3.5 % clay, a common anti-caking treatment of AN-based fertilizers at that time.[77,118] As this type of G-FGAN was not considered explosive, no precautions were taken during its handling and shipment. The G-FGAN was even packed in paper bags and stored together with other combustible materials such as twine, peanuts and tobacco, as numerous such shipments had been transported without any incidents until this disastrous event. A series of reports and investigations were performed by the US governments in the aftermath of the incident.[10,37,76-77,118-119] The explosion risks in mixing combustible materials with AN were now recognized and emphasized, leading to stricter and more restrictive handling and storage regimes for FGAN products.[9,119]

The ability of an AN fuel mixture to burn, as well as the threshold burning pressure, depend strongly on the nature of the fuel. Still, in general, additives which increase heat generation in the condensed phase will promote combustion in AN mixtures and also increase the decomposition rate.[7,14,85] Many organic substances such as fuel oil only promote burning weakly in mixtures with AN, while others compounds such as charcoal, wood and soot powders produce exceedingly combustible mixtures.[14,80,84-85,120] Moreover, addition of catalytic compounds such as chlorides will enhance the burning capability even further as well as the burning rate.[14] Metal powders are also notorious for creating highly explosive mixtures with AN, as they often can supply considerable amounts of reaction heat.[24] The enhanced chemical reactivity of mixtures of AN and combustible materials such has *n*-hexane and aluminium powder has been linked to a stabilization of the crystalline phase IV, which promotes lower decomposition temperatures.[22]

When AN is thermally decomposed with combustible material, the decomposition trigger is dissociation, just as for pure AN.[7-8,57] However, instead of oxidizing ammonia, the active species from nitric acid can now oxidize the combustible material (Figure 5.1). As highly

exothermic pathways are promoted, further decomposition in the unreacted AN is now conceivable. The importance of nitric acid was early demonstrated by Finlay and Rousebourne who observed that at approximately 100 °C AN reacts spontaneously with cellulose or starch, generating carbon dioxide (CO_2), water and nitrogen.[121] By neutralizing the nitric acid with urea, however, the reaction was prevented. Neutralization of the reaction between AN and combustible material by alkaline compounds is still a widely discussed topic in hazard prevention,[7,48] emphasizing the importance of nitric acid in promoting ignition.

$$HNO_3 \rightarrow NO_2^+ + H_2O$$
$$NO_2^+ + \text{-CH-} \rightarrow N_2 + CO_2 + H_2O$$

Ionic decomposition

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$
$$\geq 169.9 \,°C$$

Dissociation

$$HNO_3 \rightarrow {}^{\bullet}OH + NO_2$$
$${}^{\bullet}OH + \text{-CH-} \rightarrow N_2 + CO_2 + H_2O$$
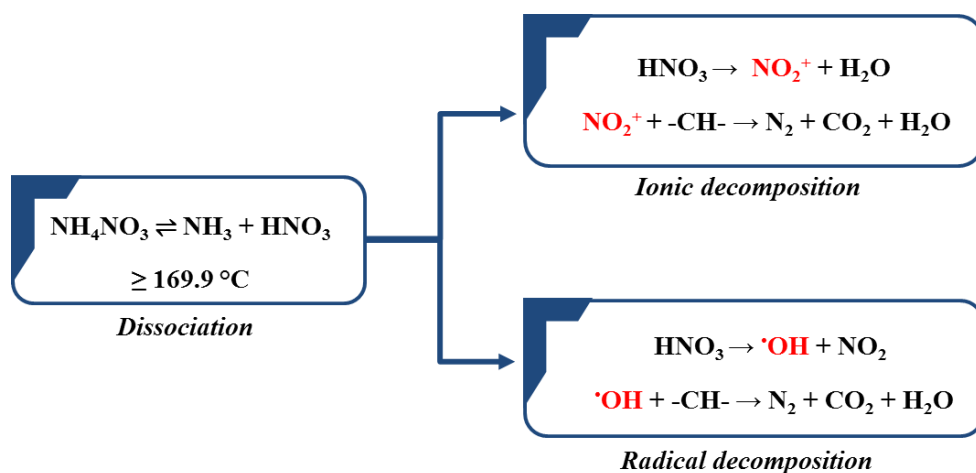
Radical decomposition

Figure 5.1   Decomposition of AN mixed with hydrocarbons following an ionic or radical pathway, respectively.[7,47] Compared to decomposition of pure AN, the reactive species can now react with the available hydrocarbons instead of ammonia.

As for many of the contaminants discussed earlier, a shift in yields from nitrous oxide to nitrogen is also observed for the decomposition of AN mixed with combustible materials.[7,47] Furthermore, other reaction products such as carbon dioxide for hydrocarbons and the corresponding metal oxide for metal powders are observed. For the latter, the nitrate is formed first upon reaction with AN, which subsequently decomposes to the metal oxide, nitrogen dioxide and oxygen under highly exothermic conditions.[47]

The ability of combustible material to lower the combustion threshold pressure compared to that of pure AN is also a crucial factor when considering the fire hazards of AN. But, as the earlier discussed experiments by van Dolah, van den Hengel *et al.* and Ermolaev *et al.* emphasized; even though the addition of combustible material increases the exothermic output and can

reduce the required pressure for combustion more than 10-fold, deflagration does not seem to take place without a certain degree of confinement.[37,79-80]

This dependence on confinement was in fact already pointed out in an investigation published by the Bureau of Mines in 1953.[77] Prompted by the Texas City disaster, the Bureau of Mines investigated the explosibility of the same type of G-FGAN stored in the vessels in a range of bomb experiments in 2–5 kg scale. The mere presence of organic matter in the amounts contained in the fertilizer (0.75 % wax) appeared to be insufficient to cause explosions at low or no confinement.[77] When heating 2.3 kg of the sample in steel bombs with limited venting, however, the G-FGAN detonated with great violence (Table 5.3). This was also the result for G-FGAN mixed with 1.5 % bag paper and even pure AN under ample confinement and heating.

Table 5.3   Parameters following explosions in electrically heated 3 by 20 inch vented (3 mm) steel bombs on 2.3 kg pure AN, wax-coated G-FGAN or wax-coated G-FGAN added 1.5 % bag paper, respectively. Adapted from Burns et al.[77]

Test mixture	Temp. before explosion [°C]	Pressure before explosion [MPa][d]
Pure AN	277–344	18–21
G-FGAN[a,b]	114–350	14–18
G-FGAN + 1.5 % bag paper[b]	134–153	1.7–2.1

[a] Coated with 0.75 % wax and conditioned with 3.5 % clay; [b] For these test mixtures, a larger critical vent diameter of 10 mm was established. The given results are only for 3 mm vented tubes; [c] Measured by burst disks.

The wax-coated G-FGAN was indeed more sensitive than the pure AN as explosion took place at lower temperatures and pressures. Still, the sensitivity was even more drastic for the mixtures containing G-FGAN and bag paper which exploded at pressures an order of magnitude less and at temperatures below the melting point of AN.

6   Discussion and concluding remarks

Even after more than two centuries of studies on the thermolytic behavior of AN, we have yet to establish the critical contributors in the transition from deflagration to detonation when AN is exposed to fire, a phenomenon which have caused some of the greatest industrial accidents in history.

The hazard of AN under elevated temperatures arises firstly from its exothermic decomposition, and secondly, from the release of gaseous products in considerable volume. Knowledge of the kinetics and decomposition of AN is thus crucial for the analysis of its potential hazards. At first glance, the decomposition of AN may seem rather straightforward; a net endothermic process involving two concurrent reactions; the endothermic dissociation of AN into the compound's precursors and the exothermic decomposition of AN into nitrous oxide and water. However, this only takes place under unconfined and controlled heating close to AN's boiling point. In fact, a molten mass of AN tends to reach a definite and predictable limiting steady-state temperature, which is a function of the ambient pressure and the heating rate. This is a result of the endothermic dissociation which, under such conditions, absorbs all the heat available from the decomposition. Deviations from this, however, such as temperatures surpassing AN's steady-state decomposition temperature (292 °C at 1 atm), confinement and exposure to contaminants, modifies the thermolysis of AN. Here, alternative and more exothermic decomposition pathways are introduced, mainly in the gas phase, and usually accompanied by an increase in nitrogen yields at the expense of nitrous oxide.

Still, if explosive and run-away reactions are to be attained in pure AN, exothermic contributions must be of such an extent that the initial, endothermic decomposition of AN is more than generously surpassed. Nevertheless, the reported literature herein does propose that deflagration-to-detonation transitions in pure AN are quite improbable without confinement. As confinement leads to greater gas and condensed phase interactions, while at the same time suppresses the endothermal dissociation, net exothermic decomposition and self-accelerating behavior is promoted. The critical pressures for such transitions have been investigated in a few small-scale experiments and have also been linked to a critical height. Still, this has yet to be established for large and bulk scale amounts of AN. Due to the difficulty in performing and reproducing experiments of such dimensions, the development of approaches and representative

approximations for evaluating the ability of self-confinement in AN heaps are consequently of great importance for forthcoming safety and risk evaluations of AN transport and storage. In addition, the resulting complexity in the thermolytic behavior of AN, even with small changes in conditions, contributes to the unpredictable consequences when AN is exposed to fire. This problematizes the design of appropriate large scale experiments even further.

Upon the exposure to combustible material and a range of different contaminants, including AN's own decomposition products, exothermal and self-accelerating behavior in AN decomposition is promoted. This is by actions such as catalysis, introduction of alternative decomposition pathways and by providing additional reaction heat. Also here, explosions in such mixtures seem to be dependent on a certain amount of confinement. These critical pressure levels are substantially reduced compared to that of pure AN and small voids and self-confinement in the molten mass can probably be sufficient. This prominent dependence on confinement, for both pure and contaminated AN, appears to involve increased interactions between the gas and condensed phases whereby further and more rapid decomposition, combustion and run-aways are conceivable. The extent of the heterogeneous gas-condensed phase chemistry thus seems to play a vital role in the unpredictable behavior of AN under fire exposure. This can probably also be a key reason for the variety of results found on investigations of AN thermolysis as experimental set-up and conditions thus will be crucial for the results.

The nature of these essential parameters and their potential presence in fire incidents makes a pending explosion difficult, if not impossible, to foresee. No investigations have been able to establish realistic, critical values for these parameters as fire incidents are rarely generic events. This has also been the conclusion in a range of post-accident reviews from the past century including the reconciliation with AN being a metastable compound. What we do know, however, is that the crucial common denominator is heat exposure itself. To prevent explosions in AN, avoiding fire and heat exposure is indisputably of great importance. If such exposure is inevitable, averting mixing with contaminants, confinement and the possibility of (projectile) shock initiation will also reduce the explosion risk. As we now have greater opportunities to utilize and develop technological solutions for such risk elimination, compared to the safety technologies in the early beginning of the 20th century, appropriate and improved safety measures are all the more achievable.

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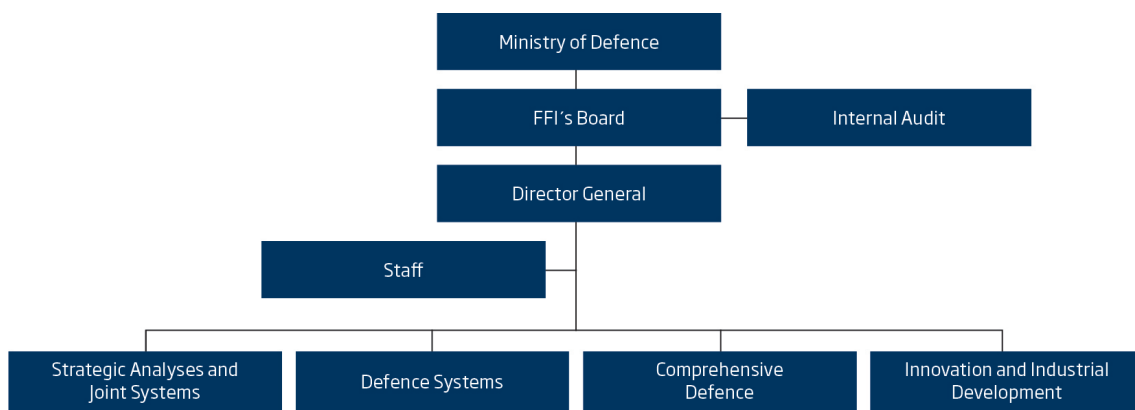
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