

Étude théorique de la décomposition thermique du nitrate d'ammonium en présence d'additifs et de contaminants

Eleonora Menicacci

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THÈSE DE DOCTORAT DE L'UNIVERSITÉ PSL

Préparée à Chimie Paris-Tech

Theoretical study of the thermal decomposition of ammonium nitrate in presence of additives and contaminants

Étude théorique de la décomposition thermique du nitrate d'ammonium en présence d'additifs et de contaminants

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Ai miei genitori

A mio fratello

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Introduction

Many substances are susceptible to incompatibility phenomena when they are brought into accidental or intentional contact with other substances or materials. The control of chemical risk in the industrial environment requires rapid and accurate identification of incompatibility problems. This identification has so far been carried out through calorimetric test such as Differential Scanning Calorimetry (DSC). However, the information provided by the DSC tests are limited and do not allow for the identification and understanding of neither the chemical mechanism nor the cause-and-effect relationship of incompatibility between two substances. In this context, the a priori prediction of reactivity between two (or more) molecules by molecular modelling can become a valuable tool, complementary to experimental trials.

The studies preceding this thesis focused on the understanding of the mechanisms of chemical incompatibilities involving ammonium nitrate (AN) using molecular modelling. Ammonium nitrate is a product widely used in the chemical industry, known to be incompatible with a large number of chemical substances (ammonia, chlorides, metals, acids, fuels, sulfates) and involved in many significant accidents from 1921 with the Oppau accident and more recently in 2001 with the Toulouse accident. The application of molecular modelling to study chemical incompatibilities is an innovative and pioneering approach that has made it possible to clarify the reaction mechanisms during the decomposition of pure AN and in contact with contaminants. Previously, a theoretical study based on DFT calculations was carried out on pure ammonium nitrate and its mixture with sodium dichloroisocyanurate (SDIC) to identify the reaction paths, the products formed and the heat released by the reactions. These theoretical methods were then applied to other chemical incompatibility systems with ammonium nitrate (NaNO₂, NaNO₃, and chlorinated substances) to test their relevance. The objective of this research is to extend the knowledge of ammonium nitrate, testing the previous theoretical approach with other additives or contaminants and thus characterize their behaviour on the decomposition of ammonium nitrate.

This thesis aims to develop a simplified approach allowing to identify and categorize different types of additives and contaminants. Their behaviour as inert, promoters or inhibitors could be identified by focusing on modelling the critical steps of the mechanisms of reaction. AN grade fertilizer presents some special formulations. For example, AN is mixed with CaCO₃ is called the CAN fertilizer, and if it is mixed with $(NH_4)_2SO_4$ (AS), the resulting formulation is called ASN. After a bibliographical study about the behavior of contaminants and additives placed in contact with AN, three systems, known experimentally for their effect on AN used to improve the fertilizers' formulations, were identified to be studied, through the application of the Density Functional Theory (DFT): AN + CaCO₃, AN + CaSO₄ and AN + (NH₄)₂SO₄.

This choice was made to study an inhibitor, an inert, and a promoter of AN's decomposition. Indeed, bibliographical study showed that $CaCO_3$ is experimentally used as an inhibitor, $CaSO_4$ as an inert and $(NH_4)_2SO_4$ as a promoter. According to literature, the behaviours of substances with AN can be defined as follows: Inhibitor: a substance that increases the thermal stability of ammonium nitrate

Promoter: a substance that reduces the thermal stability of ammonium nitrate

Inert: a substance that does not modify the thermal stability of the ammonium nitrate

In the **first chapter** of this manuscript, the context of the study is explained. In the first part, the chemical and physical characteristics of ammonium nitrate are presented. The second part illustrates the accidentology of ammonium nitrate: AN has been the cause of several disasters in the last hundred years. The regulation of AN grade fertilizer follows the accidentology. The third part deals with the global issue of chemical incompatibilities and the instruments used nowadays to prevent them in an industrial context. Subsequently, the reactivity of ammonium nitrate with various types of substances is described in detail. Finally, bibliographic knowledge on AN additives and contaminants is reported: three different sections dedicated, to promoters, inhibitors and inert substances of AN decomposition were presented.

The **second chapter** introduces the theoretical bases of the methods used in the context of this thesis. It contains a brief reminder of quantum chemistry, a general presentation of the different ab initio methods used to solve the Schrödinger equation and a more detailed description of the Density Functional Theory (DFT) which is the method used in this work.

In the **third chapter**, the study of the influence that two inorganic selected salts exert on AN is presented: $CaCO_3$ and $CaSO_4$. In the beginning, the physico-chemical characteristics of the two salts are presented, followed by a description of their stabilizing effect on AN. Various types of studies are discussed, including DSC calorimetry and Differential Thermal Analysis (DTA). Once the reactivity of these salts has been clarified, the theoretical work done between AN + CaCO_3 and AN + CaSO_4 is presented and discussed.

In **chapter four**, a discussion about the case of the Oppau accident, which occurred in Germany on September 11^{th} , 1921, is proposed. This case is still today probably the worst and most devastating accident ever recorded in the history of the chemical industry. The causes that led to this accident have never been completely understood. At the BASF plant, ammonium nitrate was diluted with ammonium sulfate $(NH_4)_2SO_4$ to improve its quality as a fertilizer and to reduce hygroscopicity. A detailed analysis of the dynamic of the accident and the experimental work carried out from it until today is presented. Finally, a theoretical work, aimed at understanding the possible incompatibility between AN and AS is highlighted. The aim was to understand the reason for which $(NH_4)_2SO_4$ acts at the same time as an inhibitor and as a promoter of AN's decomposition.

In **chapter five**, in the first part, the study is dedicated to two chlorinated substances, which are CaCl₂ and KCl. At the beginning, an introduction about their characteristics is proposed, followed by a general description of reactivity of different kind of chlorinated salts placed in contact with AN. Some calorimetric data relative to the mixture of AN with CaCl₂ and with KCl, are also reported. Finally, theoretical work on CaCl₂ and KCl has been performed with the final purpose of presenting a mechanism of these substances when they are placed in contact with AN.

In the second part of this last chapter, the theoretical behaviour of various substances known to be used as ammonium nitrate inhibitors and inerts are explored. These substances are CaCO₃, MgCO₃, Na₂CO₃, KHCO₃, NaHCO₃, CaSO₄, MgSO₄, K₂SO₄, Na₂SO₄, NaHSO₄, KHSO₄, Na₃PO₄, K₃PO₄, Na₂HPO₄, (NH₄)₂SO₄,

(NH₄)₂HPO₄, K₂HPO₄, CaHPO₄, NaH₂PO₄, and KH₂PO₄. A theoretical study was performed to investigate their mechanism of action. Since the species investigated were numerous, this study was limited to the first step of their interaction with AN.

Finally, conclusions and perspectives will complete this thesis work, proposing a global and critical analysis of the study carried out as well as some suggestions for ways forward to improve the theme addressed here.

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CONCLUSION

ANNEXE I – ADR incompatibility table, Recommendation for the segregation of dangerous substances

ANNEXE II - Attempt to build a predictive tool on ammonium nitrate reactivity in the presence of additives and contaminants

I. Research of predictive physico-chemical descriptor of the influence of additives on the thermal stability of ammonium nitrate.

I.I Proton Affinity Références

CHAPTER 1

Generalities about ammonium nitrate



This chapter is devoted to a general introduction on ammonium nitrate (AN) and its behaviour when it is placed in contact with different kind of additives. In the first part of the chapter, a focus on the physical and chemical characteristics of ammonium nitrate is presented. Then, its different uses are explained. AN regulation is reported. The third part deals with the issue of chemical incompatibilities of AN and how to prevent them. The use of predictive tools such as the labelling system, safety data sheet, incompatibility tables, experimental tools, and the theoretical tools are mentioned. In the fourth part, the reactivity of AN with various types of substances is described in detail, considering three categories: promoters, inhibitors and inerts of AN's decomposition. Then, a summary table that takes into account the behaviour of substances, when they are placed into contact with AN, is provided. Finally, the objectives of the thesis are described.

1. General information about ammonium nitrate

Ammonium nitrate (NH₄NO₃, AN) is a hygroscopic salt that presents a high solubility in nitric acid, alcohol, acetic acid, and water, with a melting point of 169.6° C.¹ The crystalline structure of AN has an extensive polymorphism, and five crystalline forms can exist by varying the pressure and temperature: at 125° C, AN presents a cubic crystalline form, between 84° C and 125° C a quadratic form, a monoclinic form between 32° C and 85° C, and an orthorhombic form between -16° C and 32° C. Below -16° C AN presents a second quadratic form.



Figure 1. Pressure-temperature diagram for NH₄NO₃.²



1.2 Uses and applications of ammonium nitrate

AN is widely used in the chemical industry as a component of explosives and as fertilizer.³⁻⁴ When we talk about industrial explosive, generally we refer to ANFO (ammonium nitrate fuel oil) formulation where AN is mixed with fuel oil, or amatol (where AN is combined with trinitrotoluene), or to the case of rocket fuels, in which AN takes the place of ammonium perchlorate.⁵ In fertilizer, AN acts as a source of ammonia and nitrate ions necessary for plant life. In explosive formulations, it acts as an oxygen source and as an oxidant. AN is also used to produce an anaesthetic, namely the nitrous oxide,⁶ for some industrial fermentations and for the preparation of citric acid.⁶ The most marked difference between ammonium nitrate used as an explosive and AN used as a fertilizer is in their different porosity of the granulate formulation.⁷ AN intended for use as an explosive has a high porosity to facilitate oil absorption. At the same time, a low bulk density ensures low resistance to detonation. Ammonium nitrate grade fertilizer presents a high granular density and a low porosity. It is also processed to have a low capacity to absorb contaminant, and a high bulk density resulting in high resistance to detonation.⁸ AN is usually stable, and its thermolysis depends on various factors such as the presence of contaminants, confinement, humidity, pressure, and temperature.^{1,7,9}. The presence of impurities during manufacturing, storage, transport and use processes such as acids, chlorides, fuels, metals can destabilize the AN formulation,⁵ dues to a catalytic effect of the contaminant on the decomposition of ammonium nitrate leading to an unexpected and sometimes dangerous reaction like selfignition and explosion. 10,11

1.3 Ammonium Nitrate's Reactivity

Many hypotheses on the decomposition of pure AN have been formulated. Experimental tests have led to the development of various possible decomposition mechanisms, which are being presented in this section. Beyond the various hypotheses^{1,4}, all reactions start with a transfer of a proton from the ammonium molecule to the nitrate (1). According to these studies, this step is a moderately endothermic process.

(1)
$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$

Different reaction mechanisms about the ammonium nitrate decomposition were reported since 1869.^{1, 4,12–}¹⁴ These works show that there is not a single mechanism of decomposition, but this one is influenced and changes with the temperature. When the salt is heated from 200°C to 230°C, the decomposition of AN follows the decomposition (2), and the heat evolved is about 86 cal/g: ¹

(2)
$$NH_4NO_3 \rightarrow \frac{1}{2}N_2 + NO + 2H_2O$$



Above 230°C, the predominant decomposition: ¹

(3)
$$NH_4NO_3 \rightarrow 3/4N_2 + 1/2NO_2 + 2H_2O$$

and the heat evolved is around 316 cal/g. When the temperature reaches 560°C, AN explodes generating these products: ¹

(4)
$$8NH_4NO_3 \rightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O$$

The heat evolved is around 201 cal/g. At 950 °C, the next decomposition is predominant: ¹

(5)
$$NH_4NO_3 \rightarrow N_2 + 2H_2O + 1/2O_2$$

The heat evolved is 354 cal/g. For all these reactions, no detail on the mechanism are available. For this reason, a theoretical study was conducted to understand the decomposition of pure ammonium nitrate better.¹⁵ Details about this work are presented in the chapter.

1.4 AN Regulation and Accidentology

Although pure ammonium nitrate is generally used without risk, its commercial formulation, exposed to contamination of impurities, presents significant dangers. Over the years, indeed, many accidents involving ammonium nitrate (See Table 1) have occurred, causing an important number of deaths and injuries.^{16,9} Looking at these tables, it is immediately clear that the most common cause that has led to accidents during production, transport and storage is the chemical contamination of AN, likes in the case of the AZF Accident in Toulouse (2001) and the West Texas Fertilizer on April 17, 2013 in which ammonium nitrate was affected by impurity. Ammonium nitrate is classified as a Class 5.1 oxidizing agent according to the U.N. Recommendation on the Transport of Dangerous Good¹⁷ and is placed in categories 2 (H319 - eye irritant) and 3 (H272 - oxidant) in CLP.¹⁸ The next paragraph presents a complete accidentology of ammonium nitrate of the last 100 years. Subsequently, regulations of AN-based fertilizers and their classification is introduced.

Place	Year	causes		
Kensington United Kingdom	1896	AN for the production of N_2O		
Oakdale, PA United States	1916	AN in the pre-boiling tank		
Gibbstown, NJ, United States	1916	AN melted, 160 ° C		
Morgan, NJ, States United	1918	AN		
Stolberg Germany	1920	AN agglutinated		
Vergiati, Italy	1920	AN + TNT		
Brooklyn, NY, United States	1920	AN agglutinated		
Kriewald Germany	1921	Caked AN		
Oppau, Germany	1921	$AN + (NH_4)_2SO_4$		
Sinnemahoning, AP, United States	1922	AN		
Muscle Shoals, AL United States	1925	Cars covered with 220 barrels of AN		
Emporium, PA, United States	1925	AN with wax in water		
Tessenderloo, Belgium	1942	piles of AN		
Milan, TN United States	1944	AN melted, 154 ° C		
Benson, AZ, United States	1944	AN 149 ° C		
Texas City, TX, United States	1947	AN + wax		
Presque Isle, ME, United States	1947	AN + fertilizer superphosphate, K, flour, etc.		
Brest, France	1947	AN + wax		
St. Stephens, Canada	1947	AN bagged fertilizer		
Pinole, CA, United States	1953	AN + NaNO ₃ + organic mixed to start manufacturing dynamite		
New Castle, PA, United States	1956	AN		
Mt. Braddock, PA, United States	1958	AN + NaNO ₃		
Norton, United States	1961	AN + ANFO		
Finland	1963	AN molten, 160 ° C		
Vernon, United States	1966	AN bagged fertilizer		
Amboy, United States	1966	AN in a truck next to the TNT bunker (2000 lb TNT and 10,000 lb NA)		
Taroom Queensland, Australia	1972	AN explosion caused by an electrical fire		
Bucharest, Romania	1974	AN+ wood powder		
Tahawas, NY, United States	1976	AN		
Delaware City, United States	1977	AN solution to 83% for the production of N_2O		
Rocky Mountain, United States	1978	AN fertilizer		
Moreland, United States	1979	AN fertilizer		
Kansas City, United States	1988	AN + fuel + Aluminum dust or pellets		
Joplin, United States	1989	Production of AN in a reactor Stengel		
Porgera Valley, Papua New Guinea	1994	Fire in an emulsion matrix reservoir near the AN oil fuel		
Port Neal, United States	1994	Acidic environment, the presence of chlorides, a low density area, containment		
Kentucky, United States	1998	AN stored with methyl bromide and pesticides		
Toulouse, France	2001	AN + SDIC ?		
Cartagena, Murcia, Spain	2003	AN self-sustaining decomposition		
Mihăileşti, Buzau, Romania	2004	road truck explosion due to an impact generated by an earthquake		
West, TX, United States	2013	Uncontrolled fire: building almost entirely of wood		
WyandraQueensland, Australia	2014	AN for the manufacture of explosives. Contamination by organic substances and metals		
Ti Tree, Australia	2014	AN+ fuel		
Tianjin, China	2015	Dangerous Goods illegally stored :AN, NaCN and nitrocellulose.		

Table 1. Ammonium Nitrate Accidentology.

<u>Chapter 1</u>

1.4.1 Regulation (EC) No 2003/2003 of the European Parliament and of the Council

The current regulation for fertilizer is the <u>"Regulation EC No 2003/2003 of the European Parliament and the council of 13 October 2003 on fertilizers</u>.¹⁹ The European regulation on fertilizers aims to give precise directives about what are the standards to be respected for a fertilizer to be declared in conformity with the EC directive. This regulation is composed of 5 parts. In the first part, called Annex I, the denominations of the most common and used fertilizers in Europe are presented. This system of the denomination is based on the element(s) constituting the fertilizer. Below is reported the subdivision of fertilizers in the various categories. Ammonium nitrate is included in nitrogen-based fertilizers. The second part, Annex II, concerns the tolerance about the quantities of the various compounds in the formulation of each type of fertilizer and the maximum percentage of impurities and contamination that each fertilizer can tolerate. However, ammonium nitrate are given in Annex III, in which the most common formulations of ammonium nitrate-based fertilizer are reported. In Annex IV, are described the sampling and analysis methods. Finally, Annex V contains a list of documents to be consulted by manufacturers and their representatives to prepare a technical dossier for a new type of fertilizer to be added to Annex I of this Regulation. Below, the list of the classification of fertilizers, presented in Annex I, is reported:

List of EC fertilizer types¹⁹

A. Simple inorganic primary nutrient fertilizers with primary nutrients

- A.1 Nitrogenous fertilizers
- A.2 Phosphate fertilizers
- A.3 Potassium fertilizers
- B. Inorganic fertilizer compound with primary nutrients
 - B.1 NPK fertilizer
 - **B.2 NP Fertilizer**
 - **B.3 NK Fertilizer**

B.4 PK Fertilizer



- C. Inorganic and fluid fertilizers
 - C.1 Simple fluid fertilizers
 - C.2 Compound fluid fertilizers
- D. Inorganic fertilizers with secondary elements
- E. Inorganic fertilizers with trace elements
 - E.1. Fertilizer reporting only one trace element
 - E.1.1. Boron
 - E.1.2. Cobalt
 - E.1.3. Copper
 - E.1.4 Iron
 - E.1.5. Manganese
 - E.1.6. Molybdenum
 - E.1.7 Zinc
 - E.2. Minimum trace element content in percentage by weight of fertiliser
 - E.3. List of organic materials authorized to chelate and complex trace elements

As specified in Annex III,¹⁹ ammonium nitrate is the main ingredient in a wide range of products, some of which are used as fertilizers and others as explosives. Considering the particular nature of ammonium nitrate and high nitrogen fertilizers and the resulting requirements for public safety, health and protection of workers, it was necessary to provide for additional rules for fertilizers of this type. Some of these products could be dangerous and used for purposes other than those for which they are intended.¹⁹ It could affect the safety of people and property. Manufacturers should, therefore, be required to take appropriate measures to avoid such uses, in particular, to ensure the traceability of such fertilizers. In the interest of public safety, it is particularly important to determine the characteristics and properties which distinguish the EC fertilizers based on ammonium nitrate and with high nitrogen content, from ammonium nitrate products used as explosives.¹⁹ EC fertilizers based on ammonium nitrate and with high nitrogen content should meet specific

characteristics to ensure their safety. Manufacturers should ensure that all ammonium nitrate fertilizers with a high nitrogen content have successfully passed a detonation test before being placed on the market. ¹⁹ It is necessary to establish rules concerning closed thermal cycle methods even if these methods may not necessarily simulate all the conditions encountered during transport and storage.¹⁹ Fertilizers can also be contaminated with substances that may pose a risk to human and animal health and for the environment. The denomination of ammonium nitrate-based fertilizers into EC regulation N° 2003/2003 is reported below, and these kind of formulations have to respect the following composition:¹⁹

1) **Calcium nitrate** formed by limestone. This product is obtained from a chemical process, and it contains, as an essential component, calcium nitrate and, optionally, ammonium nitrate. It contains as a minimum nutrient the 15 % nitrogen evaluated as total nitrogen or as nitric and ammoniacal nitrogen. The maximum quantity of ammoniacal nitrogen is 1.5%.¹⁹

2) Limestone ammonia nitrate. This product is obtained from a chemical process and has ammonium nitrate as an essential component and which may contain fillers such as ground limestone, calcium sulfate, dolomitic ground rock, magnesium sulfate, kieserite. The maximum nitrogen N is about 20% assessed as nitric nitrogen and ammoniacal nitrogen, each of which must represent about half of the nitrogen present. The designation limestone ammonia nitrate may only be used for fertilizer. In addition to ammonia nitrate, only calcium carbonate (e. g. limestone) or magnesium carbonate or both (e. g. dolomitic rock) is permitted. The minimum carbonate content of the fertilizer must be at least 20 %. The purity of these carbonates must be at least 90 %.¹⁹

3) Ammonia sulfonitrate. It is a chemically produced product containing ammonium nitrate and ammonium sulfate as essential components. The maximum nitrogen content is 25% of nitrogen assessed as ammoniacal nitrogen and nitric nitrogen. Minimum nitric nitrogen content is 5%. The total nitrogen value is 19%, evaluated as ammoniacal nitrogen and nitric nitrogen. Minimum nitric nitrogen content: 6 % wt of nitrogen. The MgO value corresponds to 5% of magnesium in the form of water-soluble salts expressed as magnesium oxide.

4) Ammonium nitrate urea solution. The product is obtained by a chemical process and by aqueous solution, containing ammonium nitrate and urea at 26 % of maximum nitrogen, evaluated as total nitrogen. The urea nitrogen represents only about half of the nitrogen present. The maximum biuret content is about 0.5 %. If the biuret content is less than 0.2 %, the words <u>"poor in biuret"</u> may be added.¹⁹

In addition to the standards for the composition of ammonium nitrate fertilizers, there are also technical requirements that must be observed to ensure that the fertilizers are not dangerous. The technical provisions cover various aspects of the mixtures such as the porosity, fuel components, the pH, the particles' size, chlorine and heavy metals contents. It is also essential to determine the detonability of the mixture. Below, the characteristics of each specification

Characteristics and limits of ammonium nitrate fertilizers with a high nitrogen content¹⁹

- Porosity (oil retention)

The oil retention of the fertilizers, which must have been previously tested with two thermal cycles at a temperature of 25 to 50 °C, do not have to exceed 4 % by mass. The thermal cycles test is presented in the next page into **Method 1**, and the test for oil retention is reported into **Method 2**.¹⁹

- Fuel components

The percentage by mass of combustible material, measured as carbon, shall not exceed 0.2 % for fertilizers with a nitrogen content of 31.5 % or more by mass and shall not exceed 0.4 % for fertilizers with a nitrogen content of 28 % or more but less than 31.5 % by mass. In the next page, into **Method 3**, more detailed are reported.¹⁹

<u>- pH</u>

A solution consisting of 10 g of fertilizer in 100 ml of water must have a pH of 4.5 or more. Into **Method 4** is reported the experimental test to determine the pH of fertilizer.¹⁹

- Particle size analysis

The fraction of fertilizer passing through a 1 mm mesh sieve must not exceed 5 % by mass, nor 3 % by mass when the mesh is 0.5 mm. Into **Method 5**, a more detailed explanation is reported.¹⁹

- Chlorine

The maximum chlorine content is set at 0.02% by mass. Into **Method 6** are reported more detail about the determination of the quantity of chlorine.¹⁹



- Heavy metals

There should be no deliberate addition of heavy metals and, for any trace of these metals resulting from the production process, the limit set by the Committee should not be exceeded. The copper content must not exceed 10 mg/kg. No limits are set for other heavy metals. In the next page, into **Method 6** and **7**, more information is reported.¹⁹

Description of the detonability test for ammonium nitrate fertilizers with high nitrogen content¹⁹

The tests necessary to determine if AN-based fertilizer respect the EC standard, a representative sample of fertilizers is taken apart, and the experimental test have to be performed. The entire sample shall be subjected to five thermal cycles before the detonation test is carried out. The fertilizer is subjected to the detonation test in a horizontal steel tube under the following conditions:¹⁹

- seamless steel tube,

- tube length: at least 1 000 mm,
- external diameter: at least 114 mm,
- wall thickness: at least 5 mm,

- priming relay: the nature and dimensions of the priming relay charge should be chosen to obtain, at the level of the sample (of material) to be tested, the highest detonating stress in terms of propagation of the detonation,

- test temperature: 15-25 ° C,

- lead indicator cylinders for detonability: 50 mm diameter, 100 mm height,

Each test has to be placed at 150 mm intervals and supporting the tube horizontally. These tests are repeated two times and they are considered concluded if the crushing of one or more lead support cylinders is less than 5 % in each test.

Method 1 - Application of thermal cycles¹⁹

The scope of application is to define the procedures for performing thermal cycles before the oil retention test on a straight ammonium nitrate fertilizer with a high nitrogen content and the detonation resistance test on a straight ammonium nitrate fertilizer or compound with high nitrogen content. This procedure is applied

before the determination of the oil retention of the fertilizer. The test sample is placed in an Erlenmeyer flask. It is heated from room temperature to 50°C and maintained at this temperature for two hours (phase at 50°C). The test sample is then cooled to 25°C and maintained at this temperature for two hours (25°C phase). The combination of the two successive phases at 50°C and 25°C constitutes a thermal cycle. After undergoing two thermal cycles, the test sample is stored at a temperature of 20 ± 3 °C for the determination of oil retention. The apparatus is composed of a thermostated water bath at 25 (± 1) and 50 (± 1) ° C respectively and an Erlenmeyer flask with its capacity of 150 ml. Each test sample of 70 (± 5) g is placed in an Erlenmeyer flask and closed. Every two hours, the sample is transferred from the 50°C water bath to the 25°C water bath and vice versa. Water is maintained in each bath at a constant temperature and ensuring continuous movement. The sample should be protected from the condensation by a rubber cap. After undergoing the required number of thermal cycles, the test sample shall be maintained at a temperature of 20 (± 3) °C pending the detonability test. A sufficient amount of fertilizer is placed into the container for a single detonation.

Method 2 – Determination of oil retention¹⁹

This method could be applied to pearl and granulated fertilizers that do not contain oil-soluble materials. For oil, retention is intended the quantity of oil retained by the fertilizer determined under the prescribed operating conditions. This quantity is expressed as a percentage by mass. The principle of this test is that the sample containing the fertilizer is immersed entirely in diesel fuel for a specified time, then the excess diesel fuel is drained under specified conditions. The mass increase of the test sample is then measured. The reactive used are diesel fuel with a maximum viscosity of 5 mPa at 40 °C, a density between 0.8 to 0.85 g/ml at 20 °C, sulfur content inferior to 1.0% (m/m) and an ash content inferior to 0.1% (m/m). The apparatus for this test is composed by a balance with an accuracy of 0.01 g; beakers with a capacity of 500 ml; a plastic funnel, preferably with a cylindrical vertical upper edge, approximately 200 mm in diameter; a 0,5 mm mesh opening test sieve fitting into the funnel, fast filter paper, crepe, soft and absorbent paper (laboratory grade). The operation to determine the oil retention is carried out by two determinations at close intervals on different partial quantities of the same test sample.

Method 3 - Determination of fuel components¹⁹

This method is used for the determination of the fuel content of straight ammonium nitrate fertilizers with high nitrogen content. The concept is that carbon dioxide produced by the inorganic filler can be removed with acid. The organic compounds are oxidized by a mixture of chromic acid and sulfuric acid. The carbon dioxide formed is absorbed in a barium hydroxide solution. The precipitate is dissolved in a hydrochloric

acid solution and measured by back titration with a sodium hydroxide solution. Reagents used are chromium trioxide (Cr_2O_3 , sulfuric acid at 60% by volume and silver nitrate solution at 0.1 mol/l).

Method 4 - pH measurement¹⁹

The measurement of the pH of an ammonium nitrate solution is obtained by using a pH meter. The reagents are distilled or demineralized water, free by carbon dioxide and a buffer solution, pH 6.88 at 20°C. The experience starts with the preparation of the buffer solution. So, $3.4 (\pm 0.01)$ g of potassium dihydrogen orthophosphate (KH₂PO₄) are dissolved in approximately 400 ml of water. Then $3.55 (\pm 0.01)$ g of sodium monohydrogen orthophosphate (Na₂HPO₄) are dissolved into 400 ml of water. Both solutions are transferred quantitatively into a 1000 ml volumetric flask; making up to volume and mixing. The solution is then in an airtight container, and 10.21 (\pm 0.01) g of potassium hydrogen phthalate are dissolved into (KHC₈O₄H₄) water to prepare the buffer solution (pH 4.00 at 20°C). Then it is transferred into a 1000 ml volumetric flask making up the volume and mixing. This solution is stored in an airtight container. Commercially available standard pH solutions may be used. The apparatus of the experience is composed by a pH meter, with glass and calomel electrodes, with a sensitivity of 0.05 pH unit. The pH meter is calibrated at a temperature of 20 (± 1) °C, using buffer solutions. A stream of nitrogen is slowly made to run over the surface of the solution, maintaining it throughout the test. The determination of the pH is done taking 100 ml of water into 10 (\pm 0.01) g of the test sample into a 250 ml beaker. The insoluble fractions are removed by filtering, settling or centrifuging the liquid. The pH of the clear solution is measured at a temperature of 20 (\pm 1) °C, using the same procedure as for calibrating the pH meter.

Method 5 - Granulometry¹⁹

In this method, the test sample is sieved, by hand or mechanically, through a set of three nested sieves. The quantity collected in each sieve is recorded; the percentages of material passing through the sieves are then calculated. The apparatus of this experience is composed by test sieves made of 200 mm diameter woven wire with a mesh width of 2 mm, 1 mm and 0.5 mm respectively, a lid and a container for these sieves, a balance with a sensitivity of 0.1 g, a mechanical device capable of imparting vertical and horizontal movements to the test sieves. The sample is divided representatively into fractions of about 100 g. One of these fractions is weighted to the nearest 0.1 g. The sieve set is arranged in ascending order of opening (0.5 mm, 1 mm, 2 mm), placing the previously weighed sample on the upper sieve. The cover is adjusted on the upper sieve, and the apparatus is shacked horizontally and vertically, by hand or mechanically for 10 minutes. Then the sieves dissembled one after the other; collect the material they contain. The material contained in each sieve is weight. Then the masses of the collected fractions are reported as a percentage of

the total mass of the fractions. The percentage of material collected in the container (particles less than 0.5 mm) is calculated. The results obtained for A must not differ by more than 1 % in absolute terms, nor those obtained for B by more than 1.5 % in absolute terms. If not, the test should be repeated.

Method 6 - Determination of chlorine¹⁹

This method is used for the determination of chlorine (in the form of chloride ions) contained in straight ammonium nitrate fertilizers with high nitrogen content. The chloride ions dissolved in water are determined by potentiometric titration using a silver nitrate solution in an acid medium. The reagents used are distilled or demineralized water, free of chloride ions, acetone, concentrated nitric acid (density at $20^{\circ}C=1.40 \text{ g/ml}$), silver nitrate standard solution at 0.1 mol/l, silver nitrate standard solution at 0.004 mol/l, a potentiometer with silver indicator electrode and calomel reference electrode (sensitivity 2 mV, potential from - 500 to + 500 mV), a bridge containing a saturated potassium nitrate solution connected to the calomel electrode and, fixed at the ends by porous plugs, a magnetic stirrer with Teflon coated rod, 0.01 ml tapered-tip micro burette.

Method 7 - Determination of copper¹⁹

This method is used to determine the copper content of straight ammonium nitrate fertilizers with high nitrogen content. The sample is dissolved in dilute hydrochloric acid, and the copper content is determined by atomic absorption spectrometry (spectrophotometer with copper lamp (324.8 nm)). The reagents used are: hydrochloric acid (density at 20 °C =1.18 g/ml), hydrochloric acid (6 mol/l solution), hydrochloric acid (0.5 mol/l solution), ammonium nitrate, hydrogen peroxide, 30% (m/m), concentrated solution of copper and diluted solution of copper.

1.4.2 New European Regulation of fertilizer of 5^h June 2019

All the above specifications are valid until 2022 when the new UE fertilizer regulation is adopted.²⁰ This new regulation was published on 5th June 2019. It contains innovations, especially about the designation of fertilizers. The old designation in the previous Regulation (EC Regulation 2003) will be abrogated, and the new way of designating fertilizers will be as follows:²⁰

1. Fertilizer

- A. Organic Fertilizer
 - I. Solid organic fertilizer



- II. Liquid organic fertilizer
- B. Organic-mineral fertilizer
 - I. Solid organic-mineral fertilizer
 - II. Liquid organic-mineral fertilizer

C. Inorganic fertilizer

- I. Inorganic fertilizer with macro elements
- a) Inorganic solid fertilizer with macroelements
 - i) Inorganic simple solid fertilizer with macroelements

A) Inorganic simple fertilizer ammonium nitrate-based with high nitrogen content

ii) Inorganic solid fertilizer composed by macroelements

A) Inorganic simple fertilizer ammonium nitrate-based with high nitrogen content

- b) Inorganic liquid fertilizer with macroelements
 - i) Inorganic simple liquid fertilizer with macro elements
 - ii) Inorganic simple liquid fertilizer composed by macroelements
- II. Inorganic fertilizer with oligo-elements
 - a) Inorganic simple liquid fertilizer with oligo-elements
 - b) Inorganic fertilizer composed by oligo-elements

1.4.3 The REACH Regulation

The REACH Regulation²¹ (Registration, Evaluation, Authorization and Restriction of Chemicals) constitutes a regulatory framework for the registration of chemicals in the European Union. The principal aim is the protection of the environment and human health. Chemical substances used in industry are listed to classify their potentially dangerous character in various situation, particularly during mixing. REACH Regulation entered in force the 1st June 2007 and the registration of substances, which began in 2008, has been recently completed on May 31st of 2018. More than 20,000 chemical substances are already known, and their potential risks have been established. However, chemical incompatibilities are not indicated with an explicit title as in the case of Safety Data Sheets, which presents a dedicated "Stability and Reactivity" section. In the case of imported substances or manufactured goods, they are subordinate to the rules of the European Chemicals Agency (ECHA), which was created to gather all the data from chemical substances produced or imported into Europe in quantities of more than one tons per year. ECHA's responsibilities essentially is to organize data sharing to reduce testing and label products according to their dangerousness. This new regulation covers a large spectrum of substances, and it is applied to all types of chemicals like radioactive substances, drugs, food additives, pharmaceuticals, pesticides, polymers and substances used for research

and development purposes and synthesis intermediaries. As far as the ammonium nitrate regulation is concerned, the following restrictions are set out in Annex XVII of the REACH Regulation:²¹

1) Ammonium nitrate shall not be placed on the market as a substance, or in mixtures that contain more than 28 % by weight of nitrogen in relation to ammonium nitrate, for use as a solid fertilizer, straight or compound, unless the fertilizer complies with the technical provisions for ammonium nitrate fertilizers of high nitrogen content set out in Annex III to Regulation (EC) No 2003/2003 of the European Parliament and of the Council.¹⁹

2) Shall not be placed on the market as a substance, or in mixtures that contain 16 % or more by weight of nitrogen in relation to ammonium nitrate except for supply to: (a) downstream users and distributors, including natural or legal persons licensed or authorized b) farmers for use in agricultural activities, either full time or part-time and not necessarily related to the size of the land area. (c) Natural or legal persons engaged in professional activities such as horticulture, plant growing in greenhouses, maintenance of parks, gardens or sports pitches, forestry or other similar activities.

1.4.4 The CLP Regulation

CLP stands for Classification and Labelling of Chemicals (officially the Regulation 1272/2008).²² In the early 1990s, United Nations developed the Globally Harmonized System of Classification and Labelling of (GHS).²³ Its aim is the harmonization of the classification of the hazard and its communication through label, datasheet and security. The GHS recommendations have been adopted in Europe through the CLP Regulation (Classification, Labeling, and Packaging).^{22,23} This text, which entered into force on 20th January 2009 covering the new rules in Europe of classification, packaging and labelling of most single substances or mixtures and chemicals. In this regulation, there is a more detailed classification of physical hazards related to substances and mixtures. The CLP distinguishes 28 hazard classes (16 for physical hazard, 10 for health hazard, and 2 for environmental hazard). For each class, there is a specific symbol or pictogram (9 in total) accompanied by sentences, i.e. "hazard statements" and "precautionary statements". In Figure 2, pictograms associated with ammonium nitrate are reported. The CLP Regulation is fundamental for the implementation of the REACH Regulation thanks to the classification and labelling of chemicals that makes possible to better identify a potential hazard such as incompatibilities, harmful events for both humans and the environment.

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Figure 2. GHS pictograms for ammonium nitrate. The first pictogram on the left means "harmful", the central pictogram means "oxidant" and the third pictogram on the right means "explosive".

1.4.5 Recommendations on the Transport of Dangerous Goods

For a given formulation of AN-based fertilizer, it is possible to determine if it meets the criteria imposed by the European Union following EC standards, as seen in the paragraph 1.4.1. In this paragraph, the classification of products based on AN is shown, starting from the nature of their composition. In the Recommendations on the Transport of Dangerous Goods (better known as Orange Book), are listed substances classified as dangerous goods.¹⁷ Ammonium nitrate-based materials are part of the list. Generally, the classification of ammonium nitrate-based products is done considering its composition, for reason of experience and knowledge, falling in different classes depending on their composition and potential hazard.¹⁷ If some formulations do not enter in the presented criteria, they must be subjected to a detonation test.¹⁷ The number of fertilizer mixtures for agricultural needs is large and a considerable amount of testing would need to be carried out, if a test-based system of classification were to be applied. To avoid such unnecessary testing and to get a consistent approach, the classification of ammonium nitrate products is sensibly based on composition. The components specified in the UN model regulations are the percentage of ammonium nitrate (AN), combustible substances, total combustible/organic material, other added materials, if any, e.g. inert diluents and nutrient source materials such as phosphate and potash type (potassium salts such as KCl, K₂SO₄ and KNO₃). Such a composition-based system inevitably has to take a pragmatic approach, and it cannot cover all possible combinations in a precise way. UN transport regulations exist alongside other rules that are designed to classify and control the use of chemicals. In the EU, chemicals are regulated by several different Directives and Regulations, such as the "Classification, Labelling and Packaging" (CLP) Regulation.¹⁸ AN, being a fertilizer has also to respect the criteria imposed by EC regulation N° 2003/2003 of the European Parliament and the council of 13 October 2003 on fertilizers. But, the AN classification system is based upon, among others, the UN transport regulations in an attempt to

harmonize the classification of chemicals. The Recommendation of transport and dangerous goods, to simplify the classification of all the relevant combinations or compositions based on AN, elaborated some logic diagrams. The official text in the Orange Book describes the entries for the products and the associated Special Provisions, to facilitate the classification.¹⁷ On the logic diagrams, notes are reported, to provide supplementary information to the boxes.¹⁷ When traced off element are reported, such in the case of Mn, Cu and Zn, products are subjected to an ulterior classification as environmentally hazardous substances in ADR (Class 9, UN 3077) or marine pollutants in IMDG depending on the concentration of the trace elements.¹⁷ The logic diagrams, represented in Figure 3, Figure 4 and Figure 5, report the ammonium nitrate-based fertilizer's classification. Just below it is also reported all the **Special Provision**, to help the understanding of the logic diagram, providing the necessary information for the AN classification.¹⁷

Special Provision:

39.1 Purpose

This section presents the United Nations scheme for the classification of solid ammonium nitrate-based fertilizers as referred to in the Model Regulations, Chapter 3.3, special provisions 307 and 193.

39.2 Scope

Any new solid fertilizer composition containing ammonium nitrate shall be subjected to the classification procedure as set out in 39.4.

39.3 Definitions

39.3.1 An ammonium nitrate-based fertilizer is a uniform mixture containing ammonium (NH4+) and nitrate (NO3-) ions. See also 39.3.3.

39.3.2 A compound fertilizer is a uniform mixture that contains at least two of the three primary nutrients nitrogen (N), phosphorus (P) and potassium (K).

39.3.3 In determining the ammonium nitrate content, all nitrate ions for which a molecular equivalent of ammonium ions is present in the fertilizer shall be calculated as ammonium nitrate.

39.3.4 Combustible substances as referred to in paragraph 39.4 also include inorganic substances that can be oxidized, e.g. elemental sulfur. For organic substances, the content of combustibles is calculated as carbon.

39.3.5 Materials that may be incompatible with ammonium nitrate include urea, acids, superphosphates with free acid, elemental sulfur, sulfides and most transition metals, including heavy metals (e.g. copper), and chlorides. Note however that this listing is not exhaustive.

39.4 Classification procedure

39.4.1 Solid ammonium nitrate-based fertilizers are classified on the basis of their composition and experience and knowledge of their hazardous behaviour. Occasionally, the classification is complemented by testing for the ability to undergo self-sustaining decomposition or for explosive properties. These principles are condensed in the flowchart in 39.5.

39.4.2, UN No. 2067 may only be used for ammonium nitrate-based fertilizers that do not show explosive properties when tested in accordance with Test Series 2 of this Manual.

39.4.3 Ammonium nitrate-based fertilizers that do not fulfil the requirements for classification as UN No. 2067, can be assigned another suitable UN number in Class 1 or Class 5, Division 5.1, provided that the suitability for transport is demonstrated and this is approved by the competent authority. This may, for instance, be when contamination has occurred in, e.g. an accident, so that the fertilizer can be transported under a suitable UN number, e.g. in Class 1 as approved by the competent authority.

39.4.4 Ammonium nitrate-based fertilizers that meet composition limits relevant for inclusion in the class of Explosives as set out in 39.5 shall be classified in that class regardless of the results when tested in accordance with Test Series 2 of this Manual.

39.4.5 Ammonium nitrate-based fertilizers that meet composition limits relevant for classification as oxidizing solids as set out in 39.5, or are otherwise classified as oxidizing solids, shall not be exempted from that classification on the basis of the results from tests O.1 sand/or O.3 in Section 34 of this Manual. See also paragraph 34.3.1 in Section 34 of this Manual.

39.4.6 Fertilizers that contain 70 % or more ammonium nitrate shall not contain ammonium sulfate as a nutrient unless they are compound fertilizers with less than 90% ammonium nitrate and with at least 10% inorganic materials excluding ammonium nitrate and ammonium sulfate.

39.4.7 Compound fertilizers that meet the composition limits relevant for potential inclusion for transport in Class 9 shall be tested for their capability to undergo self-sustaining decomposition according to the method given in paragraph 38.2.4 of this Manual (test S.1, trough test) and classified according to criteria given there and in 39.5.

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Figure 39.1 (a)



Figure 3. Logic Diagram for the classification of ammonium nitrate according to the Recommendation of Transport of Dangerous Goods, part 39.1 (a)

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Figure 39.1 (b)



Figure 4. Logic Diagram for the classification of ammonium nitrate according to the Recommendation of Transport of Dangerous Goods, part 39.1 (b)

Figure 39.1 (c)



Figure 5. Logic Diagram for the classification of ammonium nitrate according to the Recommendation of Transport of Dangerous Goods, part 39.1 (c)



2. Tools dedicated to chemical incompatibilities

In order to evaluate the incompatibility of chemicals with other materials, tools have been proposed for this purpose. These tools exist to facilitate the information sharing about the reactivity of substances, their physical-chemical properties and, most importantly, their incompatibilities. In these tools, the properties of substances and their chemicals risks are indicated by appropriate labelling.

2.1 Labeling of chemicals

The first date of the legislation on poisonous substances was drawn up by the Health Code (Decree No. 88-1232 of 29th December 1988). This was an old way of labelling, which were used to specify the precautions for the used product, the instructions for the storage, disposal, and what to do in case of an accident. All these instructions were marked on the package containing the chemical. Currently, following the CLP regulation, the main text dealing with packaging labelling must include an evident and legible label, firmly fixed on its support and following the dimension of the container. This tool provides an immediate idea in terms of the compatibility or incompatibility of two substances thanks to the pictograms, precautionary statements and hazard classes. The label must include the following information in the language of the country of use: the name of the substance, address and telephone number of the manufacturer, distributor or importer; the hazard symbol(s) (proposed in CLP regulation); hazard classes and category; precautionary advice; the international CAS identification number of the substance and the CE hazard nine-digit number.

2.1.1 Safety Data Sheets (SDS)

An SDS is a document containing information about physical-chemical data, the risks presented under different conditions of employment as well as the employment and prevention precautionary measures to be implemented on chemicals. An SDS document provides the necessary knowledge for the protection of worker's health, safety and the protection of the environment, and the measure of protection to take in case of an emergency. CLP and REACH regulations require that importers and sellers must provide users with a safety data sheet ²⁴ on the hazardous chemical, written in French. The Safety Data Sheets are more exhaustive and more flexible than the labelling on the package of chemicals: SDS is a communication tool which enables manufacturers, importers, distributors and the final users to ensure the safe use of the substance or the mixture, to manage the assessment of the risks, to inform the staff about the risks and dangers and to train them in the correct and safe use of the product taking the right collective and individual measures. SDS contains 16 headings information related to the safe use of the product:

1. identification of the substance/preparation of the company



- 2. hazard identification,
- 3. composition/information on components,
- 4. first aid,
- 5. fire-fighting measures,
- 6. measures to be taken in the event of accidental dispersion,
- 7. handling and storage,
- 8. exposure controls/personal protection,
- 9. physical and chemical properties,
- 10. stability and reactivity,
- 11. toxicological information,
- 12. ecological information,
- 13. disposal considerations,
- 14. transport information,
- 15. regulatory information,
- 16. other information.

In the SDS of ammonium nitrate proposed in Table 2 below,²⁵ it is specified that AN is a reactive hazard substance, an oxidizer that in contact with combustible/organic material may cause fire, it presents many incompatibilities such as strong oxidizing agents, strong reducing agents, strong acids and powdered materials. It should be avoided the exposition to heat and combustible material. To complete the information contained in the SDS, other tools for predicting hazards due to chemical incompatibilities exist, i.e. the incompatibility tables and software that have appeared more recently.



10. Stability and reactivity				
Reactive Hazard	Yes			
Stability	Oxidizer: Contact with combustible/organic material may cause fire. Hygroscopic.			
Conditions to Avoid	Incompatible products. Excess heat. Combustible material. Avoid dust formation. Exposure to moist air or water.			
Incompatible Materials	Strong oxidizing agents, Strong reducing agents, Strong acids, Powdered metals, Combustible material			
Hazardous Decomposition Products Nitrogen oxides (NOx), Ammonia				
Hazardous Polymerization	Hazardous polymerization does not occur.			
Hazardous Reactions	None under normal processing.			

Table 2. Section 10 of the SDS for ammonium nitrate prepared by ThermoFisher Scientific²⁵

2.1.2 Chemical incompatibility tables

Tables dedicated to chemical incompatibility and compatibility phenomena are very useful tools widely applied by academic laboratories and by industries. Their function is to identify the compatibility between two substances or between a substance and the material of its container.²⁶ An example of this kind of tables are the double-entry tables, represented in Figure 6 and 7, where only two substances can be crossed at the same time. The danger related to the generated incompatibility can be shown by pictograms. Thanks to these tables, it is possible to have easy access to a variety of information such as if two products can be stored together if they can be mixed or simply if they are compatible. Each cell represents two substances coming into contact and generating different kinds of hazard due to the incompatibility that can be produced by the encounter of two substances. Here are reported four different types of danger: oxidizing, harmful, flammable and toxic.

		4	ser -	X
1	+	-	-	+
0	-	+	-	0
See.	-	-	+	+
X	+	0	+	+

Figure 6. Example of incompatibility table.²⁷

	**	*				
()	+	×	×	×	×	+
03	×	+	×	×	×	•
	×	×	+	×	×	×
A	×	×	×	•	×	×
	×	×	×	×	+	+
	+	•	×	×	+	+

Figure 7. Example of incompatibility table.²⁸

However, these tables do not provide complete information on incompatibilities. The ADR recommendation proposed another type of table based on the segregation system in which some entries more complicated are presented. This table has been developed to meet the requirements for the transport of dangerous goods. This table is based on the segregation recommended by the ADR (Transport of Dangerous Goods by Road)²⁹ regulation, which defines the rules for the transport of dangerous goods by road. This table, presented in Annexe I, contains as entries, six of the nine classes defined in the ADR and a large amount of fairly precise information in the cells within the matrix. In this table are included recommendations on compatible products ("Separation may not be necessary") or not ("Segregate from") for their storage, minimum safety distances to be maintained ("Keep apart") and also an exclusive legend for organic peroxides ("Isolate"). Even if this is an improvement, the information provided is not yet sufficient and rather limited because, in some cases. Indeed, different substances listed as compatible, depending on their main hazard, may react together due to their secondary hazard. Incompatibilities tables have the advantage of being immediate and easy to understand for workers who handle chemicals, but for complex cases such as multiple products, they are not predictive of danger. The incompatibilities tables have been proposed with the intention to generalize and simplify the reactivity of a large range of substances. Each kind of table emphasizes a different type of hazard. However, different versions of incompatibility tables exist which are not always consistent with each other, and that may lead workers into error. This depends on the fact that each chemical owns several hazardous properties that are not all taken into account at the same moment in a table. Another problem that is difficult to manage is the so-called "secondary danger" that occurs between substances that are normally compatible and do not present a real danger. The secondary danger is never put in evidence in the tables of incompatibility, which therefore represent a valid tool but, in some cases, too simplistic. For this purpose, software-type tools have been developed to compile more information. The next step in chemical hazard and risk management was the invention of software that would provide more exhaustive and extensive information on substances, especially with regard to their compatibility or incompatibility with other chemicals.

2.2 The software

Computer software is a powerful and very useful instrument in risk management. The panorama is vast and includes freeware and commercial software. Generally, they present all the same way of utilization: to enter a chemical compound of interest in the database; it is necessary to specify the CAS number, the chemical name and formula. This allows to select the substance and to have access to the specific table of incompatibility in which are specified the following information: physico-chemical data, as well as information on the reactivity between the two substances involved and the expected effects (compatible,
incompatible, corrosive, explosive, flammable, gas generation, heat generation, intense or potentially dangerous, toxic. The knowledge contained in the software are taken from different sources, such as books on the risks of chemical reactivity ³⁰, datasheets from the safety of each product, and collected by the results of experimental tests and industrial chemistry encyclopedias.^{3,10}

The most known and used software are:

1) CAMEO Chemicals (Computer-Aided Management of Emergency Operations)³¹

2) WISER (Wireless Information System for Emergency Responders)³²

3) Chemical Reactivity Worksheet³³

CAMEO is a freeware software developed and released in 1986 by the Office of Emergency Management of Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA). The information that we can get from its utilization is the risk associated with a specific substance. CAMEO presents a dynamic view of incompatibility. Other softwares, such as WISER (Wireless Information System for Emergency Responders) and Chemical Reactivity Worksheet exist, but they are not yet ready to become the tools of excellence in risk prevention and control. The cause is that the information provided is limited to a number of chemicals registered in the respective databases. Most importantly, this software does not consider environmental conditions, such as dilution, humidity and temperature. In recent years the NOAA Chemical Reactivity Worksheet has gone towards improvements: the 26th March 2016 the ameliorated version 4.0 was introduced. For WISER software, the version 5.4 was released the 24th May 2019. Right now, a detailed bibliography is available and some other small improvements. Regardless of the specific characteristics of each software, their limits are linked to the impossibility to understand the phenomena related to an incompatibility mechanism of the reaction. Other tools can be used to collect more detailed and refined information about the phenome that is the cause of unexpected reactions, such as the experimental tools.

2.3 Experimental tools

Calorimetric tests are valid tools to study the thermal decomposition of single substances, binary mixtures or of a mélange of substances.³⁴⁻³⁵ Examples of different type of calorimetric instruments are:

1) DSC (Differential Scanning Calorimetry)

2) DTA (Differential Thermal Analysis)



3) Isothermal calorimetry C80

DSC is widely used in the search for information such as melting temperature, decomposition temperature, polymorphic transitions, co-presence of crystalline phases, reaction temperatures and degree of reaction etc..36,37 It allows to obtain both thermodynamic and thermo-kinetic data of the substances under examination. Through the DSC, it is possible to measure the heat absorbed or released by a sample when it is heated or cooled. The information provided, both qualitative and quantitative and relating to endothermic and exothermic processes, is obtained by scanning the variations of the heat of the sample under examination over a range of temperatures. These measurements are all carried out by comparing the heat flows absorbed or released by the sample with a reference. From a practical point of view, the sample to be analyzed and the reference are subjected to a linear temperature ramp, where the fixed heating rate is set by the operator according to the requirements of the experiment. Throughout the operation, sample and reference are kept at the same temperature. When a sample undergoes endothermic phenomena, the heat provided to keep it in isothermal is greater. On the contrary, if a sample undergoes exothermic phenomena, the heat supplied is lower. The differential measurement of the system is fundamental because it allows receiving at the output the proper behaviour of the material. When the interest is in decomposition reactions, some thermograms allows reading the Tonset temperature and the amount of heat released during the decomposition reaction, which provides a quick overview of the behaviour of the substance of interest. The Tonset is ideally the temperature at which the decomposition starts. In this case, the DSC's thermogram of pure chemical is compared to that of a mixture. The chemical incompatibility is identified if the Tonset of the mixture is lower than the Tonset of pure substances. When the heat released from the mixture is higher than the one of the pure substances, there is an incompatibility. In Figure 8 is given an example illustrating a chemical incompatibility between two substances in DSC thermograms. Substance A undergoes to decomposition at 310°C, releasing heat of -1570 J/g. Substance B decomposes at 310°C, releasing an exothermic peak of -250 J/g. The mixture of substance A and substance B decomposes at about 125°C, releasing the energy of -2600 J/g. The greater limitation of DSC is the impossibility to detach the mechanism of reaction behind an incompatibility due to a possible promoter of ammonium nitrate decomposition, or a stabilizing effect due to AN's inhibitor.





Figure 8. Chemical incompatibility between substances A and B obtained by DSC. Tests carried out at INERIS.

2.4 Theoretical tools

The tools described in the previous paragraphs used in the prediction and management of chemical risk do not provide an exhaustive analysis of incompatibility phenomena. They focus only on describing the consequences and precautions to be taken in case of danger but do not provide information on the chemical origins of the problem. In this context, the study of chemical reactivity by molecular modelling represents a solution to go deeper into the description of the causes at the base of chemical compatibility or incompatibility. The theoretical approach applied to issues related to industrial risk has already proved to be a promising tool for this type of analysis^{38–40} by showing satisfactory results. More recently, a theoretical study has been applied to understand the behaviour of pure ammonium nitrate¹⁵ and its reactivity with other substances. In the following paragraphs, the theoretical studies previously carried out on AN are briefly summarized.



2.4.1 Decomposition of pure ammonium nitrate

The decomposition mechanism of the pure ammonium nitrate in the gas phase was studied in detail with the identification of five reaction channels. In the first step, ammonium nitrate decomposes into ammonia and nitric acid ($\Delta G \neq = 4.9$ kcal/mol). Then HNO₃ decomposes into radicals NO₂[•] and OH[•] with an energy barrier of 40.2 kcal/mol, and this represents the rate limiting step of the decomposition of AN.¹⁵ This barrier is not so easy to be overcome, and this could explain why ammonium nitrate is stable at standard conditions.

2.4.2 Chemical Incompatibility between ammonium nitrate and the sodium salt of dichloroisocyanuric acid

The interaction of AN and the sodium salt of dichloroisocyanuric acid (SDIC) was studied due to the possible implication of these molecules in the accident happened in Toulouse in September 2001.⁴¹ The chemicals generated by this mixture have been investigated with the use of techniques such as MS, DSC, FTIR, TG, and the final products identified were: N₂, NO, HCl, NO₂, Cl₂, H₂O, CO₂, N₂O, and NCl₃.^{42,43} After a theoretical study on this system, it has been estimated that the interaction between SDIC and ammonia leads to the formation of the salt of monochloroisocyanuric acid (SMIC) and a monochloroamine (NH₂Cl), passing through a transition state, TS_{SDIC+NH³}, of 58.0 kcal/mol (Figure 9).⁴⁴ Monochloroamine (NH₂Cl) can go under decomposition following two different paths of reaction, namely A and B. In path A, the monochloroamine reacts with the hydroxyl radical (OH'), generated from the decomposition of nitric acid HNO₃, forming hydroxylamine (NH₂OH) and Cl[•] (chlorine radical).⁴⁴ Cl[•] reacts with amidogen radical NH₂[•] (amidogen radical), to form monochloroamine, hypochlorous acid, and a chlorine molecule.⁴⁴ The relative Gibbs free energies of these chemicals are very exothermic, and respectively -53.1, -46.6, and -49.4 kcal/mol. Hydroxylamine isomerizes, and after the elimination of hydrogen, it leads to the formation of molecular hydrogen and the HNO• (nitroxyl radical). Looking at pathway B, NH₂Cl reacts with the NO₂, generated by the decomposition of HNO₃, to form the NH₂NO₂ (nitramide) and another chlorine radical.⁴⁴ NH₂NO₂ decomposes in N₂O, N₂, and O₂ while chlorine radical continues to react in the environment of reaction.⁴⁴ Pathway A and B gives both the production hypochlorous acid, a reaction between the hypochlorous acid (HClO) and the monochloroamine was characterized, forming a molecule of dichloramine (NHCl₂) and water.⁴⁴ NHCl₂ can react with another molecule of hypochlorous acid molecule leading to trichloramine (NCl₃) and water.⁴⁴ The complete mechanism of reaction allows the identification of the direct mechanism of AN with SDIC and justifying the formation of the observed products (Cl₂, H₂O, HCl, N₂, N₂O, NO, NO₂).⁴⁴ The rate-determining step for the proposed mechanism of the reaction is the transition state TS_{SDIC+NH3}, of 58.0 kcal/mol.⁴⁴ A scheme about this mechanism is presented in Figure 11.



Figure 9. Decomposition of ammonium nitrate (blue), and in the presence of SDIC salt (red).⁴⁴



Figure 10. Effect of a water molecule on the reaction barrier between NH₃...SDIC salt.⁴⁴

Including the effect of the presence of water the reaction barrier decreases of 25.9 kcal/mol (from 58.0 to 32.1 kcal/mol) because water catalyzes the transfer of the hydrogen atom between SDIC and NH₃ in the transition state (See Figure 10). ⁴⁴ The water molecule is regenerated at the end of the reaction so that a real catalytic effect is observed.⁴⁴ These results indicate that in presence of a water molecule, the reaction between AN and SDIC becomes competitive with the decomposition of pure AN, the difference being 8.1 kcal/mol (32.1 vs 40.2 kcal/mol, respectively).⁴⁴ Therefore, it could be hypothesized that the presence of water, even in small quantities, could ignite the incompatibility reaction between AN and SDIC.



Figure 11. Scheme reaction mechanism between AN and SDIC salt.⁴⁴



2.4.3 Ammonium nitrate reactivity in the presence of other two sodium salts (NaNO₂ and NaNO₃)

For these cases of study, the identification of the reaction mechanism between AN+NaNO₂ and AN+NaNO₃ was essentially focused on the rate-determining step: the direct reaction between the products of the first decomposition of ammonium nitrate (NH₃ or HNO₃) and contaminants. ^{,45} As shared before, AN decomposes into nitric acid and ammonia, passing through a slightly endothermic step ($\Delta G = 4.9$ kcal/mol). For NaNO₂ and NaNO₃, were considered for both the reaction with NH₃ and HNO₃ previously formed in the environment.⁴⁵ It has been evidenced that NaNO₂ reacts with HNO₃ in a more favorable way, leading to NaOH and two molecules of NO₂, as shared in reaction 6. A transition state has been identified, with a relative Gibbs free energy of 44.1 kcal/mol.⁴⁵

(6) $NaNO_2 + HNO_3 \rightarrow NaOH + 2 NO_2$

The energy barrier for previous transition state is higher than the decomposition of AN (44.1 vs 40.2 kcal/mol), excluding an incompatibility between the substances.⁴⁵ In the case of NaNO₂ and ammonium nitrate, it is HNO₃ that plays a key role in the interaction with ammonium nitrate.⁴⁵ Also in the case of the reaction between NaNO₃ and NH₄NO₃, the reaction with nitric acid is favored than the reaction involving ammonia.⁴⁵ Here, the resulting products are sodium hydroxide (NaOH) and a dinitrogen pentoxide molecule (N₂O₅), passing through a transition state with an energy barrier of 50.7 kcal/mol, as shared in reaction 7.⁴⁵

(7)
$$NaNO_3 + HNO_3 \rightarrow NaOH + N_2O_5$$

Comparing the energies obtained for the decomposition of pure ammonium nitrate ($\Delta G = 40.2 \text{ kcal/mol}$) with the ones obtained for the reaction between ammonium nitrate and sodium nitrate ($\Delta G \neq = 50.7 \text{ kcal/mol}$), the study confirms experimental data: no incompatibility exists between the two chemicals.⁴⁵ But, it must be taken into account that AN, NaNO₂ and NaNO₃ are very hygroscopic salts and, as seen in the previous case between AN and SDIC, the role of water has been taken into account.⁴⁵ A molecule of H₂O was introduced in the reaction environment, to reproduce the experimental conditions to better understand the reactivity of AN in the presence of sodium salts and nitric acid. In the case of sodium nitrite, the presence of a molecule of H₂O, in the geometry of the transition state, causes a decrease in the activation barrier for the reaction of 7.4 kcal/mol that makes the reaction between the ammonium nitrate and sodium nitrite ($\Delta G \neq = 36.7 \text{ kcal/mol}$) competitive in comparison to the decomposition of the pure ammonium nitrate ($\Delta G = 40.2 \text{ kcal/mol}$).⁴⁵ This result, in agreement with experimental data, demonstrated the possibility of an incompatibility between the AN-NaNO₂.⁴⁵ For NaNO₃, when a water molecule is present in the environment of reaction, it modifies the geometry of transition state (TS_{NaNO3+HNO3}), with a decrement in the value of the activation barrier of the reaction of 9 kcal/mol: this is not a sufficient gap able to justify an incompatibility between the two substances, even in the presence of humidity.⁴⁵ The energy barrier is higher ($\Delta G \neq = 41.7$)

kcal/mol) than the barrier associated with decomposition energy of pure ammonium nitrate ($\Delta G = 40.2$ kcal/mol). An energy diagram, summarizing the reactions of two salts is shown in Figure 12.



Figure 12. Left: interaction of NaNO₂ and NaNO₃ in the presence of HNO₃ with or without water molecule. Right: CERL calorimetric results.

These examples demonstrate the capability of the theoretical approach, specifically the DFT method, to predict the reactivity of substances placed in contact with ammonium nitrate. The same approach has been applied to new systems presented in this thesis work, in order to better understand the reactivity of AN, studying its reaction in presence of a number of substances chosen after a deep bibliographic work.

3. The effect of additives on ammonium nitrate

AN is generally used in formulations mixed with additives or contaminants. Additives can be added to improve the efficiency of AN formulation in fertilizers, on the contrary contaminants are used to ameliorate the explosion effect in explosive applications. Some additives are also used as stabilizer (like carbonates, sulfates, phosphate of sodium, potassium, calcium) to avoid the decomposition during transport and storage. Moreover, AN's formulations could be also accidentally subjected to contamination by impurities. These contaminants can lower the thermal stability of AN and promote auto-ignitions and explosions, caused by their catalytic effects on the decomposition of AN. Many experimental studies have been conducted on a wide range of substance, with the aim was to clarify the behavior of ammonium nitrate in the presence of different kind of substances. The need to understand in advance the behavior of substances derives from the

large number of accidents caused by the not always appropriate composition of AN's formulations. Today, there is a new tendency to classify the substances that can enter in contact with AN, into three categories: promoters, inhibitors, and inerts of ammonium nitrate decomposition. Zhe Han⁴⁶ defined a promoter as a species that generally reduces the thermal stability of ammonium nitrate. This effect can be observed indeed as a negative variation of the decomposition temperature with respect to the decomposition temperature of ammonium nitrate. Inhibitors,⁴⁶ on the other hand, are substances that thermally stabilize ammonium nitrate, causing at least an increase in decomposition temperature when added to AN. Finally, inerts produce only a dilution effect that do not alter the thermal stability of AN.⁴⁶ When a promoter destabilizes ammonium nitrate, it could lead to chemical incompatibility. In this case, three types of scenario are possible^{6,47}

1) a decomposition with the formation of toxic gases.

- 2) fire due to the oxidant characteristic of ammonium nitrate
- 3) detonation, deflagration, and explosion.

In the next section of the paragraph, the effects of inorganic and organic additives and contaminants placed in contact with AN is reported.

3.1 Examples of inorganic promoters of AN decomposition

Inorganic promoters are numerous among AN's contaminants. Inside this category are present various types of chemicals such as halide salts,¹⁶ sulfates and nitrates of chromium, iron, copper, aluminum, barium and inorganic acid such as HCl and H₂SO₄.⁴⁸,⁴⁹ DSC and RSST experiments conducted on a large series of contaminants clearly demonstrated the destabilizing effect of these incompatible contaminants given by lowering the decomposition temperature (Tmax and Tonset) of the neat ammonium nitrate.^{46,50} Example sof promoters are chlorine salts such as KCl, NH₄Cl, CaCl₂, NaCl, FeCl₂, PbCl₂, NiCl₂, AlCl₃ Calorimetric data show that the Tmax (maximal temperature of the decomposition) obtained from a DSC experiment for pure ammonium nitrate is around 326 °C.¹⁶ Adding to AN a 5% wt of various chlorine salts, it leads in the case of NaCl to a Tmax equal to 262°C, for KCl Tmax it assumes a value of 256°C.¹⁶ With NH₄Cl at 5% wt, the maximum decomposition temperature of the mixture drops to a value equal to 257°C.¹⁶ In the case of CaCl₂ the value of Tmax, under the same experimental conditions, is equal to 261°C.¹⁶ These calorimetric values demonstrate the promoter and destabilizing effect of CaCl₂, NaCl, KCl and NH₄Cl in contact with pure ammonium nitrate. Another example of promoters of AN decomposition are chromium, aluminum, copper, iron nitrates (Cr₁(NO₃)₃, Cu(NO₃)₃, Al(NO₃)₃, Fe(NO₃)₃) and chromium, aluminum, iron, copper and barium sulfates (Cr₂(SO₄)₃, Al₂(SO₄)₃, FeSO₄, Fe₂(SO₄)₃, CuSO₄, BaSO₄). Through the results of other DSC

calorimetric test, it has been analyzed the effect on AN of the promoters listed above, ever adding a quantity equal to 5% wt of incompatible substances. The temperature of decomposition taken into account was the Tonset measured at 10% of the decomposition of the sample of the mixture under examination. Considering that in these DSC experiments the Tonset of pure ammonium nitrate was equal to 289°C, adding 5% of these promoters the following values have been obtained: 251°C, 258°C, 262°C, 280°C in the case of Cr(NO₃)₃, Fe(NO₃)₃, Al(NO₃)₃, Cu(NO₃)₂.⁴⁸ On the other hand, for Cr₂(SO₄)₃, Fe₂(SO₄)₃, FeSO₄, Al₂(SO₄)₃, CuSO₄, BaSO₄ added always in quantities equal to 5% wt, the Tonset measured result be equal to 263°C, 274°C, 271°C, 274°C, 277°C, 286°C. The table 3 below summarizes of the main classes of inorganic promoters of ammonium nitrate decomposition.

Metallic Substances ³⁰	Chloride Salts ^{16,47,48}	Nitrates ⁴⁸	Sulfates ⁴⁸
Aluminum, antimony,	KCl, NH ₄ Cl, CaCl ₂ ,	Chromium(III),	Chromium(III),
chromium, cobalt,	NiCl ₂ , AlCl ₃	Copper(II), Iron (III)	Iron(III), Copper(II),
iron, lead, magnesium,			Barium (II)
titanium,			Pyrite: FeS ^{47,48}
Inorganic Acid ⁴⁹	Cations ^{30,47,48}	Sodium Hyponitrite ³⁰	Sodium nitrite ^{16,30}
HCl, H ₂ SO ₄	Co ²⁺ /Co ³⁺ , Cu ⁺ /Cu ²⁺ Al ³⁺ , Cr ³⁺ , Fe ³⁺	Na ₂ N ₂ O ₂	NaNO ₂

Table 3: Examples of inorganic promoters of AN's decomposition

3.2 Examples of inorganic inerts of AN decomposition

For NaNO₃, Ca(NO₃)₂ and KNO₃, some calorimetry experiments show that these substances did not influence the temperature of decomposition of AN, even if they are added in a quantity higher that 10% wt, and most important by adding increasing amounts of substance, the decomposition temperature is not affected by it.¹⁶ Chemicals that do not influence the thermal behavior of AN, are defined as inerts.¹⁶ They are compatible substances with respect to ammonium nitrate, and their stabilizing power becomes evident looking at the heat generated during the decomposition process, that is inferior rather than the heat released

during the decomposition of pure AN. Adding a quantity equal to 5% wt of NaNO₃, KNO₃ and Ca(NO₃)₂, the decomposition temperature (expressed as Tmax) for AN passes from 326° C to 328° for NaNO₃, 326° C for KNO₃ and 330° C for Ca(NO₃)₂.¹⁶ Otherwise, the literature reports a possible incompatibility between potassium nitrate and AN, due to the strong oxidative character of KNO₃. ^{47,30}

3.3 Examples of inorganic inhibitors of AN decomposition

According to different studies, it has been noticed that most of the oxyanions $(A_xO_y^{2^*})$ raised the temperature of the AN exotherm.^{16,51-52}. The anions SO₄²⁻, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, CO₃²⁻, and HCO₃⁻ are conjugate bases of weak acids and can be protonated. The carbonate anion CO₃²⁻ is especially basic and in the presence of ammonium nitrate, it can generate carbonic acid, which decomposes spontaneously into water and carbon dioxide gas. In contrast, HSO₄⁻ is a weak base. Rubtsov et al.^{53,51} also observed that salts that having anions more basic than nitrate caused a marked reduction in the decomposition rate. Solutions containing the most basic anions (CO₃²⁻, HCO₃⁻ and HPO₄⁻) yielded pH values in the range of 7.4–8.3. These species, when added to AN, are able to stabilize it, producing an exothermic peak 40–60 °C higher than the one of neat AN¹⁶. Additives producing pH values in the range 4–5 such as SO₄²⁻ and H₂PO₄⁻ only raised the maximum by 10–20 °C when included with AN¹⁶ at the 20 wt.%. Bisulfate (HSO₄²⁻) produces strongly acidic aqueous solutions¹⁶ and does not lower the temperature of the AN exotherm at a small concentration (5% wt). At higher concentration (>5% wt) it does.¹⁶

Most of the anion additives were examined in the presence of several different counter ions. It seems that varying the cation (Na⁺, K⁺, NH₄⁺, and Ca₂⁺) does not significantly affect the position of the exotherm or the rate constant.¹⁶ It was already known that that ammonium ion is not entirely innocuous due to its acidity.⁵⁴ Its destabilizing effect is not evident all the time when it is associated with a basic anion, but at certain concentration, as for the case of (NH₄)₂SO₄, the presence of NH₄⁺ could lead to an incompatibility reaction with AN.^{48,55,56}

Most of the additives shifted the exothermal peak of AN proportionally with the added concentration of salt. However, this was not the case with CaSO₄ and CaHPO₄ for which increasing amounts of the two salts; they showed no further increase of the decomposition temperature. The interpretation of the results is that these salts do not have an inhibitor effect on AN, but they behave more as inerts.¹⁶ Figure 13 shows the stabilizing effect of various salts compatible with AN (inhibitors and inerts) expressed as Tmax, depending on their pH.

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Figure 13: Oxyanions's pH versus Tmax decomposition temperature of AN placed in contact with compatible substances (inorganic inerts and inhibitors), data extracted by the Oxley's article (2002).¹⁶

3.4 Substances difficult to classify

Ammonium sulfate, as reported in the precedent paragraph, has a not totally clear behavior. In fact, it has been involved in the year 1921 in a major accident happened in Germany, in the village of Oppau, where $(NH_4)_2SO_4$ was co-crystallized with AN in a 1:1 formulation. Until today, no study has investigated the mechanisms of reactions of mixtures with ammonium nitrate and the possible incompatibility is therefore not yet fully explained. It is known that the addition of $(NH_4)_2SO_4$ affects the phase IV-III transition of ammonium nitrate and that the cation NH_4^+ in presence of oxygen has the capability to be oxidized.^{56,57}

Oxides of iron, copper, cadmium, lead, nickel, and zinc exhibit behavior that is not entirely clear. Some sources report that they are promoters of AN decomposition³⁰, but some calorimetric experiments show that these cations in the form of oxides appear a stabilizer effect on ammonium nitrate.⁴⁸ The basicity of these

compounds could have a stabilizing effect on AN, but at the same time the possibility of these cation to be subjected to oxidation/reduction cycles do not make them completely safe substances.⁴⁸

The behavior of fluorides is controversial too. As it appears in some DSC tests,¹⁶ that KF is capable of stabilizing ammonium nitrate: AN in mixture with KF would have a decomposition temperature higher than the decomposition temperature of pure AN. As there are no other data on this subject, the reactivity of fluorides in the presence of ammonium nitrate still needs to be clarified.

3.5 Effect of organic substances on AN

Energetic organic molecules such as trinitrotoluene (TNT) are promoters of ammonium nitrate decomposition. Organic explosive mixtures require special attention because, depending on the ratio between the components, their sensitivity to impact may increase in such unexpected way. When ammonium nitrate is added to TNT to form amatol, the impact sensitivity of the mixture becomes much higher compared to one of TNT alone.⁵⁸ Complex nitroarens (2,4,6-trinitroaniline, 1,3,5triaminotrinitrobenzene or orthonitrotoluene and ortho-nitroaniline) also catalysis the AN decomposition reaction at 270° C. A possible explanation is the production of nitrogen dioxide (NO₂) and nitrous acid (HONO) during the decomposition of nitroaren. These products destabilize AN.⁵⁹ Among the organic molecules sensitive to contact with ammonium nitrate is also the carbohydrates. This molecule shows to be an ideal candidate as an alternative fuel for explosives based on ammonium nitrate (ANCHO). The use of sugar for the production of explosives is not permitted. However, it has not been exploited due to of their high cost of sugar and the large quantity required. Besides, the detonation rate of an ANCHO explosive is lower (2300 m/s) than that of an ANFO explosive (31500 m/s). In the case of mineral oils (paraffin), ammonium nitrate mixture decomposes, in fact, with an energy lower than that of pure ammonium nitrate.⁵⁴ Ammonium nitrate mixtures -mineral oils, analyzed by DSC, show two exothermic regions: a peak (292°C) at a temperature lower than that of pure ammonium nitrate (304°C) and a doublet at 356°C - 387°C. However, it has also been observed that this behavior depends on the mineral oil concentration.¹⁶ An increase in the oil content raises the temperature of the first exothermic peak without shifting the second peak. Urea $(CO(NH_2)_2)$ is one of the incompatibilities of ammonium nitrate and the main reason of this incompatibility is due to hygroscopicity of this compound.^{30,60} The absorption of atmospheric or internal water from the solid can lead to undesirable consequences.

Among organic substances there are also some inhibitor of ammonium nitrate thermal decomposition, i.e. the oxalate, formate, and acetate salts added to AN at the 10 mol% level, substantially raised the pH (5.9–6.3 pH units) and the temperature of the DSC exotherm. Both the ammonium acetate, potassium acetate,

and ammonium formate increase the hygroscopicity of AN. Oxalate salts increase the stability of AN, but there is some concern about its toxicity.⁶¹ HMTA and guanidinium carbonate also stabilize AN, but the stabilizing effect of HMTD appears to disappear at 320 °C.

3.6 Synthesis about AN's additives and contaminants

All the information presented in the literature about ammonium nitrate's additives and contaminants are numerous and sometimes contradictory data are presented. This does not allow to have a clear and concise view of the real knowledge available on AN and its reactivity in the presence of different types of additives and contaminants. For this reason, it has been thought to synthesize the knowledge on AN in a schematic way. Figure 14 shows a simple scheme about the substances that may come into contact with AN, that are essentially inorganic or organic compounds. However, while a limited number of studies on AN reactivity when it is placed in contact with organic substances, there is a much greater amount of information concerning inorganic substances. It's for that, that it was believed necessary to resume the data in literature schematically, especially for inorganic contaminants and additives.

Figure 14 shows that it is possible to divide inorganic substances into promoters (colored red), inhibitors (green), inerts (blue), and finally there is a fourth category of substances representing composites which is difficult to classify because there is not enough experimental data or because the existing experimental data are inconsistent. In Table 6, a summary table of the effects of all inorganic salts and oxides, which has been discussed in paragraphs 3, are reported. This table is easy to read: each cell represents a hypothetical salt given by the crossing of the cation (columns) or anion (rows). The last column to the right is dedicated to some oxides. Only the colored cells represent substances for which tests have been carried out in the presence of AN. For hypothetical inorganic salts found in empty or white cells there is no experimental data about the reactivity of ammonium nitrate in their presence. By simply looking at this table it is possible to trace the effect that each inorganic contaminant or additive exerts on AN by referring to the color of its cell.





Figure 14. Summary diagram of the different types of compounds that can be brought into contact with AN





Table 4. Effect of certain known inorganic compounds on AN

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4 Objective of the thesis

AN has been involved in numerus major accidents during the last century. For this reason, is extremely important extend the knowledge about the interaction mechanisms of ammonium nitrate with contaminants and additives. This thesis has the aim to investigate the AN's reactivity with a certain number of chemicals, which can be grouped into three categories: promoters, inhibitors, and inerts. The aim of this study is to identify a possible common reaction pathway inside of each category to finally build a predictive tool able to determine if a contaminant may involve a chemical incompatibility with AN or not, with the help of computational chemistry approach. AN is incompatible with a wide range of substance. Besides, the identification and the prevention of incompatibility problems represent an important safety challenge in industrial context. The control of chemical risk in the industrial environment requires a quick and accurate screening. Currently, this information is mostly provided by Differential Scanning Calorimetry tests (DSC). The limitation of this approach relies on the fact that it is not possible to identify and understand the detailed mechanism involved in the reactions between two or more substances. The collaboration between INERIS et Chimie ParisTech has leaded to the development of a molecular modeling approach to complete and improve experimental knowledge about chemical incompatibilities with ammonium nitrate. The previous theoretical works were based on Density Functional Theory (DFT) calculations, and they were intended to provide information in terms of energetics and products formed by interaction between ammonium nitrate and some AN's contaminants (SDIC salt, NaNO₂ and NaNO₃). The previous computational studies helped to face some difficulties by clarifying the reaction mechanisms of the previous chemicals when they interacted with AN.

The thesis work presented today, aims to extent the use of this computational chemistry approach and to investigate and predict the effect of the different types of AN's additives and contaminants that can be found in AN's formulations. To reach this goal, new contaminants were studied for a possible future development of a simplified tool able to predict the behaviors of contaminants and additives in AN's formulations. The aim of this thesis is to extend the theoretical knowledge about ammonium nitrate reactivity, starting from the analysis of these substances:

- AN and CaCO3
- AN and CaSO₄
- AN and (NH₄)₂SO₄
- $AN + KCl/CaCl_2$



- AN + various oxyanion salts

The goal was to detach for each additive its own behavior, trying to distinguish among them a promoter behavior from an inhibitor and an inert behavior when placed in contact of ammonium nitrate. In general, thanks to the versatility of DFT methodology, it could be possible associate a theoretical descriptor to the type of reaction that a contaminant or an additive performs practice on AN. This approach has been searched, in order to build a simplified predictive tool able to determine if a substance could be identified as a promoter, inhibitors or an inert of AN decomposition.

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CHAPTER 2

Theoretical Methods



This chapter is devoted to the description of the theoretical methods used in this thesis work. The first part will cover the basics of theoretical chemistry and Hartree-Fock theory. The second part will be devoted to the description of the density functional theory (DFT).

1. The electronic problem and the Schrödinger equation

The laws of classical mechanics can explain the description of macroscopic objects. However, they do not describe the behavior of particles such as electrons. The behavior of these particles can only be described by the laws of quantum mechanics, which is based on the wave properties of matter and in particular on the Schrödinger equation, which, in a non-relativistic and time-independent form, takes the form of an eigenvalue equation:

(1)
$$\widehat{H}\Psi = E\Psi$$

 \hat{H} represents the Hamiltonian operator, Ψ the wave function and E the energy associated with the system. Solving the Schrödinger equation means finding the eigenvalue E and the corresponding wavefunction Ψ . The molecular Hamiltonian operator presents this form:

$$(2) \qquad \widehat{\mathbf{H}} = -\sum_{i} \frac{1}{2} \nabla_{i}^{2} - \sum_{k} \frac{1}{2} \nabla_{k}^{2} - \sum_{i} \sum_{k} \frac{Z_{k}}{r_{ik}} + \sum_{i} \sum_{i < j} \frac{1}{r_{ij}} + \sum_{k} \sum_{k < l} \frac{Z_{k} Z_{l}}{r_{kl}}$$

Where the indexes i and j are referred to as electrons, k, and l to nuclei. The first and second terms ∇_i^2 and ∇_k^2 describe the kinetic energy of electrons and nuclei. The remaining terms are, in order: a Coulombian electron-core attraction term to which follows a core-core repulsion term and finally an electron-electron repulsion term. This equation can only be solved analytically in the case of a hydrogen atom in which there is only one electron. On the other hand, when an electron-electron repulsion term (multielectron system) is present, approximations are necessary. All the theoretical details about paragraphs 1.1, 1.2 and 1.3 are present in the references from [1-9].

1.1 The Born-Oppenheimer approximation

The Born-Oppenheimer approximation introduces a separation between the movement of electrons and the movement of nuclei.¹ It was accepted on the basis that nuclei have a mass at least 1836 times greater than the mass of the electron, which moves much faster than the nuclei. In practice, the nuclei perceive the interaction of the electronic cloud, and they move in the average potential generated by it. These significant differences make the electronic cloud follow nuclear motion adiabatically. As a consequence, the motions can be considered decoupled, leading to a separation

of the molecular Hamiltonian into the electronic Hamiltonian \hat{H}_{el} and the nuclear Hamiltonian \hat{H}_{nucl} . Thus, the Hamiltonian, considering this approximation, can be written as follows:

(3)
$$\widehat{H} = \widehat{H}_{el} + \widehat{H}_{nucl}$$

 \hat{H} can be considered as the sum of an operator depending only on the electron coordinates and an operator depending only on the nucleus coordinates. If we develop H_{el} and H_{nucl} we get:

(4)
$$\widehat{H}_{el} = -\sum_{i} \frac{1}{2} \nabla_i^2 - \sum_{i} \sum_{k} \frac{Z_k}{r_{ik}} + \sum_{i} \sum_{i < j} \frac{1}{r_{ij}}$$

(5)
$$\widehat{H}_{nucl} = -\sum_{k} \frac{1}{2} \nabla_k^2 + \sum_{k} \sum_{k < l} \frac{Z_k Z_l}{r_{kl}}$$

 \hat{H}_{nucl} can be considered as a constant value. Now, the following electronic equation should be solved:

(6)
$$\widehat{H}_{el}\Psi = E_{el}\Psi$$

The total energy of the system can be assimilated to electronic energy to which a nuclear electrostatic repulsion contribution can be added:

(7)
$$E_{tot} = E_{el} + \sum_{k} \sum_{k < l} \frac{Z_k Z_l}{r_{kl}}$$

The term nuclear repulsion, the terms related to electron kinetic energy and the electron-nuclear interaction can be calculated in a straightway. The presence of the contribution of electron-electron repulsion does not allow to solve the exact equation for many-electrons systems, and other approximations are necessaries. Different strategies have been developed to solve this equation which can be divided into two main groups: the methods based on the wave function as the Hartree-Fock theory and the methods based on the electron density (Density Functional Theory). These two methods will be presented in sections 2.2 and 2.3.



1.2 The Variational Principle

The Variational Principle permits to obtain the approximated solution of the Schrödinger equation without having to solve it directly. This principle establishes that the energy of a molecular system calculated using a trial wave functions Ψ_i will always be higher than or equal to the real energy E_0 of the fundamental state Ψ_0 :

(8)
$$\langle \Psi_i | \hat{H} | \Psi_i \rangle = E_i \ge E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

The quality of the approximated wave function is assessed according to the energy of the system it describes: the lower the energy, the better the wave function. In practice, it is impossible to try every possible combination of trial wave functions; therefore, it is necessary to select a group of well-behaved functions: for instance, the approximated wave-function should be continuous everywhere and quadratically integrable. One strategy is to take as trial functions the exact solutions to the Schrödinger equation of a solvable problem, as for the hydrogen-like atoms.

1.3 The Hartree approximation

The central problem in Schrödinger equation is that, except for one-electron systems, it cannot be solved analytically due to the simultaneous interactions electron-electron and nucleus-electron. To solve this inconvenient, Hartree's approximation describes the interacting electrons system using a trial reference system in which the electron repulsion is neglected. In this way, electrons are independent of each other. The wave function can be written as the simple product of mono-electronic wave functions ϕ_i :

(9)
$$\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = \phi_1(\vec{x}_1)\phi_2(\vec{x}_2) ... \phi_1(\vec{x}_N)$$

This equation is known as the Hartree product. The functions ϕ_i are called spin-orbital and are decomposed as the product of a space function $\phi(\vec{r})$ by a spin function $\sigma(s)$ ($\sigma = \alpha, \beta$):

(10)
$$\phi(\vec{x}) = \varphi_1(\vec{r})\sigma(s)$$

However, this wave-function does not respect the Pauli principle, as the product (9) is not antisymmetric respect to the exchange of two electrons. Slater proposed to rewrite the Hartree's product in the form of a determinant, then named Slater's determinants:

(11)
$$\Psi_{SD}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_1(\vec{x}_2) & \dots & \phi_1(\vec{x}_N) \\ \phi_2(\vec{x}_1) & \phi_2(\vec{x}_2) & \dots & \phi_2(\vec{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\vec{x}_1) & \phi_N(\vec{x}_2) & \dots & \phi_N(\vec{x}_N) \end{vmatrix}$$

The true N-electrons wave-function is thus approximated by the Slater's determinant. Finding the best approximation to the wave-functions means to minimize the energy of the Slater's determinant. This operation requires to vary the spin-orbitals under the constraint of the orthonormality.

(12)
$$E_{HF} = \min_{\Psi_{SD} \to N} E[\Psi_{SD}]$$

This constraint is maintained by using the formalism of the Lagrange multipliers that will not be presented here. The following development of the expression is detailed and reported in many reference books², here will be presented the resulting equation:

(13)
$$\left[-\frac{1}{2}\Delta_i - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{j=1}^N (\widehat{J_j} - \widehat{K_j})\right]\phi_i = \sum_j \lambda_{ij}\phi_j$$

The λ_{ij} are the Lagrange multipliers, then identified with the spin-orbitals energies ϵ_i . The operator \hat{J} is called the Coulomb operator:

(14)
$$\hat{J}_j(\vec{x}_1) = \int \phi_j(\vec{x}_2) \frac{1}{r_{12}} \phi_j(\vec{x}_2) d\vec{x}_2 = \int |\phi_j(\vec{x}_2)|^2 \frac{1}{r_{12}} d\vec{x}_2$$

In the equation 13, the bi-electronic repulsion is replaced by a mono-electronic potential obtained by averaging the electronic interaction over all the spin and space coordinates of electron 2, weighted by the probability $|\varphi_j(x_2)|^2 dx_2$ of finding electron 2 in the volume dx_2 . The sum on j thus makes it possible to obtain the total average potential acting on electron 1 from the other N-1 electrons. \hat{K} is the exchange operator, which corrects the Coulomb repulsion term by taking into

account the anti-symmetry of the wave-function. It has no classical equivalent and it is defined by its action on the spin-orbital ϕ_i .

(15)
$$\widehat{K}_{j}(\vec{x}_{1})\phi_{i}(\vec{x}_{1}) = \int \phi_{j}^{*}(\vec{x}_{2}) \frac{1}{r12} \phi_{i}(\vec{x}_{2})\phi_{j}(\vec{x}_{1}) d\vec{x}_{2}$$

Equation 13 is thus rewritten in the more straightforward form of an eigenvalue equation called Hartree-Fock equations:

(16)
$$\hat{f}_i \phi_i = \varepsilon_i \phi_i$$

 \hat{f} is called Fock operator, which acts on the i-th electron:

(17)
$$\hat{f}_i = -\frac{1}{2}\Delta_i - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{j=1}^N (\hat{f}_j - \hat{K}_j)$$

The ε_i represent the energies associated with the molecular orbitals defined by the spin-orbitals ϕ_i .

1.3.1 The Roothan-Hall equations

Roothan and Hall proposed a method to solve the Hartree-Fock equations based on molecular orbital theory, which is now widely used.^{8,9} Its interest is that it transforms the Hartree-Fock equations in matrix form, whose resolution is then much easier. In the context of molecular orbital theory, each orbital ϕ_i is written as a linear combination of L atomic orbitals χ_v

(18)
$$\phi_i = \sum_{\nu=1}^L c_{i\nu} \chi_{\nu}$$

This is an approximation since the number of χ_v basis functions is finite, whereas an exact expression of the ϕ_i orbitals would require $L \rightarrow \infty$. Equation 16 then becomes:

(19)
$$\widehat{f}_{l}(\vec{x}_{1}) \sum_{\nu=1}^{n} c_{i\nu} \chi_{\nu}(\vec{x}_{1}) = \varepsilon_{i} \sum_{\nu=1}^{n} c_{i\nu} \chi_{\nu}(\vec{x}_{1})$$

By multiplying on the left by χ_{μ^*} , and introducing the matrix elements

(20)
$$S_{\mu\nu} = \int \chi_{\mu}^*(\vec{x}_1) \chi_{\nu}(\vec{x}_1) \, d\vec{x}_1$$

(21)
$$F_{\mu\nu} = \int \chi_{\mu}^*(\vec{x}_1) \widehat{f}(\vec{x}_1) \chi_{\nu}(\vec{x}_1) d\vec{x}_1$$

we finally get the Roothan-Hall equations:

(22)
$$\sum_{v} F_{\mu v} C_{vi} = \varepsilon_i \sum_{v} S_{v\mu} C_{vi}$$

or more simply in matrix form:

$$(23) FC = SCE$$

C is the matrix of the coefficients c_{iv} and E the matrix of the orbital energies. By orthogonalizing the atomic base functions, we can reach the eigenvalue equation FC = CE. In the previous paragraph, the Fock operator was introduced (Equation 17). However, since the Coulomb and exchange operators are dependent on the spin-orbitals ϕ_i (equations (14) and (16)) so that F itself depends on its own solutions. Therefore, the resolution requires to adopt an iterative procedure.

From an initial set of molecular orbitals, it is possible to calculate the value of the Hartree-Fock potential (\hat{J} and \hat{K} and therefore of the Fock operator). The eigenvalue equations are then solved, giving both the energies ϵi and a new, improved set of molecular orbitals. A new itertion can then begin. The process ends when the convergence criterion (variation of the energies below a certain threshold) is reached. This iterative procedure is called SCF, for Self-Consistent Field.



1.3.2 Basis functions

Each molecular orbital (MO) can be written as a linear combination of atomic orbitals (LCAOs). Atomic orbitals (ϕ_i) can, in turn, be represented by a linear combination of basis functions:

(24)
$$\phi_i = \sum_j c_j \chi_j$$

Where χ_j is the basis function to which the expansion coefficient c_j is associated. The basis functions form a basis set (BS). To perform calculations, the number of basis functions must be finite; therefore, a first approximation is undertaken by truncating the BS. According to the variational principle, the more basis functions are used to expand the orbitals, the higher the variational flexibility and the better the results. However, since the computational resource required to perform quantum chemical calculations scale-up with an exponential factor of the number of the basis functions, it is crucial to limit the size of the BS. Usually, a BS of suitable size to describe the properties of interest accurately is chosen.

For quantum chemical calculations are adopted essentially two types of atomic centered basis functions: Slater functions (STO, eq (25)) and Gaussian functions (GTO, eq (26)). For a standard function 1s of the hydrogen atom, for example, they have the following form:

(25)
$$\chi_{1s}^{\text{STO}}(r) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} \exp(-\zeta r)$$

(26)
$$\chi_{1s}^{\text{GTO}}(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2)$$

Where ζ and α are the respective exponents of the Slater function and the Gaussian function, Slater functions describe the atomic orbitals accurately, but the associated integrals are solvable only numerically, which makes STO computationally inefficient for large systems.

Gaussian functions, instead, provide a less accurate description: they don't reproduce well the asymptotic behavior of the atomic orbitals close to the nucleus (no cusp), but the associated integrals are solvable analytically. Moreover, by adopting a linear combination of Gaussian functions to

expand an atomic orbital is then possible to reproduce the correct asymptotic behavior. In general, the higher requirement of basis functions for the GTO respect to the STO is mostly compensated by the advantage of the analytical calculations of the integrals for the former. For this reason, most quantum chemical codes implemented GTO BSs. For minimal basis set, a single set of primitives for each occupied atomic orbital of the atoms is used. To improve the quality of the resulting wave-function, additional set can be used, called contractions. Moreover, polarization functions characterized by a higher angular momenta respect the occupied valence orbitals can be included to give angular flexibility in the descriptions of chemical bonds. Lastly, diffuse functions, characterized by small exponents, are used to better describe the tail of the wave-function, which is particularly necessary for the accurate description of intermolecular interactions.

1.3.3 Limitations of the Hartree-Fock approach

The variational principle tells us that the approximated wave function always has an energy higher than the exact wave function of the fundamental state. Hartree-Fock, in the non-relativistic framework, under the Born-Oppenheimer approximation and in the limit of an infinite basis set, would provide a ground state energy E_0 still higher than the exact one ε_0 . The difference between ε_0 and E_0 is then called electron correlation energy.

The electronic correlation may be separated in two contributions: dynamic and a static correlation. The dynamic correlation represents the instantaneous electron-electron interaction. In the Hartree-Fock approximation, the inter-electronic repulsion is considered only as an average effect on an electron given by the N-1 other electrons, while the static correlation is related to the fact that a single determinant does not always describe the fundamental state of a system. Although it amounts to about 1% of the total electronic energy, its neglecting severely affects the chemical description of the system. Starting from the Hartree-Fock solutions, many methods have been developed to account for the missing electronic correlation; for instance, we recall here the Interaction Configuration (CI), Multiconfigurational, Perturbative, and Coupled-Cluster methods. All of them, also known as Post-Hartree-Fock methods, can provide very accurate results, but they are very computationally demanding.

In this chapter, they will not be presented, and in the next paragraph, we will focus on another method: the density functional theory.

2. Density Functional Theory

In the previous section, the foundations of the Hartree-Fock method have been discussed. We present here the DFT (Density Functional Theory), a theory that goes far beyond the intrinsic limits

of the Hartree-Fock method. The fundamental idea is that the energy of an electronic system can be described from its electronic density. The first attempt in this direction dates back to the work of Thomas and Fermi in 1927,¹⁰ later supplemented by the Dirac exchange formula to give the Thomas-Fermi-Dirac model. ¹¹ However, this model returns poor results, systematically predicting that molecules are less stable than the atoms that make them up. In the 1950s, Slater proposed an approximate expression of Hartree-Fock exchange, in a form similar to the Dirac exchange: ¹²

(27)
$$E_x[\rho] = C_x \int \rho(\vec{r})^{4/3} d\vec{r}$$

where C_x is constant. Initially, this formula was introduced independently from the DFT. It is only in 1964, however, that a real theory was built around electron density, with the publication of Hohenberg and Kohn about their famous theorems.¹³ These theorems found a framework for their application the following year thanks to the Kohn-Sham's approach.¹⁴ The DFT and its application elaborated by Kohn and Sham are in theory exact methods. In practice, however, approximations are necessary. In the next paragraph it will be presented the work of Hohenberg and Kohn and then of Kohn and Sham. In the meanwhile, the approximations used in the DFT will be discussed as well.¹⁵⁻²⁰

2.1 First theorem: proof of the existence

The first theorem of Hohenberg and Kohn shows simply that the electron density $\rho(r)$ is the only function necessary to obtain all the electronic properties of a system: the external potential V_{ext} of an electronic system is, except for a constant, a unique functional of the density $\rho(r)$. The electron density also determines the number of electrons N of the system via the condition of normalization:

(28)
$$N = \int \rho(\vec{r}) \, d\vec{r}$$

 V_{ext} and N, in turn, determine the Hamiltonian of the system H, which is itself connected to the energy of the system by the Schrödinger equation. The fundamental state is a unique functional of electron density whose energy can then be written as:

(29)
$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{eN}[\rho_0]$$

Where T and E_{ee} represent respectively kinetic energy and electron-electron repulsion while E_{eN} corresponds to electron-nuclei interaction. It is then common to separate the system-dependent terms (E_{eN}) from those called "universal" (T and E_{ee}) in that their expression is independent of the system:

(30)
$$E_0[\rho_0] = F_{HK}[\rho_0] + \int \rho_0(\vec{r}) V_{eN} d\vec{r}$$

The F_{HK} functional is called universal functional, thus brings together kinetics energy and interelectronic repulsion. Note that it is not based on an approximation, so that the energy of the fundamental state is a priori accessible in an exact way. Let us recall that the density of the fundamental state uniquely determines the Hamiltonian of the system, which in turn characterizes all states, fundamental and excited. It, therefore, formally gives access to all the properties of all states. Thus, it is essential to be able to determine it, which is the subject of the second theorem of Hohenberg and Kohn.

2.2 Second theorem: a variational principle in DFT

The functional FHK gives the energy of the fundamental state only if the density used corresponds to the density of the fundamental state $\rho 0$. This theorem is the direct application of the variational principle to the DFT, i.e., for a trial density $\tilde{\rho}$:

(31)
$$E_0[\rho_0] \le E[\tilde{\rho}] = T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] + E_{eN}[\tilde{\rho}]$$

Note that this theorem is only rigorously valid if ρ satisfies the boundary conditions and if it is v-representable and associated with an external potential. A less strict condition can replace N-representability since it follows that the density comes from an antisymmetric wave-function (N-representability) to be valid. With a given wave-function, the corresponding electron density can be easily associated with it. The reciprocal is false since many wave-functions can correspond to the same density.

2.3 The Kohn-Sham approach

The absence of good approximations to evaluate the universal functional F_{HK} explains why the DFT was not used for quantitative predictions until 1965 when Kohn and Sham proposed an approach to

overcome the problem.¹⁴ Until then, only the Thomas-Fermi's method (then Dirac's) was used to solve the Schrödinger equation based on electron density.¹⁰As mentioned in the introduction to this section, this method provides inaccurate results due to the poor description of the kinetic energy of electrons. Kohn and Sham's idea was, therefore, to treat the kinetics term as accurately as possible. To do this, they used an approach similar to that used in the Hartree-Fock calculations by placing themselves in a hypothesis of an average field: the electrons evolve independently of each other in an effective potential V_s generated by the nuclei and the other electrons:

$$(32) \qquad \widehat{H} = -\frac{1}{2}\sum_{i}^{N} \Delta_{i} + \sum_{i}^{N} V_{S}\left(\vec{r}_{i}\right)$$

The advantage of such an approach is that the kinetic energy of an N-electron system without interaction is accurately known by using its spin-orbitals ϕ_i :

(33)
$$T_{S} = -\frac{1}{2} \sum_{i}^{N} \langle \phi_{i} | \Delta_{i} | \phi_{i} \rangle$$

Moreover, it contains most of the kinetic energy of the real system.^{22, 23} Similarly, since electronic movements are uncorrelated from each other, the exact wave function can be written as an antisymmetric product of mono-electronic wave functions (spin-orbitals ϕ i) in the form of a Slater determinant:

(34)
$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \dots & \phi_N(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(\vec{x}_2) & \dots & \phi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{x}_N) & \phi_2(\vec{x}_N) & \dots & \phi_N(\vec{x}_N) \end{vmatrix}$$

By analogy with the Hartree-Fock method, the spin-orbitals ϕ_i is determined by solving the equation at eigenvalues:

(35)
$$\hat{f}^{KS}\phi_i = \varepsilon_i\phi_i$$

where Kohn-Sham's single-electronic operator f^{KS} , is defined by:

(36)
$$\hat{f}^{KS} = -\frac{1}{2}\Delta + V_S(\vec{r})$$

The spin-orbits ϕ_i is then called Kohn-Sham orbitals, or KS orbitals. The connection between the fictitious system and the real system is made by choosing a fictitious potential V_s for which the electron density ρ_s defined in Equation (37) is equal to the one of the real system ρ_0 .

(37)
$$\rho_S(\vec{r}) = \sum_i^N \sum_S |\phi_i(\bar{r}, s)|^2 = \rho_0(\vec{r})$$

The originality of the Kohn and Sham's method is that, since the calculation of the exact kinetic energy is complicated, the best strategy is still to approximate it by separating the known part (classical kinetic energy T_s , equation (33)) from the unknown part. This logic is applied to the expression of the universal functional:

(38)
$$F_{HK}[\rho_{\vec{r}}] = T_S[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$

 T_s , the kinetic energy of the fictitious system without interactions, and J, the Coulomb interaction, can be easily computed. All unknown terms are grouped in the expression of the exchange-correlation energy E_{XC} :

(39)
$$E_{XC}[\rho] = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho])$$

Contrary to its name, E_{XC} actually contains all the corrections that are not in the other terms: the correction to the real kinetic energy (T-T_S), and the not classical effects related to the exchange (X) and the correlation (C), and other possible corrections due to the self-interaction error in the expression of the Hartree potential J. After these considerations, it remains now to find the expression of the effective potential V_S such that the same density characterizes the solution to the fictitious system as the real system. To do this, let's rewrite the expression of the total energy of the real system:
(40)
$$E[\rho] = T_{S}[\rho] + J[\rho] + E_{XC}[\rho] + E_{eN}[\rho] =$$
$$= -\frac{1}{2} \sum_{i}^{N} \langle \phi_{i} | \Delta_{i} | \phi_{i} \rangle + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} |\phi_{i}(\vec{r}_{1})|^{2} \frac{1}{r_{12}} |\phi_{j}(\vec{r}_{2})|^{2} + E_{XC}[\rho(\vec{r})]$$
$$+ \sum_{i}^{N} \int \sum_{A}^{M} \frac{Z_{A}}{r_{iA}} |\phi_{i}(\vec{r}_{1})|^{2} d\vec{r}_{1}$$

By analogy with the Hartree-Fock method, we apply the variational principle to the expression of $E[\rho]$ with the constraint that the spin-orbitals ϕ_i are orthonormal ($\langle \phi_i | \phi_i \rangle = \delta_{ij}$). The resulting equations allow us to find the eigenvalue equations: ¹⁶

(41)
$$\left[-\frac{1}{2}\Delta + V_{eff}(\vec{r}_i)\right]\phi_i = \varepsilon_i\phi_i$$

to identify the effective potential V_s to the potential V_{eff} :

(42)
$$V_{s} \equiv V_{eff} = \int \frac{\rho(\vec{r}_{2})}{r_{12}} d\vec{r}_{2} + V_{XC}(\vec{r}_{1}) - \sum_{A}^{M} \frac{Z_{A}}{r_{1A}}$$

Equations (42) are called Kohn-Sham equations. They are dependent on spin-orbit ϕ_i through J and must be solved in a self-consistent way. It should be noted that they are not based on an approximation and they permit in theory to determine exactly the fundamental state of a system. In practice, the term exchange-correlation is unknown. Approximations are necessary to find an explicit form. The main objective of the current research in DFT is thus to develop increasingly accurate exchange-correlation functionals, a point that we will detail in paragraph 2.3.5

Since the KS equations are very similar to the HF equations, their resolution is made according to the same scheme. Spin-orbitals are expanded as a linear combination of atomic orbitals (LCAOs), which are then expanded in turn with a basis set of primitive functions according to the same Roothan-Hall method developed for the HF. The KS equations form than a set of pseudo-eigenvalues equations solved self-consistently. However, the evaluation of the exchange-correlation integrals differs slightly. The computational codes use more efficient technics to calculate the Coulomb contribution, in order to save calculation time. The term exchange-

correlation is generally approached by rather complex mathematical functions. An analytical evaluation of the integral is therefore excluded, and the calculation codes instead perform a numerical quadrature integration. It consists in replacing the integral by a finite sum on a grid of points, where the value at each point is weighted by a coefficient noted here W_p :

(43)
$$\int \chi_{\mu}^{*}(\vec{r}_{1})V_{XC}(\vec{r}_{1})\chi_{\nu}(\vec{r}_{1}) d\vec{r}_{1} \approx \sum_{p}^{P} \chi_{\mu}^{*}(\vec{r}_{p})V_{XC}(\vec{r}_{p})\chi_{\nu}(\vec{r}_{p})W_{p}$$

Becke proposed the most commonly used integration grid in 1988, which splits the molecular space into atomic contributions.²⁴

2.3.1 Kohn-Sham orbitals

Molecular orbitals represent an essential conceptual tool in chemistry because they allow interpreting in a rather intuitive way the electronic phenomena of a system. Within the framework of the Hartree-Fock method, Koopmans' theorem makes it possible to give the energies and molecular orbitals of HF a physical significance by showing that the HF energy of the highest occupied orbital (HOMO) is equal to the first ionization potential.²⁵ It should be noted, however, that this theorem inherently contains two approximations, as it does not hold up the account for the relaxation of the chemical system after electronic excitation, nor the correlation effects. These two effects partially compensate each other, so that Koopmans' theorem generally provides a good approximation of ionization potentials. The validity of Koopmans' theorem in the context of the DFT has been, and is in progress, the subject of many articles.²⁶⁻³³ For a long time, it was considered that Kohn-Sham's orbitals (KS) had no physical significance, except that the sum of their squares allowed to find the electron density. However, Stowasser and Homan pointed out that the shapes and symmetry of KS orbitals were very close to those of HF orbitals.²⁷ More generally, the work of Baerends and Parr has shown that Kohn-Sham's orbitals are quite relevant for qualitative studies ^[34, 35] Provided that the exchange-correlation functional is known exactly, Koopmans' theorem can be applied to the highest occupied orbital (HOMO), whose energy must be equal to the first ionization potential:²⁸

$$(44) \quad \varepsilon_{HOM0}^{DFT} = -PI_1$$

However, L. Kleinman²¹ recently challenged the equation 44 by highlighting some of them in the demonstration by Perdew et al.²⁶ In practice, most comparative tests show that the DFT underestimates by several eV the opposite of the experimental ionization potential.^{26, 27, 33} For example, for the hydrogen atom, the DFT predicts an ionization potential of about 7 eV, compared to 13.6 eV experimentally. This error is mostly due to the problem of "self-interaction" and the asymptotic misbehavior of the exchange-correlation functional that decrease too quickly at long electron-core distances, and overestimates the energy of the HOMO.^{27,36,37} This error can be improved by using a hybrid functional whose exact exchange contribution partially corrects the problem of self-interaction. However, several studies have shown that the variation of the energy error $\varepsilon_{\text{HOMO}}$ for different chemical systems was remarkably homogeneous from one exchange-correlation functional to another.^{26,33} This underlines that Koopmans' theorem is qualitatively correct in the DFT framework, but that a systematic error occurs when calculating the HOMO energy.

2.4 Different exchange-correlation functional

The central problem of the DFT is that the exchange-correlation functional is unknown. Thus it forced the developing of approximations. Some environmental criteria have been suggested, but they do not guarantee the performance of the functionals thus obtained.³⁸ In practice, the best test remains to compare the exchange-correlation functionals with experimental databases used as a reference.

2.4.1 LDA functionals

Kohn and Sham proposed the Local Density Approximation (LDA) in parallel with the establishment of their equations.¹⁴ Again, their idea is to operate a reference system for which accurate data are known. At that time, many studies had focused on the homogeneous electron gas and had determined its properties over a wide range of densities, including exchange and correlation energies. It is naturally on this model that the LDA is based. The basic idea is that it is possible to estimate the exchange-correlation energy of an inhomogeneous system by using, on infinitesimal portions, the results of a homogeneous electron gas with a density equal to the local density of the real system. The sum of all point contributions yields the exchange-correlation energy according to the equation:

⁽⁴⁵⁾
$$E_{XC}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC} [\rho(\vec{r})] d\vec{r}$$

In a second step, ε_{XC} is divided into exchange contributions, respectively. This division, even if it has no physical meaning, dramatically simplifies the calculations:

(46)
$$\varepsilon_{XC}[\rho(\vec{r})] = \varepsilon_X[\rho(\vec{r})] + \varepsilon_C[\rho(\vec{r})]$$

Some division, even if it has no sense physique, allows simplifying the calculations. The exchange energy of an electron in a uniform gas is exactly known, thanks to the exchange equation of Dirac:¹¹

(47)
$$\varepsilon_X[\rho(\vec{r})] = -\frac{3}{4} \sqrt[3]{\frac{3\rho(\vec{r})}{\pi}}$$

The correlation energy $\varepsilon_{\rm C}$, on the other hand, is not known exactly. The Vosko, Wilk, and Nussair (VWN) approximation is the most commonly used. It is based on Monte-Carlo calculations of the homogeneous electron gas to give an approximate expression.⁴⁰ The treatment of open-shell systems is done formally as in the Hartree-Fock method, distinguishing between the spin α and β of the electrons ($\rho(\vec{r}) = \rho_{\alpha}(\vec{r}) + \rho_{\beta}(\vec{r})$). This approach, generally called LSD (Local Spin Density), has the advantage of giving to the system additional flexibility, and provides, in general, better results. In practice, the LDA approach represents an improvement over the Hartree-Fock results, but it is still affected by large deviations from the experiment (the exchange energy is underestimated by about 10 to 15%). Binding energies are generally too high, while activation barriers are largely underestimated. In principle, the LDA approximation is only valid for systems with smooth variations of the density and in regions where the exchange hole is more or less spherical. More elaborate functionals were later developed.

2.4.2 GGA functionals

The guiding idea of the GGA approximation (Generalized Gradient Approximation) is that it is important to consider the inhomogeneity of density by introducing its first derivative $\nabla \rho$ in the expression of the exchange-correlation energy:

(48)
$$E_{XC}[\rho] = \int \varepsilon_{XC} \left(\rho(\vec{r}), \nabla_{\rho}(\vec{r}) \right) d\vec{r}$$

The form of ε_{XC} is extremely variable from one function to another, but in most cases, exchange and correlation contributions are treated separately and then combined to form the total functional.

The exchange portion is expressed from the exchange energy LDA, but it includes an enhancement factor (F_X^{en}) and the reduced density gradient $s(\nabla \rho(\vec{r}))$, which improve the description of inhomogeneous systems:

$$E_X[\rho(\vec{r})] = \int d\vec{r} \rho_X(\vec{r}) \varepsilon_X(\rho(\vec{r})) F_X^{en}(s(\nabla \rho(\vec{r}))$$
$$s(\nabla \rho(\vec{r})) = \frac{|\nabla \rho_r(\vec{r})|}{\rho^{\frac{4}{3}}(\vec{r})}$$

 F_X^{en} either uses empirical data as the noble gas exchange energy (Becke 1988)⁴¹, or it is expressed based on physical considerations (as the PBE functional, for instance).⁴² The correlation part often has no immediate physical meaning, and as for the exchange energy, it is based on experimental data (P86),⁴³ or it is based on physical considerations (PW91).⁴⁴ GGA-type functionals significantly improve LDA results for lengths and binding energies. However, they never take into account the static correlation so that long-distance effects are often poorly described.

2.4.3 Adiabatic connection

The Kohn-Sham's model shows a kinetic correction in the exchange-correlation functional that the theory of adiabatic connection (see in particular ref ⁴⁵⁻⁴⁷) allows to include in the expression of the exchange-correlation hole, yet designed to take into account only potential terms. To realize that, a system interactions-free is "connected" to the real system by gradually increasing the value of the coupling parameter λ . The Hamiltonian can then define partially interacting systems:

(50)
$$\hat{H}_{\lambda} = \hat{T} + \hat{V}_{ext,\lambda} + \lambda \sum_{i} \sum_{j < i} \frac{1}{r_{ij}}$$

The parameter λ gradually reduces the intensity of the Columbian interelectronic repulsion. For $\lambda=0$, the electrons do not interact, and only the exchange is taken into account, while for $\lambda=1$, we find the real system. For each value of λ , the potential external V_{ext} adapts to maintain a constant density equal to the one of the real system.

2.4.4 Hybrid functionals

To improve the form of the exchange-correlation potential, a new generation of functionals was introduced. These functionals, called meta-GGA, depend not only on the density gradient but also on the Laplacian of the density ($\Delta \rho$). Despite this improvement, this approximation still suffers from the inadequate consideration of the exchange, which contributions are much more relevant than the

ones of the correlation. The next approach to improve the exchange-correlation functional was to take into account the exchange adopting the same formation used in the Hartree-Fock model.

The first attempt in this direction was to replace the exchange contribution in previous functionals with its exact value, and thus to keep approximations only on the correlation term, which is known to be quite weak.⁴⁸ Unfortunately, this approach provided poor results, as the exact exchange term is not adapted to the approximations made on the correlation term. For example, if the long-range correlation is poorly or not described at all, long-range exchange contributions will not be offset, and the results will be generally false. A possible alternative is thus to introduce only a fraction of the exact exchange into the exchange-correlation functional by adopting the formalism of the adiabatic connection. Assuming that the exchange-correlation functional varied linearly with λ , Becke first proposed the half-half functional (HH)⁴⁸:

(51)
$$E_{XC}^{HH} = \frac{1}{2} E_{XC}^{\lambda=0} + \frac{1}{2} E_{XC}^{\lambda=1}$$

Where the value E_{XC} for $\lambda=0$ assumes the value of the exact Hartree-Fock exchange, while for $\lambda=0$ E_{XC} assumes the value of the approximated LSD exchange. Subsequently, to improve its performance, Becke introduced three semiempirical parameters (a_{x0} , a_{x1} , and a_c) into its functional system to improve the basis of G2 data:⁴¹

(52)
$$E_{XC}^{hybrid} = a_{X_0} E_X^{LSD} + (1 - a_{X_0}) E_X^{HF} + a_{X_1} \Delta E_X^{GGA} + E_C^{LSD} + a_c \Delta E_C^{GGA}$$

Functionals that include the exact exchange in their expression are commonly referred to as hybrid functionals which contain a fixed amount of exact exchange are called global hybrids, some of them are PBE0, B3LYP, M06.⁴⁹⁻⁵¹ In the range-separated hybrids; instead, the fraction of the exact exchange is introduced as a function of the interelectronic distance. Among them there are functionals such as CAM-B3LYP or LC- ω PBE.⁵²⁻⁵³ The most sophisticated approximation is represented by the double-hybrid functionals, which include the dependence on the unoccupied orbitals and can describe weak interactions such as those arising from the dispersive forces, which are neglected by the standard formulation of the other approximations. An example of a double-hybrid functional is B2PLYP⁵⁴.

A classification based on the functional complexity, the physical constrains satisfied by the functional and the general performance has been proposed by Perdew,⁵⁵ which was inspired by the

biblical Jacob's ladder, sorted the different families of density functional approximations (DFAs) on the rungs of a ladder, from the simplest (LDA, 1^{st} rung) to the most complex (double hybrids, 5^{th} rung), with in between GGA(2^{nd}), meta-GGA (3^{rd}) and hyper-GGA or hybrid (4^{th}). Along with the functional complexity, also the associated computational cost increase climbing the ladder, with a much larger increment for hybrid and double hybrids functionals.

Following an assessment of the performances of several exchange-correlation functionals and GTO basis sets, carried out during Stefania Cagnina's thesis,⁵⁶ the functional M06-2X,⁵¹ coupled with the basis set 6-311+G(2d,2p) is the method chosen and used in the rest of the work. M06-2X is a highly parameterized functional which provides good results for both thermochemistry and reaction kinetics of a large class of main-group elements-based compounds. It is classified as a meta-GGA hybrid functional (4th rung). It contains 54% of Hartree-Fock exchange but the exchange-correlation term also includes the dependence from the kinetic energy density, other than the density (ρ) and the density gradient ($\nabla \rho$). This allows also the description of non-local effects, improving the results obtained.

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CHAPTER 3

Theoretical study of the decomposition of ammonium nitrate in presence of two inorganic salts: calcium carbonate and calcium sulfate



In this chapter the chemical-physical characteristics, and influence on the thermal stability of ammonium nitrate (AN) of two inorganic salts, namely calcium carbonate (CaCO₃) and calcium sulfate (CaSO₄) will be illustrated. Then, a detailed theoretical study aimed to understanding their reactivity with AN will be presented.

1. The state of the art of AN decomposition in presence of CaCO₃ and CaSO₄

1.1 Physico-chemical properties of calcium carbonate

Calcium carbonate is a salt produced by carbonic acid (H_2CO_3). It appears as a white crystalline solid, with a certain basicity. Calcium carbonate is soluble in acid solutions, such as hydrochloric acid. CaCO₃ presents a molecular weight of 100.09 g/mol, a melting point of 825°C and a density in water of 2.93 g/cm.

If calcium carbonate is heated to 650°C, it decomposes into CaO and CO₂, through an endothermic process called calcination ^{1,2}:

(1)
$$CaCO_{3 (s)} = CaO_{(s)} + CO_{2(g)}$$

 $\Delta H = +182.1 \text{ KJ/mol}$

As reported by Clifford Y. Tai and F.B. Chen³, calcium carbonate is subjected to the phenomenon of polymorphism, giving rise to three different types of crystalline forms: calcite, aragonite, and vaterite. Calcite is the most stable form under standard conditions, compared to the other two crystalline forms, and its precipitates may consist in mixtures of polymorphs or one of its three dominant crystalline forms. Despite the numerous works carried out to explain the polymorphism of CaCO₃, the most favorable conditions for the development of each polymorphic form have not yet been clarified. The factors that affect the polymorphism of $CaCO_3$ are the pH of the solution, the temperature, the ratio of the components, the supersaturation, the ionic strength of the solution, the type and the concentration of additives.³ At room temperature, the pH of the solution is the most significant factor.³ Temperature also plays a significant role: at very high temperatures, aragonite becomes the predominant product in solution with a pH of 12. Calcite is the anhydrous and stable form of CaCO₃ at standard conditions and it has three main transformation forms: calcite I, calcite II and calcite III.⁴ The transformation between calcite I and II takes place between 1.45 and 1.5 GPa.⁴ Transformation between calcite II and calcite III between 1.74 and 2.2 GPa. However, the calcite III is meta-stable and becomes complete stable only between 25 and 30 GPa.⁵ In addition to these three canonical polymorphic forms of calcite, there is also a IV polymorphic form that is not present in nature but can be achieved by shock compression.^{6,5} At standard conditions, aragonite can be also found, but it is unstable and it tends to retransform into calcite. Aragonite becomes stable only when it is subjected to high pressures (40 GPa) even if other polymorphic forms in competition have been identified.⁷ The safety

Data Sheets for calcium carbonate share that it is a not combustible substance, it decomposes over 825°C producing corrosive fumes pf calcium oxide. It reacts with acid, aluminum, ammonium salts, fluorine and magnesium and it may cause mechanical irritation. CaCO₃ is widely used as additives in ammonium nitrate formulation, because it ensures excellent stabilization capabilities ⁸ and it can be obtained at low cost from dolomite and limestone.^{9,10}

1.1.1 Calcium carbonate as CAN Fertilizer

One of the uses of calcium carbonate is in the domain of fertilizers. In fact, the production of AN grade fertilizers involves the addition of additives to improve AN chemical-physical characteristic, to increase its thermal stability, and to add nutrients to the soil. CAN fertilizer are a category of ammonium nitrate-based fertilizers. The production of CAN fertilizers takes place by adding calcium carbonate to ammonium nitrate during the production phase.¹¹ The addition of CaCO₃ brings several advantages to the formulation, for example, the increase of pH due to the neutralization of nitric acid and the production of $Ca(NO_3)_2$.¹² The latter, is able to positively stabilize the phase transition IV III of ammonium nitrate (as it has been introduced in chapter 1), increasing the temperature required for this phase transition by 50° C. ^{10,11,13} However, there are also negative aspects. In particular, the production of CO_2 generated during granulation leads to products that have a higher porosity than the one of pure AN. The most important aspect of this type of AN-based fertilizers is their reduced capacity to detonate, so that they are a valid option to pure ammonium nitrate.¹⁴ Among all the substances capable of reducing the explosive power of AN, as demonstrated previously by Oxley¹⁵ and Kiilski¹¹, carbonates play the most important role in stabilizing and reducing the decomposition of AN, as also recently reminded by Baubraskas.¹⁶ Fire tests have shown that the addition of CAN made fire controllable and easier to extinguish.¹⁷ Sensitivity tests determined that the CAN formulation can detonate if properly stressed, but the boost necessary for a detonation has to be much more intense than the one needed to make detonate pure AN.¹⁸ Ballistic mortar investigation on explosive power of CAN for a mixture containing 20% of calcium carbonate was performed indicating lead to a decrement of the explosive power almost of 90%.^{19,20}

1.1.2 Experimental data about NH4NO3 in presence of CaCO3

Several experimental studies, mainly calorimetric, have been conducted, leading to the proposition of the following reaction for the decomposition of AN in the presence of CaCO₃: ^{8,10,21,22,}

(2) $2NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + H_2O + CO_2$

Kaljuvee and other researchers (2008) studied the effect of additives such as limestone and dolomite on ammonium nitrate decomposition.²¹ In this work, different kind of limestone and dolomite were used. X-ray diffraction studies (XRD) reported that in the limestone used in these experiments, the content of CaCO₃ was 93.4% for Karinu type and 97.1% for Vasalemma type. As far as the composition of the dolomite is concerned, the amount of $[CaMg(CO_3)_2]$ was between 2.2%-6.3% for Kurere dolomite and in the case of Analema the quantity of $[CaMg(CO_3)_2]$ was between 96.4-92.6%. Looking at the differential thermal analysis (DTA) data of curve s of AN samples, four endotherms were observed.



Figure 1. Thermal curves of AN in a – air and b – nitrogen, from Kaljuvee article $(2008)^{21}$

As shown in Figure 1, the first transition of ammonium nitrate ($AN_{IV} \Leftrightarrow AN_{III}$) in air and in nitrogen atmosphere was evidenced at 53.0 and 53.7°C. The second one, ($ANIII \Leftrightarrow ANII$) and the third one transition ($ANII \Leftrightarrow ANI$) were detached at 88.1 and 90.8°C, and at 127.1 and 128.0°C. At the end, the melting point transition ($ANI \Leftrightarrow ANmelt$) endotherms the minima have been evidenced in air at 164.8 °C, and in nitrogen at 168.4°C. The addition of different quantity of limestone and dolomite (5-20 mass%), does not leaded to shifts in temperature of the $ANVI \Leftrightarrow ANIV \Leftrightarrow ANIII$, $ANII \Leftrightarrow ANI$ phase transitions. On the contrary, depending on the type and amount of additive, a shift has been evidenced for the melting point and the

decomposition temperature of AN of 1.5–2 °C and 8–45°C towards higher temperatures, as shown in Figure 2.



Figure 2. DTA curves of AN and its blends with Kurevere dolomite, from Kaljuvee article (2008)²¹

All the samples with lime-containing additives exhibited the endotherms on the DTA curves in the temperature range of decomposition of $Ca(NO_3)_2$ or $Mg(NO_3)_2$, suggesting the possibility of their formation during decomposition of AN.²¹ The analysis of the gaseous compounds produced during the experiments on neat AN, suggested some differences between the decomposition of AN in air and in N₂, as it is possible to see in Figure 3.²¹



Figure 3. FTIR spectra of gaseous compounds evolved at thermal treatment of AN in a – air and b – nitrogen, from Kaljuvee article $(2008)^{21}$

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If limestone and dolomite are added to AN, there is a variation in the gaseous products formed, as shown in the FTRI spectrum in Figure 4.



Figure 4. FTIR spectra of gaseous compounds evolved at thermal treatment of AN blends with a – Karinu limestone and b – Kurevere dolomite at mole ratio of AN/(CaO+MgO)=2:1 in air, from Kaljuvee article (2008)²¹

The formation of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ was deduced from the different composition of the gases released during the DTA experiments, as it is possible to see in Figure 4, by making a simple comparison with Figure $3.^{21}$ In fact, the presence of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ can be deduced from the fact that these two compounds, decomposing would form CO_2 , which appears in fact in the spectrum FTIR, and this would suggest the establishment of the reaction 2 and also of the reaction number $3.^{21}$

3) $2NH_4NO_3 + MgCO_3 \rightarrow Mg(NO_3)_2 + 2NH_3 + H_2O + CO_2$

The thermal treatment experiments of AN blends with CaCO₃, MgCO₃, limestone and dolomite samples suggest that the decomposition of AN proceeds through a completely different mechanism – depending on the origin and the content of additives - partially, or completely, through the formation of Mg(NO₃)₂ and Ca(NO₃)₂ which decompose at 370–630°C.²¹ The AN reaction with MgCO₃, and dolomite samples was not as complete as with CaCO₃ or limestone samples, because MgCO₃ is less reactive towards AN than CaCO₃.²¹ Rubstov's work has shown that at kinetic level CaCO₃ is more performing than MgCO₃, reaching the same reactions number 2 and 3, for the decomposition of AN in the presence of CaCO₃ and MgCO₃.²³ Other experimental tests have been conducted on the influence of CaCO₃ on the decomposition of AN :

they will be reported below. As explained in chapter 1, typical parameters to rationalize the behavior of mixture with respect to pure compound are the onset temperature (T_{onset}), that is the temperature at which the calorimetric reaction starts, and the maximum temperature (T_{max}) , corresponding to the maximum to the peak of the calorimetric plot. For the decomposition of pure ammonium nitrate the Tmax of decomposition is 263 °C with DTA analysis, while it ranges between 270,7 and 308,8°C when mixed with 5% of weight of different type of dolomite and limestone.²¹ Oxley's studies about the effect of various substances on the reactivity of ammonium nitrate, led to the conclusion that among all the additives stabilizing the formulation of AN grade fertilizer, calcium carbonate (CaCO₃) was the most performing.¹⁵ From these DSC experiments, the T_{max} of decomposition of pure AN is 326°C, a value that increases to 360.0°C, when mixed with 5% in weight of pure CaCO₃, and to 389.0°C with 20 %.¹⁵ The decomposition of pure AN generates a heat of 1255 J/g but when it is mixed with 33% wt of CaCO₃ the heat generated decrease to 397 J/g.¹⁵ In addition, Vytenis Babrauskas, while studying the stability of CAN stabilizers, has also demonstrated that there has been no incident involving ammonium nitrate that was in formulation with CaCO₃. In fact, calcium carbonate is able to drastically reduce the detonability of AN, as can be seen from Figure 5. This image represents the different detonability of various AN's formulations, tested with ballistic mortar. In pink is reported the curve related to CAN formulation.¹⁶



Figure 5. The effect in the Mark III RARDE ballistic mortar of AN with various additives (Clancey and Turner)^{16,19}

To conclude, CAN formulations are so much stable than pure AN that even if it contains 0.4% organic material it still resist to detonation compared to pure AN added by the same quantity of organic compound.²⁴

1.2 Physico-chemical properties of calcium sulfate

Calcium sulfate is a white solid salt, poorly soluble in water. It is generally used as desiccant. Anhydrous calcium sulfate presents a melting point at 1460 °C. It exists in three different degrees of hydration that generate three different crystalline structures:²⁵

- CaSO₄ anhydrous (molar mass: 136.14 g/mol, density: 2.96 g/cm³, water solubility: 0.21g/100ml at 20 °C)
- CaSO₄ 2H₂O dihydrate, which gives rise to gypsum or selenite (molar mass: 172.172 g/mol, density: 2.32 g/cm³, water solubility: 0.24 g/100ml at 20°C)
- CaSO₄ 1/2 H₂O hemihydrate, known as Paris plaster (molar mass: 145.15 g/mol)

In the Safety Data Sheets, $CaSO_4$ is considered as a not combustible substance, that gives off irritating or toxic fumes (or gases) in a fire. In case of fire in the surroundings it is suggested to use appropriate extinguishing media. In case irritation for the eyes and in case of ingestion abdominal pain.

As in the case of CaCO₃, it's difficult to determine a phase diagram for calcium sulfate. As reported by Daniela Freyer and Wolfgang Voigt, hemihydrate forms of CaSO₄ can be obtained by dehydration of gypsum in dry solid state or in aqueous solutions at enhanced temperatures.²⁶ These forms (β -, α -hemihydrate) show different thermal and hydration characteristics, which cannot be traced back to their specific structural features.²⁶ Because of the importance for gypsum-based binder and building materials, other studies on crystallization and setting kinetics of gypsum have been performed to detach the retarding and accelerating effects of additives: unlikely, despite the efforts, no mechanistic model able to explain most of the effects observed with respect to kinetics and crystal morphology has been developed.

1.2.1 Calcium sulfate as additive for ammonium nitrate grade fertilizer

The most abundant form of calcium sulfate is gypsum, which is used in agriculture. Sulphur is absorbed by soil as sulfate, which is the major plant nutrient, and is essential for crop growth. Calcium sulfate is used to improve soil quality thanks to its capability to improve Ca- and S-nutritional elements in agriculture. In contrast to what has already been seen for calcium carbonate, at the best of our knowledge, there are no studies on the influence that calcium sulfate exerts on ammonium nitrate in terms of improvement on the crystalline structure of AN. Contrary to the calcium carbonate, for calcium sulfate just few experimental information is available about calorimetric experiments describing its effects on the decomposition of ammonium nitrate. Experimental data suggest a lower stabilizing effect than CaCO₃ on the thermal stability of AN. Indeed, according to DSC test, the T_{max} increases to 333.0°C when AN is mixed with 5% wt of pure CaSO₄ and with 20% wt of CaSO₄ T_{max} is 334°C.^{15,27} Moreover, the heat generated by a mixture of AN

with 33% in weight of CaSO₄ is 669 J/g, about one half of AN decomposition heat. These data suggested that CaSO₄ behaves closer to an inert substance than to an inhibitor of ammonium nitrate decomposition.

2. Theoretical study of ammonium nitrate in contact with calcium carbonate

In order to study the reactivity of calcium carbonate, two different structures were considered at first: the minimum geometries, obtained by M06-2X/6-311+G(2d,2p) level of theory, are represented in Figure 7 for the monomer and dimer (Figure 7).

The dimer was taken in consideration because other theoretical studies on calcium carbonate modeling has been performed, through hartree-fock calculations. Calcite, or the dimer of CaCO₃ is the smallest structure that is representative of the cluster.²⁸ In this model, the calcite is composed by two calcium atom that are linked with two carbonate ion through four coordination bounds given by four oxygen atom. The same structure proposed by the Hartree-Fock calculation was taken as model for our calcite molecule, which image is presented in Figure 6. However, during preliminary studies of the calcite reactivity with AN, the dimer molecule was discarded because the structure was too flexible to be taken as a reference for theoretical studies performed in the gas phase. Therefore, the CaCO₃ monomer was adopted as the starting model for the study of reactivity with ammonium nitrate. The final and optimized geometry of CaCO₃ presents a carbonate molecule, whose planar carbon atom is bound to three oxygen atoms, which two are coordinated to the calcium atom.







Figure 7. Dimer of CaCO₃

Starting from the geometry presented in Figure6, a study on the interaction of $CaCO_3$ with ammonium nitrate was conducted in order to highlight the reactivity of calcium carbonate. Starting from the procedure previously used to study chemical incompatibilities of $AN^{29-,30}$, the emphasis was placed on identifying the

steps in contact in the reaction mechanism between the two substances involved, considering that ammonium nitrate easily decomposes into nitric acid and ammonia ($\Delta G = 5.4$ Kcal/mol) as discussed in chapter 1. The reaction between AN and CaCO₃ was therefore investigated by considering that CaCO₃ could react with nitric acid, here after referred to as *path A*, and ammonia, *path B*. Total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.

2.1 Reaction between CaCO₃ and HNO₃

2.1.1 Interaction between a first HNO₃ with CaCO₃

As first step of *path* A, a reaction between calcium carbonate and nitric acid lead to a proton transfer from a molecule of HNO₃ to CaCO₃ through a barrier-less and exothermic reaction, with the formation of the aggregate [NO₃···CaCO₃H] as intermediate product, in which nitrate ion is coordinated to calcium atom. The structure of [NO₃···CaCO₃H] is reported below, in Figure 8. The Gibbs free energy released in the process has a value of -67.1 kcal/mol.

In this thesis by aggregate is meant the product formed by the encounter of an additive or a contaminant, with a molecule of HNO₃, NH₃ or AN, forming more or less a stable interaction. An example is the case of [NO₃…CaCO₃H] seen above. The term aggregate will continue to be re-proposed in this manuscript while maintaining the same meaning explained here.



Figure 8. Aggregate [NO₃…CaCO₃H]

The purpose of the stability studies of this aggregate, and of the others presented later, is to identify secondary reactions, which under certain conditions may be able to destabilize ammonium nitrate. The decomposition of the aggregate [NO₃---CaCO₃H], provides the following possible reactions:

(4) $[NO_3 \cdots CaCO_3H] \rightarrow NO_3^- + Ca^{2+} + HCO_3^-$ (5) $[NO_3 \cdots CaCO_3H] \rightarrow [NO_3 \cdots CaCO_3]^- + H^+$ (6) $[NO_3 \cdots CaCO_3H] \rightarrow [NO_3 \cdots - Ca]^+ + CO_3H^-$ (7) $[NO_3 \cdots CaCO_3H] \rightarrow NO_3^- + [CaCO_3H]^+$

The possible decomposition pathway has been calculated by DFT. All the Gibbs free energies of dissociation for the aggregates [NO₃···CaCO₃H] are shown in Figure 9.





Figure 9. Possible reaction paths for the dissociation of the aggregate [NO₃···CaCO₃H]

As shared before, $[NO_3 - CaCO_3 H]$ can decompose into $NO_3 + Ca^{2+} + HCO_3$, as reported in reaction (4) and the ΔG associated is about 381.7 Kcal/mol. Another possibility is the dissociation into $[NO_3 - CaCO_3]^+$ H^+ (reaction (5)) with a ΔG equal to 249.5 Kcal/mol. Reaction (6) proposes as decomposition the production of two ionic species: $[NO_3 - Ca]^+ + CO_3 H^-$ with a ΔG associated of 99.4 Kcal/mol. In reaction (7), the generated products are $NO_3^- + [CaCO_3 H]^+$, and the necessary ΔG is 91.4 Kcal/mol. The energies required for the decomposition of the aggregate $[NO_3 - CaCO_3 H]$, are so high that it can be considered as a stable intermediate.

2.1.2 Interaction between a second HNO₃ and CaCO₃

After the first interaction, the aggregate $[NO_3 \cdots CaCO_3H]$ can still react with a second molecule of nitric acid, forming the $[NO_3 \cdots CaCO_3H_2 \cdots NO_3]$ aggregate, which is shown in Figure 10. Even in this case, the reactions involved are an interaction of a HNO₃ molecule with $[NO_3 \cdots CaCO_3H]$, and the protonation of the bicarbonate. Both reactions are concerted and exothermic (by -27.9 kcal/mol), showing no barrier. Stability tests have been carried out by DFT, also to investigate if this second generated aggregates can cause side reactions able to destabilize ammonium nitrate. The decomposition of the aggregate $[NO_3 \cdots CaCO_3H_2 \cdots NO_3]$ involves the possible following reactions (Figure 11):

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Figure 10. Aggregate [NO₃···CaCO₃H₂···NO₃]

(8) $[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \rightarrow 2NO_3^- + Ca^{2+} + H_2CO_3$ (9) $[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \rightarrow 2NO_3^- + [CaCO_3H_2]^+$ (10) $[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \rightarrow NO_3^- + Ca(NO_3)^+ + H_2CO_3$ (11) $[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \rightarrow NO_3^- + [NO_3 - CaCO_3H_2]^+$ (12) $[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \rightarrow Ca(NO_3)_2 + H_2CO_3$



Figure 11. Reaction paths for the dissociation of [NO₃...CaCO₃H₂...NO₃]

Looking at the energy values shared in Figure 11, the only favorable decomposition is that leading to the formation of Ca(NO₃)₂ and H₂CO₃ (Δ G= -76.9 kcal/mol) with a barrier of 18.1 kcal/mol. Ca(NO₃)₂ is one of the reaction products found experimentally.^{8,10,21,22}. Other decomposition reactions are possible, but they are all higher in energy (see Figure 11). Ammonium nitrate is known to exhibit an incompatibility for acidic substances³¹, and carbonic acid (H₂CO₃) is one of those and it could represent a problem for AN stability. H₂CO₃ is still able to react in two ways. In this first path, AN in presence of H₂CO₃ leads to the formation of an adduct [NH₄NO₃···H₂CO₃] (Δ G= -63.6 kcal/mol). This one evolves into [NH₃···HNO₃···H₂CO₃] (Δ G= -69.6 kcal/mol), through a TS_{3A} with an energetic barrier of 0.8 kcal/mol. In the transition state, a double displacement of protons occurs: one directly from carbonic acid to nitrate anion, and a second one from ammonium to bicarbonate (HCO₃⁻), which forms again H₂CO₃ (by an endothermic decomposition of 3.5 kcal/mol). The other possible reaction for carbonic acid is its decomposition into carbon dioxide and water with a relative free energy of 17.3 kcal/mol. Among these two pathways, the most favorable reaction is the decomposition of H₂CO₃ into H₂O and CO₂, as confirmed by experimental data.^{8,10,21,22} The energy involved in the reactions are reported in Table 1, the pathway of reaction is presented in Scheme 1. Gibbs free energy profile is in Figure 12.

Table 1 Relative energies (kcal/mol) for the decomposition reaction of NH_4NO_3 in presence of $CaCO_3$. This table concerns only the reaction of $CaCO_3$ in presence of HNO_3 .

	ΔΕ	ΔH	ΔG
NH4NO3	0.0	0.0	0.0
$NH_3 + HNO_3$	13.5	14.0	5.4
Path A			
[NO ₃ ···CaCO ₃ H]	-69.4	-68.5	-67.1
[NO ₃ ···CaCO ₃ H ₂ ···NO ₃]	-108.8	-108.0	-95.0
$Ca(NO_3)_2 + H_2CO_3$	-80.5	-79.9	-76.9
[NH4NO3···H2CO3]	-71.8	-71.3	-63.6
TS _{3A}	-70.7	-70.4	-62.8
[NH ₃ ···HNO ₃ ···H ₂ CO ₃]	-76.1	-75.0	-69.6
$NH_3 + HNO_3 + H_2CO_3$	-53.5	-52.0	-66.1
$H_2O + CO_2$	-89.7	-87.4	-94.2

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 $Ca(NO_3)_2 + H_2CO_3$

 $H_2O + CO_2$





 $\mathsf{TS}_{\mathsf{3A}}$

 $+ NH_4NO_3$

[NH₄NO₃···H₂CO₃]



Figure 12. Gibbs Free Energy profile for the reaction between CaCO₃ and HNO₃

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2.2 Reaction between CaCO₃ and NH₃: a less favorable reaction pathway

2.2.1 Interaction between NH₃ and CaCO₃

Following *path B*, the calcium carbonate interacts with ammonia. The interaction between CaCO₃ and NH₃ can be described as a reaction in which a molecule of ammonia interacts with an atom of calcium, leading to the formation of the aggregate. The resulting aggregate, $[NH_3...CaCO_3]$, is stable and the Gibbs free energy released is about ΔG =-12.4 kcal/mol. This species undergoes to a proton displacement from a molecule of ammonia to the carbonate, with an energetic barrier of 13.1 kcal/mol, via a transition state TS_{1B} (Figure 13), leading to a aggregate $[NH_2...CaCO_3H]$, (Figure 13) and releasing an energy equal to -5.9 kcal/mol.



Figure 13. Representation of the TS_{1B} and the aggregate [NH₂...CaCO₃H]

In transition state TS_{1B} , the proton presents on the molecule of ammonia is displaced on the oxygen of carbonate, leading the final optimized structure presented in Figure 13. Using the same approach seen for the path A, the stability of [NH₂···CaCO₃H] was also investigated, evidencing the following decomposition reactions:

(13) $[NH_2 CaCO_3 H] \rightarrow NH_2 + Ca^{2+} + CO_3 H^-$ (14) $[NH_2 CaCO_3 H] \rightarrow NH_2 + CaCO_3 H^-$ (15) $[NH_2 CaCO_3 H] \rightarrow [NH_2 - Ca]^+ + CO_3 H^-$

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Figure 14. Reaction paths for the dissociation of the aggregate [NH₂···CaCO₃H]

As shown in Figure 14, all these decomposition reactions are endothermic. Decomposition energies are all higher than 135 Kcal/mol, so that it is possible conclude that the aggregate is stable and it does not undergo to side reactions, able to decrease the stability of ammonium nitrate.

2.2.2 Interaction between a second NH₃ with CaCO₃

The last adduct $[NH_2...CaCO_3H]$ can accept a second molecule of ammonia, resulting in another aggregate: $[NH_2...CaCO_3H...NH_3]$ (ΔG = -14.2 kcal/mol,), which does not undergo to further proton displacement. Also for $[NH_2...CaCO_3H...NH_3]$, showed in Figure 15, calculations on the possible decomposition were performed.



Figure 15. Aggregate [NH₃···CaCO₃H···NH₂]



The aggregate [NH₂…CaCO₃H…NH₃] foresees the following decomposition:

 $[\mathrm{NH}_2 \cdots \mathrm{CaCO}_3 \mathrm{H} \cdots \mathrm{NH}_3] \twoheadrightarrow \mathrm{NH}_2^- + \mathrm{Ca}^{2+} + \mathrm{CO}_3 \mathrm{H}^- + \mathrm{NH}_3 \qquad 14)$

 $[NH_2 \cdots CaCO_3 H \cdots NH_3] \rightarrow [NH_2 \cdots CaCO_3 H] + NH_3 \qquad 15)$

The Gibbs free energies related to the decomposition are reported in Figure 16. In the first reaction, the aggregate to decompose into NH_2^- , Ca^{2+} , HCO_3^- and NH_3 and it requires a Gibbs free energy of 465.7 Kcal/mol. In the second reaction, the decomposition products are $[NH_2--CaCO_3H]^+$ and NH_3 and the free energy required is about -18.3 Kcal/mol. The energy involved in the reactions are reported in Table 2, the pathway of reaction is presented in Scheme2. Gibbs free energy profile is in Figure 17.



Figure 16. Possible reaction paths for the dissociation of the aggregate [NH₂---CaCO₃H---NH₃]

We can conclude, as can be seen on Figure 18, *path B* leads to energetically less stable aggregates than *path A*. This latter leads to the formation of stable species, experimentally observed (in particular $Ca(NO_3)_2$). For this reason, *path A* (where $CaCO_3$ reacts with HNO₃) is the most probable. The whole pathway of reaction and Gibbs free energy profile is reported in Figure 18 and Scheme 3.







Figure 17. Gibbs Free Energy profile for the reactions between CaCO₃ and NH₃

	ΔΕ	ΔH	ΔG
NH ₄ NO ₃	0.0	0.0	0.0
$NH_3 + HNO_3$	13.5	14.0	5.4
Path B			
[NH ₃ ···CaCO ₃]	-12.8	- 12.8	- 12.4
TS _{1B}	- 0.9	- 1.5	0.7
[NH ₂ ···CaCO ₃ H]	- 17.7	-17.2	-18.3
[NH ₂ ···CaCO ₃ H···NH ₃]	-22.3	-22.5	-14.2

Table 2 Relative energies (kcal/mol) for the decomposition reaction of NH4NO3 in presence of CaCO3.This table is focused on the reaction of CaCO3 in presence of NH3.



Figure 18. Gibbs Free Energy profile for the reaction between AN and CaCO₃.

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3. Theoretical study of ammonium nitrate in contact with calcium sulfate

In the case of calcium sulfate, no preliminary theoretical studies have been necessary in order to identify the geometry of the salt. In fact, the only reasonable geometry is the one in which a calcium atom coordinates three oxygen atoms of the four present in the CaSO₄ structure. The minimum geometry, obtained by M06-2X/6-311+G(2d,2p) level of theory, is represented in Figure 19. Considering the only few experimental data available for AN/CaSO₄ mixture, the reaction mechanism proposed for this system has been identified in analogy to that for the AN/CaCO₃ system. As before, reaction *path A* corresponds to the reactions between CaSO₄ and HNO₃, and *path B* corresponds to the reaction between CaSO₄ and NH₃. Total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.



Figure 19. Molecule of CaSO₄

3.1 Reaction between CaSO₄ and HNO₃

3.1.1 Interaction between a first HNO₃ with CaSO₄

Like for CaCO₃ in *pathA*, the first reaction for CaSO₄ is exothermic and barrier-free, where HNO₃ simultaneously forms a bond with the calcium atom and a proton is transferred to SO₄²⁻, leading to the aggregate [NO₃···CaSO₄H] (ΔG = -56.8 kcal/mol, Figure 20).

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Figure 20. Aggregate [NO₃···CaSO₄H]

3.1.2 Interaction between a second HNO₃ with CaSO₄

[NO₃···CaSO₄H] can react with another molecule of HNO₃ through two possible protonation sites: site **a** and site **b** (see Figure 20) leading to two different possible isomers, namely $[NO_3 \cdots CaSO_4H \cdots HNO_3]_a$ (ΔG = -83.6 kcal/mol) and $[NO_3 CaSO_4 H H O_3]_b$ ($\Delta G = -68.1$ kcal/mol). The first isomer, $[NO_3 - CaSO_4H - HNO_3]_a$ evolves into $[NO_3 - CaSO_4H_2 - NO_3]_a$ ($\Delta G = -66.1$ kcal/mol) passing through the transition state TS_{2Aa} that presents a barrier of 24.1 kcal/mol. The structures of these latter systems are reported in Figure 14. Starting from [NO₃...CaSO₄H...HNO₃]_b, the other possible isomer is $[NO_3 - CaSO_4H_2 - NO_3]_b$ ($\Delta G = -64.9$ kcal/mol passing through the transition state TS_{2Ab} with a barrier of 6.3 kcal/mol (see Table3). In both cases, the same products, $Ca(NO_3)_2$ and H_2SO_4 , are formed. Indeed, the two transition states, TS_{2Aa} and TS_{2Ab}, are characterized by the displacement of a proton from HNO₃ to CaSO₄, albeit from a different site (see Figure 21). As previously considered for H₂CO₃, H₂SO₄ is also able to react with AN in two different ways. In the first path, ammonium nitrate in presence of H_2SO_4 can lead to the formation of $[NH_4NO_3 H_2SO_4]$ (ΔG =-47.1 kcal/mol) which evolves into the species $[NH_3 HNO_3 H_2SO_4]$ (ΔG =-46.9 kcal/mol), through a TS_{3A} with an energetic barrier of 1.3 kcal/mol (ΔG =--45.8 kcal/mol, see Table 2 for energy values and Figure 17 for Gibbs free energy profile). The TS presents a double and simultaneous proton displacement from sulfuric acid to nitrate and from ammonium to sulfate. At the end, H_2SO_4 is regenerated, producing NH_3 and HNO_3 again with a barrier of 9.9 kcal/mol. The other

possibility is the endothermic sulfuric acid decomposition by 11.1 kcal/mol. So, the catalytic destabilizing effect of H_2SO_4 on AN is in competition with its decomposition. The aggregates mentioned before, are all reported in Figure 21, the reaction pathway is reported in Scheme4, energy values are reported in Table4, and Gibbs Free Energy profile in Figure 22.



Figure 21. Transition states and aggregates of the reactions of HNO₃ and CaSO₄.

	ΔΕ	ΔH	ΔG
NH4NO3	0	0	0
$NH_3 + HNO_3$	13.5	14.0	5.4
Path A			
[NO ₃ ···CaSO ₄ H]	-58.6	-57.6	-56.8
[NO ₃ ···CaSO ₄ H···HNO ₃] _a	-97.1	-96.1	-83.6
TS _{2Aa}	-74.3	-73.6	-59.5
$[NO_3 \\ \cdots \\ CaSO_4H_2 \\ \cdots \\ NO_3]_a$	-79.8	-78.8	-66.1
[NO ₃ ···CaSO ₄ H···HNO ₃] _b	-82.0	-81.0	-68.1
$\mathrm{TS}_{2\mathrm{Ab}}$	-77.2	-76.7	-61.8
$[NO_{3} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	-78.8	-77.7	-64.9
$Ca(NO_3)_2 + H_2SO_4$	-50.0	-48.9	-47.9
$[NH_4NO_3\cdots H_2SO_4]$	-47.5	-54.0	-47.1
TS _{3A}	-47.3	-53.9	-45.8
[NH ₃ ···HNO ₃ ···H ₂ SO ₄]	-47.3	-54.5	-46.9
$NH_3 + HNO_3 + H_2SO_4$	-23.0	-21.0	-37.0
$H_2O + SO_3$	-30.0	-27.6	-36.8

Table 3. Relative energies (kcal/mol) for the decomposition reaction of NH_4NO_3 in presence of CaSO₄. This table is focused on the reaction of CaSO₄ in presence of HNO₃.



Scheme 4. Pathway of reaction between CaSO₄ and HNO₃


Figure 22. Gibbs Free Energy profile for the reaction between CaSO₄ and HNO₃

3.2 Reaction between CaSO₄ and NH₃

3.2 Interaction between NH₃ and CaSO₄

Following *path B*, the ammonia reacts with CaSO₄ forming a first aggregate, $[NH_3...CaSO_4]$ (ΔG = -14.0 kcal/mol, Figure 23), with an exothermicity of 19.4 kcal/mol.



Figure 23. Aggregate [NH₃···CaSO₄]

To this first reaction follows a similar one, where a second molecule of NH₃ interacts with [NH₃···CaSO₄]. The resulting species, [NH₃···CaSO₄···NH₃] is very stable (ΔG = -32.0 kcal/mol). While no proton transfer is observed upon the addition of the first ammonia molecule, the interaction with a second NH₃ makes such

a reaction possible. The species $[NH_3...CaSO_4H...NH_2]$ (Figure 24) is stable (ΔG = -16.8 kcal/mol), passing through a transition state TS_{2B} (Figure 24) with a barrier of 21.9 kcal/mol.



Figure 24. Representation of the TS_{2B} and the aggregate [NH₃···CaSO₄H···NH₂]

Reaction *path B* rests, however, energetically less favorable, than *path A*. The aggregate $[NH_3 \cdots CaSO_4H \cdots NH_2]$ can potentially undergoes other decomposition. Nevertheless, previous experimental studies on AN's reactivity in presence of $CaCO_3^{25-30}$ demonstrated that reactions with HNO₃ were more favored than the ones with NH₃. The same was proved for CaSO₄. So, the decomposition of $[NH_3 \cdots CaSO_4H \cdots NH_2]$ was not studied.

	ΔΕ	ΔH	ΔG
NH4NO3	0	0	0
$NH_3 + HNO_3$	13.5	14.0	5.4
Path B			
[NH ₃ ···CaSO ₄]	-14.9	-15.2	-14.0
[NH ₃ ···CaSO ₄ ···NH ₃]	-41.3	-42.0	-32.0
TS_{2B}	-20.5	-21.5	-10.1
[NH ₃ ···CaSO ₄ H···NH ₂]	-25.2	-25.0	-16.8

Table 4. Relative energies (kcal/mol) for the decomposition reaction of NH_4NO_3 in presence of $CaSO_4$. This table is focused on the reaction of $CaSO_4$ in presence of NH_3 .

The whole reaction mechanism and the Gibbs free energy profile are represented in Scheme 6 and Figure 26.





[NH₃···CaSO₄H···NH₂]



Figure 25. Gibbs Free Energy profile for the reaction between CaSO₄ and NH₃



Scheme 5. Pathway of reactions between ammonium nitrate and CaSO₄



Figure 26. Gibbs Free Energy profile for the reaction between AN and CaSO₄

4. Conclusion

The results obtained suggest that CaCO₃ can capture a proton from HNO₃, avoiding the decomposition of nitric acid, since the interception of the proton is strongly exothermic and therefore favored from the thermodynamic point of view (ΔG =-67.1 kcal/mol), while the production of radicals from the decomposition of pure AN is endothermic (ΔG = 40.2 kcal/mol). When AN is in presence of this stabilizing substance, the production of reactive species (OH[•] and NO₂[•] radicals) is avoided, and the formation of stable aggregates that evolve into stable molecules, such as H₂O, CO₂ and Ca(NO₃)₂, as reported experimentally is promoted. It can be concluded that the reactions between AN and CaCO₃ are more favorable than the decomposition of pure AN. Besides, there is the production of stable species that do not encourage the development of radical phenomena, which tends to produce a chain of highly destabilizing reactions. The theoretical results of this study are consistent with the behavior of the additive observed experimentally. The ability of the carbonate to accept the proton from the nitric acid and thus to form a stable aggregate is the key characteristic of this reaction mechanism.

As far as CaSO₄ is concerned, we observe a similar behavior. However, compared to CaCO₃ the energy release is slightly lower (ΔG =-83.6 kcal/mol for more stable products) and the proton transfer is less

exothermic (ΔG =-56.8 kcal/mol). Moreover, for CaSO₄, only the first reaction with HNO₃ is spontaneous (ΔG =-56.8 kcal/mol). The second passes through a transfer of protons in two distinct transition states that have similar relative free energy (ΔG TS_{2Aa}=-59.5 kcal/mol with a barrier of 24.1 kcal/mol and ΔG TS_{2Ab}=-61.8 kcal/mol with a barrier of 6.3 kcal/mol). CaSO₄ has a lower tendency to absorb a proton from the second molecule of HNO₃, compared to the case of CaCO₃, explaining a less important inhibitory.

Finally, the reaction between ammonium nitrate and CaCO₃ or CaSO₄ leads to similar reaction products: in both cases Ca(NO₃)₂ and an acid molecule, H₂CO₃ or H₂SO₄. This last step represents another significant difference between CaCO₃ and CaSO₄ in terms of stabilization effect on AN. H₂CO₃ decomposes preferentially into CO₂ and H₂O. H₂SO₄ can decompose into SO₃ and H₂O, or react with AN. This latter reaction produces NH₃ and HNO₃ with a barrier of 9.9 kcal/mol while H₂SO₄ decomposes into SO₃ and H₂O with a Δ G of 11.1 kcal/mol. H₂SO₄ exerts a catalytic effect of AN decomposition, as seen experimentally,³¹ that would balance the stabilizing effect of inhibition due to the production of stable aggregates. This could explain the inert behavior rather than inhibitor observed experimentally for CaSO₄. Theoretical results are consistent with the results shows in the experimental tests, in which increasing the concentration of CaSO₄ in the AN mixture does not cause an increase in the decomposition temperature.¹⁵

To conclude, the detailed analysis of the reaction energy profile of ammonium nitrate decomposition in the presence of CaCO₃ and CaSO₄ reveals the molecular mechanisms, which support their role as stabilizer substances in AN formulation. Indeed, both carbonates and sulfates, capturing an acid proton from the AN, can avoid the production of highly reactive radicals from the decomposition of pure AN. They lead to similar reaction mechanisms, characterized by the formation of a stable product $Ca(NO_3)_2$ and an acid: H₂CO₃ for calcium carbonate and H₂SO₄ for calcium sulfate. However, while carbonic acid decomposes into H₂O and CO₂, sulfuric acid could interact with AN, partially balancing the above mentioned stabilizing effect of deprotonation. These results are in agreement with the experimental observation: CaSO₄ has a profile more similar to an inert than to an inhibitor of AN decomposition (clearly observed in the case of CaCO₃). More generally, these results show how modern computational techniques, based on accurate quantum mechanical methods (e.g., DFT), can make an important contribution to improve the knowledge about the aggregate reaction mechanisms, such as compatibility and incompatibility phenomena. In particular, this study shows how the theoretical approach can complement experimental tests to reach an understanding of the stabilizing or destabilizing effect observed in the various types of additives that are put in contact with AN.

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Chapter 3

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CHAPTER 4

Theoretical study of the decomposition of ammonium nitrate in presence of ammonium sulfate

In this chapter, the study on the reactivity of ammonium nitrate in the presence of ammonium sulfate is presented. The mixture of these two salts was the cause of a major accident at the beginning of the 20th century in Germany. So far, no explanation has been found to justify the unpredictable behaviour of ammonium sulfate in the presence of ammonium nitrate, so a theoretical study was performed to clarify the reaction mechanism between these two salts. The chapter will be structured as follows: the physical and chemical properties of ammonium sulfate (AS) are firstly described; then the various industrial production processes and its uses are reported. A detailed description of the incident of Oppau, where ammonium nitrate was in formulation with ammonium sulfate, is presented. All experimental studies on the behaviour of ammonium sulfate in presence of ammonium nitrate are given. The aim is to better understand the nature of the AN/AS mixture. Finally, a theoretical study is presented, trying to provide a possible reaction mechanism between the two salts. The last part of the chapter is devoted to another theoretical work of ammonium salt similar to ammonium sulfate: the di-ammonium phosphate (DMP). The aim was to determinate if DMP, due to the structural similarity with AS could present its same unpredictable behaviour.

1 Properties and production of Ammonium Sulfate

1.1 Physical-chemical properties

As reported in Ullmann's Encyclopedia of Industrial Chemistry¹, ammonium sulfate (AS, (NH₄)₂SO₄) was industrially produced at the beginning of the 20th century from coal firing gases. At that time, ammonia started to be synthesized at the industrial scale; and given the abundance of ammonia, ammonium sulfate became a widely used fertilizer. However, its fame has diminished over time, due to the advent of more concentrated nitrogen fertilizers. Since 1960, (NH₄)₂SO₄ has been mostly produced as a co-product in organic synthesis. Nowadays, its production is made in different ways, such as from gypsum.¹ Ammonium sulfate has a molar mass of 132.14 g/mol, and its average specific heat capacity between 2 and 55 degrees is equal to 1.423 J/gK.¹ In this range, AS has a bipyramid rhombic crystalline structure. The size of the crystals can be influenced by the substances contained in the crystallization solution; this is a factor that has to be taken into account carefully in the commercial sector. Figure 1 shows the solubility of (NH₄)₂SO₄ in water: the salt does not form hydrates, the integral heat of the solution at dissolution is 6.57 kJ/mol at 30 °C. The addition of ammonia influences the solubility of the ammonium sulfate. Therefore, the solubility of AS is considerably reduced by the addition of ammonia: at 10 °C, from 73 g of (NH₄)₂SO₄ in aqueous solutions of ethanol, propanol, butanol, acetone, pyridine, is very low. Two phases are formed: one aqueous

and the other of the organic solvent. The unique stainless steel Cr-Ni is resistant to solutions of ammonium sulfate and solutions of salt in sulfuric acid. ¹



Figure 1. The solubility of ammonium sulfate in water¹

1.2 Production of ammonium sulfate

The procedures to synthesize ammonium sulfate essentially are:1

- 1. Production from coke-oven gas
- 2. Production from ammonia and sulfuric acid
- 3. Production from organic syntheses, such as the production of caprolactam
- 4. Production from gypsum, ammonia, and carbon dioxide.

These processes are described to introduce the accident of Oppau plant (Germany, 1921).



1. Production from coke-oven gas

In the last thirty years, the production of ammonium sulfate from coke oven gas has declined significantly. One of the leading causes has been the partial closure of steelworks and the development of coke oven processes, with a consequent decrease in the production of ammonium sulfate. This process involves the direct use of non-purified coke oven gas, which is introduced into sulfuric acid, giving the production of ammonium sulfate, but which is contaminated with colored tar products. In the long treatment process, water is used to remove ammonia from the coke oven gas. The ammonia is then released with a lime suspension which is placed inside the sulfuric acid, generating ammonium sulfate.

2. Production from ammonia and sulfuric acid

With an acid concentration of 70%, it is possible to evaporate all the water using the reaction heat generated by the reaction between the ammonia and sulfuric acid.

(1)
$$2NH_3(g) + H_2SO_4(1) \rightarrow (NH_4)_2SO_4(s)$$
 $\Delta H = -274kJ/mol$

This reaction is done in devices called saturators, where the process of saturation neutralization and crystallization are carried out in a single device. Sulfuric acid is sent to the suction side and ammonia to the pressure side of the forced circulation pump. The salt generated is discharged to the lower end of the saturator, centrifuged, dried, and cooled.

3. Production from organic syntheses, such as the production of caprolactam

In this kind of process, ammonium sulfate is a waste product generated by the production of synthetic fiber intermediates. Examples are caprolactam, acrylonitrile, and methyl methacrylate. Caprolactam, used for the production of nylon 6, produces between 2.5 and 4.5 ton of ammonium sulfate per ton of solution. Crystallizers are used to precipitate it from the reaction environment, to separate the ammonium sulfate from the solution.

4. Production from gypsum, ammonia, and carbon dioxide

This process was developed by BASF during the First World War and involved finely divided gypsum $(CaSO_4)$ and ammonium carbonate $((NH_4)_2SO_4)$:

(2)
$$CaSO_4*(2H_2O) + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$$

The products of the reaction are a mixture of calcium carbonate and ammonium sulfate. The ammonium sulfate solution is filtered, then acidified with H_2SO_4 , and finally processed in multistage evaporation crystallizers to form coarse-grained ammonium sulfate.

2 The accident at Oppau plant, Germany (1921)²

The chemical plant of Oppau was an industrial center of the BASF (originally: Badische Anilin- & Soda-Fabrik). In this plant, nitrogen fertilizers were produced according to an innovative new method, which allowed the high-pressure synthesis of ammonia.

The BASF production plant site was located close to the Rhine river near the Oppau village. On Wednesday 21st September 1921, at 07:32:14 local time, the Oppau factory was semi-destroyed by two apocalypticsized explosions within four seconds of each other (the second explosion was at 07:32:18 local time). The second explosion was the most devastating. The number of deaths recorded, according to official investigations, were around 559, 1977 injured and 1870 homeless. The Oppau plant has been severely damaged (Figure 2), and at the center of the explosion, an enormous circular-shaped crater was formed: 96 meters wide, 165 meters long, with a depth of 18.5 meters.



Figure 2. Photograph of the BASF Oppau factory after the accident of the 21st September 1921 explosion, with the Rhine river in the background and a northeastern direction.²

The Oppau plant has been severely damaged (Figure 2), and at the centre of the explosion, an enormous circular-shaped crater was formed: 96 meters wide, 165 meters long, with a depth of 18.5 meters. After a short period from the explosion, it was filled with groundwater. At that time, the municipality of Oppau had about 7500 habitants. Buildings that were at a distance of 500-1500 meters were destroyed or severely compromised. 1036 buildings located at a distance of up to 600 meters were razed to the ground, 928 buildings at a range of 900 meters were damaged. The remaining 89 were slightly damaged. The sound of the explosion was heard in Munich, almost 300 km south-east, as well as in Zurich and Göttingen.

2.1 Investigations after the disaster of Oppau

As described in the report of Tor E. Kristensen, the Oppau case was the most catastrophic accident in the history of the chemical industry, and it remained among the worst industrial disasters to the present day.² The Oppau plant had integrated all the ammonium sulfate production processes: from the reception of coal to the production of gas, ammonia synthesis, conversion into solid nitrogen fertilizers, storage of fertilizers nitrogen in silos and the shipment of finished products.² Investigation clarified that the explosion did not occur at the ammonia production level, but during storage in the silo number 110.² This storage silo contained about 4500 tons of AS of which only 10% gave rise to the explosion.² From that moment, all hypotheses were focused on the content of this silo. Ammonium nitrate, which was used for war purposes, was converted to agricultural fertilizer at the end of the First World War.² The reaction of the Bavarian state to the accident was immediate, with the appointment in the same afternoon of the crash of a commission, called the Bavarian Commission that became operational a week later on September 28th, 1921. The Weimar Republic (Reichstag) too appointed a committee of inquiry on September 28th, 1921. It was then decided that the two commissions should work independently from each other, but that they should hold joint meetings in Oppau or Berlin.² The Bavarian Commission was composed of members with technical and scientific expertise. It focused its interest on clarifying issues relating to the production, storage, and transport of ammonium nitrate and ammonium sulfate.² Their work consisted of studying documentary materials such as drawings, protocols, plants, interviewing staff, and analyzing data.² The Reichstag commission was composed of political members representing the Reichstag. Famous scientists from outside Germany also took part in the study of the Oppau case, such as: the Scottish chemist and engineer Sir Robert Robertson, the chemist and engineer Sir Richard Threlfall, the Nobel prize winner Sir William Henry Bragg, and the explosives and ammunition specialist Godrey Rotter, who worked at the Woolwich Research Department in London.²

2.2 Characteristics of Oppau salt

Ammonium nitrate is exceptionally hygroscopic and deliquescent, and it was decided to improve its composition through the addition of potassium or AS (ammonium sulfate) also called Ammonsulfatsalpeter in German or ASN.² The ideal composition of Oppau's ASN salt had a ratio of 50% by weight of AN and 50% by weight of AS, and its content of mechanical mixtures compared to double salts was not entirely controlled. Since 2AN:AS double salt in its pure form contains 54.8% AN and 45.2% AS, close to that used in Oppau, the product involved in the explosion is often, but inaccurately, identified as 2:1 double salt (or 55:45 mixtures by weight).² A more precise characterization of the crystalline structure of the double salts of AN/AS has only been done recently, in 2010.^{3,4}

As said before, the origin of the explosion occurred in silo 110. So in the first hypothesis, the caused was the use of explosives to break the agglomerated zones of the fertilizing salt. The use of explosives for the demolition of packed areas of a solid mixture is a very drastic measure, mainly when applied to a known explosive substance (AN). The ASN salt, despite the reduced hygroscopicity given by the addition of ammonium sulfate, is still tended to solidify during storage. The explosive used to break ASN solid cake was Perastralit in cartridges, composed exactly of 72% AN, 16% aluminium and 12% trinitrotoluene and ten parts of the army explosive loss (72% AN, 10% potassium perchlorate, 15% nitrogen compounds, and 3% wood flour).²

2.2.2 The hypothesis of contamination of ASN salt with incompatible substances

To justify the intrinsic explosive character of ASN, the focal point of the research became the study of AN contamination. which could be due to contamination by azides, hydrazine, chlorates, perchlorates, elemental sulfur, and nitrogen trichloride.² Very accurate researches were then carried out into the purity of Oppau's salt, getting negative result about its contamination: the absence of these substances was established definitively thanks to the use of targeted experiments that excluded not only the total contamination of the substances mentioned above but also other substances such as sulfides, sulfites, thiocyanates, and pyridine.² The only contamination found was a minimal amount of organic material (carbohydrates) equal to 0.03%.² Although the presence of the contaminants mentioned above had been excluded, the salt of Oppau contained known impurities due to the production processes: ASN contained 0.3% of sodium chloride (NaCl),⁵ and up to 0.35% of rust (iron oxides) that gave a yellow-brown colour to the salt of Oppau.² The last one specific impurity came from the production plants that were built of ferrous materials.² Furthermore, ASN salt was very hygroscopic, even if it was less than pure AN, containing humidity ranging from 1 to 4%.² Besides, several samples were collected by investigators shortly after the start of the investigation. Sample analyses were carried out in both Germany and Great Britain.⁶⁻¹² After the explosion, some samples of the silo 110

112 (the silo closest to 110 one) were sent to analyze in an attempt to understand its causes: primarily the accidental phenomenon of contamination was investigated.² The results of the analysis confirmed that the salt of Oppau had been seen to be rather pure, and the explanation lies to the fact that ammonium sulfate is produced from gypsum, a process that makes it mainly free from the most of possible contamination.² No contaminants such as free acids, pyridine, or thiocyanate have been found. However, ASN contains a small percentage of water.² No explosive substances, such as hydrazine or nitrogen chlorides, which can act as detonators for the salt of Oppau have been found.² Neither ammonium nitrite nor any other substantial ammonium nitrite that is easy to oxidize, have been found.^{2,12} Even the hypothesis of spontaneous heating is to be eliminated.² The Oppau salt contains so few impurities that this scenario was considered impossible.¹¹ It is essential to specify that the salt of Oppau did not contain free ammonium nitrate but consisted entirely in the combination of its two components. The only possible contamination seen is the content of a small amount of water that seems to have an influence only in the cooking of the salt.² This can be explained more easily by assuming that small crystals would form from the small amount of solution and it was also found that in the presence of a small percentage of water, the salt tended to bind.² This investigation seems to demonstrate that there is nothing intrinsically dangerous or suspicious about Oppau salt in that it regains the content of impurities that could lead to chemical decomposition, or through the possession of particular physical properties that could induce heat on undergoing some transformations.¹¹ Once it had been demonstrated that Oppau salt did not present any contamination, a new hypothesis has been introduced.² A possible explanation could be in a different sensitivity of ASN salt to detonation based on the composition in terms of the ratio AN/AS.¹³ In this regard, the Bavarian Commission in a report of 1922 carried out a study on the effects of the introduction of a spray system presented in the Oppau production.² It is important to note that AN and AS have different solubility in water and AS has the lowest one.² The ASN mixed salt is produced by adding solid AS to a boiling and concentrated ammonium nitrate solution, maintaining the stoichiometric quantity of 50/50. Because of the different solubility, AS is generally not well dissolved in the solution, and to improve the dissolution a spraying system was introduced to help AS to better mix in the AN solution. It has been seen that AS crystallizes before AN, leading to a demixed zone, further separating the two salts instead of joining them in the single ASN salt.¹² This inhomogeneity may have led to an increase in the explosiveness of ASN salt. The formation of the fine dust, generated from the demixing process, can have been accumulated in the silo, presenting a concentration of AN higher than 55%. To summarize, the introduction of the spraying process can have the following disadvantages:¹³

- Formation of a quantity of fine fraction with AN content higher than 55% more sensitive to detonation than the ASN salt with 50/50 AS-AN composition.¹³

- An undefined amount of ASN in a 50/50 ratio with increased sensitivity due to the variation in diameter and density of salt particles, with an increased amount of water and irregular crystals.¹³

Already during the production of ASN salt at the Oppau site it was well known that if AN exceeded the concentration of 55 %, the mixture of the two salts could be explosive. However, according to the technical knowledge of the time, all necessary measures had been taken to ensure that the concentration and ratio between the two salts AS and AN remained stable at 50:50.¹³ Unfortunately, the effect of the spray system and the potential demixing that it could have had not considered. The variation of the size of salt granules, combined to the demixing effects could have formed a much more sensitive area predisposed to detonation.¹³ Unfortunately, if the events went in this way, nowadays it is not anymore possible to know because the possible sensitized to detonation salt has been lost during the explosion. What can be done right now is to study the various effects that ammonium sulfate exerts on AN, through different techniques, i.e., ballistic and calorimetry experiments, software capable of predicting explosive reactions and, last but not least, molecular modelling. In the following paragraphs are reported all the experimental data available in the literature about the interaction of ammonium sulfate in the presence of ammonium nitrate, in order to have a global view of its reactivity.

2.3 The state of the art on the interaction of ammonium nitrate in the presence of ammonium sulfate

2.3.1 Analysis conducted by the Royal Armament Research and Development Establishment¹⁴

Royal Armament Research and Development Establishment (RARDE) experiments conducted on mixtures of ASN salts, with the variable-ratio between AS and AN, are in contrast with the conclusion of the previous studies about the stability of the Oppau salt.¹⁴ The experiments carried out by RARDE, consist on measuring the different effects in the ballistic mortar generated by different types of AS-AN mixtures, to measure the possible explosiveness of these at different concentrations of the two salts.¹⁴



Figure 3. B.M. values of $AN/(NH_4)_2SO_4$ mechanical mixture.¹⁴



Figure 5. B.M. values of co-Cryst AN/(NH₄)₂SO₄1:1, 2:1, 3:1 molar, nominal.¹⁴



Figure 4. B.M. values of AN/(NH₄)₂SO₄ co-Cryst 1:1 salt.¹⁴



Figure 6. Theoretical B.M. values of AN/(NH₄)₂SO₄ mixture.¹⁴

Figure 3 shows the behaviour of a mixture of ammonium nitrate and sulfate obtained mechanically, i.e., the two salts were mixed and not crystallized together.¹⁴ Here three different concentrations of the salt are shared: in the first one the AN percentage is less than 50%, and the explosiveness of the mixture is inferior to the one of pure AN.¹⁴ But at AN concentration higher than 50% the explosiveness is higher than the one of pure AN.¹⁴ In Figure 4 is shown the trend of a 1:1 mixture of co-crystallized ammonium nitrate and sulfate salts.¹⁴ Here it is evident that when AN concentration is higher than 50% the explosiveness of the mixture is higher than the one of pure AN.¹⁴ Figure 5 shows three mixtures of co-crystallized ammonium nitrate and ammonium sulfate salts in different ratios: 1:1, 2:1, 3:1. Figure 6 presents a trend in which the mixture of AN:AS is a curve with a shape reminiscent of the letter S.¹⁴

Comparing these curves, it is clear that the ASN salt, contrary to the results of previous analyses conducted on the salt of Oppau, has an intrinsic hazard that is expressed only in some conditions.¹⁴ It is possible to affirm that AS behaves in some circumstances as an inhibitor of decomposition of ammonium nitrate and in others as a promoter of AN decomposition.¹⁴ The different explosiveness presented in Figure 6 are values obtained by theoretical calculation about the different explosive oxidation of AS in the presence of AN given by the generation of oxygen.¹⁴ In other words, the explanation given by the RARDE tests is that when AS acts as a promoter, it is because the following reaction occurs, where (NH₄)₂SO₄ is oxidized by the oxygen generated by the decomposition of ammonium nitrate:¹⁴

(3)
$$(NH_4)_2SO_4 + O_2 \Rightarrow N_2 + 2H_2O + H_2SO_4 + 85$$
 Kcal/mol

Figure 6 reports the results extracted from the previous reaction at different concentration of AS and O₂. The area where the values in which the explosiveness is less intense can be attributed to an endothermic decomposition of $(NH_4)_2SO_4$.¹⁴ Here AS acts as an inhibitor. When the explosive values are higher, AS tends to be oxidized, generating exothermically as products of the reaction N₂, H₂O, and H₂SO₄.¹⁴ According to RARDE experience, the oxidation of AS is an exothermic reaction (-85 Kcal/mol), more exothermic than the decomposition of pure ammonium nitrate (-27.6 Kcal/mol).¹⁴ The oxygen released by AN is used by the ammonium sulfate to oxidase itself.¹⁴ This means that the quantity of ammonium nitrate required to oxidase the maximum quantity of ammonium sulfate occurs when the explosion heat of the ammonium nitrate (E_{explAN}) is equivalent to the oxidation heat (E_{ossAS}) of the ammonium sulfate.¹⁴

(4) $E_{explAN} = E_{ossAS}$ x=AN's quantity ; y = 1-x = AS's quantity $\frac{27.6}{80}x = \frac{85}{132}(1-x)$ X = 0.65 Y= 0.35

The equation number 4, once solved, shows that the maximal oxidation of AS from AN happens when the concentration of AN is 65% of the mixture, and thus 35% of AS .^{13,14} In Figure 6 this point corresponds to the maximal peak, where the explosiveness is the highest represented. Also Vythenis Babrauskas, in its study about the influence of additives and contaminants on ammonium nitrate, reports the same trend of the behavior of the salt of ASN.¹⁵

2.3.2 New information about the Oppau accident given by the EXPLO5 V6.02 program

After the Oppau accident, researchers have strengthened their analysis of the dynamics disaster proceeding through thermochemical considerations.⁶ The initial results presented during the immediate years following the accident have now been re-evaluated and brought about through the application of modern calculation methods, using software capable of deriving these thermochemical values very accurately.² In Figure 7, the values calculated by the specialists of the Reichstag commission for the heat of AN-AS mixtures are shown in blue. With the techniques available at the time, the explosion heats were calculated by choosing mixtures corresponding to available stoichiometric ratios of the two salts; then possible reaction products were postulated (H₂O, N₂, SO₂, H₂ or O₂).⁶



Figure 7. The (negative) heat of explosion of AN-AS mixtures as calculated by the Reichstag commission in the 1920s (blue line), compared to the (negative) isobaric heat of combustion of the same mixtures calculated with EXPLO5 V6.02 (red line). Image is taken by Tor E Kristensen Report.²

The researchers of 5% Reichstag commission calculated the explosion heat through a simple enthalpy analysis starting from the products they hypothesized had been formed.⁶ In the report presented by Tor E. Kristensen were presented the results obtained by a thermochemical calculation program, EXPLO5 V6.02, which determined with reasonable accuracy the isobaric heat of a combustion reaction. Figure 7 shows the two explosion graphs; the curves calculated are the blue one proposed by the Reichstag commission and the red one by the EXPLO5 V6.02 program. The sign of the heat involved during the reactions represented has been inverted from negative to positive for simplicity of reading. Figure 7 shows that the curve generated by the computational analysis does not differ significantly from the curve proposed in the 1920s. However, it should be noted that the combustion heat of the AN-AS mixtures presented in Figure 7, it is shown that

starting from the composition of ASN equal to 55:45 of AN: AS (which corresponds to the double salt 2AN: AS) an inversion point occurs so that one enters a rich zone of oxidizing reactions.² This event occurs because of the transition from an oxidant-poor decomposition zone below point 55:45 to a highly oxidizing decomposition zone above this point.² In point 55:45, decomposition products consist almost exclusively of H₂O, N₂, and SO₂.² In conclusion, the range up to 55:45 AN: AS has been identified as particularly critical concerning the energy behaviour of AN-AS.⁶ The Oppau explosion, however, is almost certainly coupled with the detonation rather than the isobaric explosion.² In a detonation event, as opposed to isobaric combustion in atmosphere conditions (Figure 7), the detonation products first reach equilibrium at the end of a reaction, at very high pressures and temperatures, and then expand in an attempt to reach the environmental conditions.² In the 1920s, the theoretical frameworks that could predict such an event of detonation did not yet exist.² So scientists had to rely more on their intuition than on the available knowledge.² For this reason, the technical-scientific experts of both commissioners appointed in September 1921, were unable to highlight a specific behaviour of AN: AS, during a possible event of detonation.² Thanks to the use of a more recent tool, EXPLO5 V6.02, to study the reactions of detonation, the picture obtained (Figure 8) is more different than that presented in the graph of the heat of the previous explosion.² The detonation heat for AN: AS mixture increases until it reaches an inversion point corresponding to the AN: AS ratio of about 65:35, where the stoichiometry is the 3AN: AS, and then decreases slowly towards the pure AN (Figure 8).²



Figure 8. The (negative) heat of detonation of AN-AS mixtures calculated with EXPLO5 V6.02 at a constant density of 1.1 g·cm-3 (using the BKW EOS) compared to the (negative) heat of explosion (combustion) as calculated by the Reichstag commission in the 1920s. Image is taken by Tor E Kristensen Report.²

Unlike the thermochemical analysis conducted in the 1920s, according to the results of EXPLO5 V6.02 software, the heat developed by the AN-AS mixtures continues to grow significantly beyond point 2AN: AS (55:45) to point 3AN: AS (65:35).² This is crucial because it suggests that the decomposition heat generated by the AN: AS mixtures does not decrease beyond inversion point 55:35, but decreases after rotation point 65:35.² It could mean that the AN-AS mixtures acquire an oxidative boost in the range between 50:50- 65:35 AN: AS.² The point 65:35, pronounced in both Figures 8 and 9, looking at the prediction software results, are associated with the formation of H₂O, N₂, and H₂SO₄ as the only majority detonation products.²



Figure 9. The number of gaseous reaction products and detonation temperatures of AN-AS mixtures calculated with EXPLO5 V6.02 at a constant density of 1.1 g·cm-3 (using the BKW EOS). Image is taken from Tor E Kristensen Report.²

In Figure 9 are showed and compared the curves obtained in Figure 7 (isobaric heat of explosion) and Figure 8 (heat of detonation).² The most marked difference between the area around the composition of ASN 55:45 and that around 65:35 is given by the formation of sulfuric acid which is predominantly in liquid form (it is condensed given the high pressures to which it is subjected).² All this is shown in Figures 8 and 9.² Sulfuric acid is a detonation product where the sulfur is in its maximum state of oxidation.² The Reichstag Commission of 1920 considered as a possible initial product of the explosion sulfur trioxide (SO₃) which decomposed into SO₂ and oxygen.² Consequently, only the latter species were considered credible end products, as in Figure 7.² Since the process of dissociation of sulfur trioxide is endothermic, part of the evolved heat of detonation is consumed, lowering the temperature of detonation: this is the origin of the differences between Figures 7 (isobaric conversion) and 8 (detonation conversion). In the analysis presented by Tor E. Kristensen, the role and the formation of sulfuric acid was not well clarified.² Anyway, the formation of sulfuric acid between the ASN decomposition products could shed light on another aspect of the Oppau explosion.² Some cases of harmful irritation due to the cloud of gas and dust formed after the explosion was reported in the press.¹⁶ A cloud of dust perhaps combined with aerosols of sulfuric acid

(possibly containing other types of irritating sulfur) could have had an unpleasant and detectable influence on the people who were in the vicinity of the Oppau factory after the explosion.²

2.3.3 Other experimental studies

More recent calorimetry work has been conducted to determine whether ammonium sulfate is capable of stabilizing or destabilizing ammonium nitrate. However, this results would go against what emerges in calorimetric tests where AS concentrations equal to 5% would increase the decomposition temperature of AN, showing clear inhibitory behaviour,¹⁷ passing from a temperature of decomposition for pure ammonium nitrate of 292°C to 312°C when AN, during DSC calorimetric test. However, in the same article, J.C. Oxley affirmed that when AN formulations were enriched with a variety of sodium or ammonium salts (SO_4^{2-} , BF4⁻, B4O7²⁻, HCO²⁻), AN formulations containing sodium salt were slightly more stable than those containing ammonium salt. It was concluded that the addition of the ammonium cation accelerates the decomposition of AN formulations, although this destabilization is not always evident if the anion is stabilizing. According to Oxley,¹⁸ solutions containing SO_4^{2-} produce pH values in the 4-5 range, and they are more basic than nitrate. When sulfate is mixed with AN as an additive, the SO_4^{2-} anion functions as a conjugated base of weak acids, which forms H_2SO_4 in the presence of NH_4^+ , and decreases the decomposition rate of AN,¹⁵ thus inhibiting its decomposition. The results of the RSST calorimetric experiments conducted by Zhe Han^{2,20-21} led to the conclusion that AS stabilizes ammonium nitrate and increases its decomposition temperature, passing from a Tonset of 200°C for pure AN, to 247 °C and 260°C for AN mixed with 0,1 % and then 0,5% of AS. So we have controversial results: on the one hand, the confirmation that the salt of Oppau ASN did not have the presence of contaminants capable of destabilizing it and the apparent behaviour as an inhibitor witnessed by the experiments of calorimetry. On the other hand, RARDE ballistic mortar experiments that tell us instead that there is an intrinsic danger of ammonium nitrate in the presence of ammonium sulfate that occurs because there is possible oxidation of $(NH_4)_2SO_4$ by the oxygen produced by NH_4NO_3 . The maximum oxidation of AS occurs when the AN: AS ratio is 65:35. These data are confirmed by the simulations carried out by the software EXPLO5 V6.02, which shows that starting from the ratio AN: AS equal to 50:50 to 65:35 creates an oxidation zone in which the two salts can give rise to products such as H₂SO₄, N₂, H₂O. These products are the same as those presented by the RARDE studies. There is, therefore, a coincidence of the data obtained at the ballistic mortar and those presented by the simulation software. In Figure 8, we also see that once the inversion point where AN: AS is in ratio 65:35 has passed, the heat of detonation decreases. The calorimetry experiments reported above were performed with percentages of AS between 5% and 20%, then in an area outside the oxidation zone where the incompatibility between AN and AS occurs. Therefore, in the theoretical study, the behaviour of AS in the

presence of AN will be first studied in an attempt to try to understand if a different behaviour as promoter or inhibitor emerges from AS when it comes into contact with AN.

3 Theoretical study of ammonium nitrate in contact with ammonium sulfate

As a first point in the study of the reactivity of $(NH_4)_2SO_4$, a full geometry optimization was carried out, for which the structure we refer to is reported in Figure 10. The level of theory used is M06-2X/6-311+G(2d,2p).



Starting from this structure, a study on the interaction of $(NH_4)_2SO_4$ with ammonium nitrate was conducted to highlight the reactivity of ammonium sulfate. The emphasis was placed on identifying the steps involved in the reaction mechanism between the two substances involved, considering that ammonium nitrate easily decomposes into nitric acid ($\Delta G = 5.4$ Kcal/mol, as discussed in Chapter 1), the reaction of ammonium nitrate with each of these species has been then studied. The $(NH_4)_2SO_4$ can react with nitric acid, hereafter referred as *path A*, or decomposing into ammonia and sulfuric acid as reported in *path B*. The reaction between ammonium sulfate and NH₃ did not present any results: it is for this reason that they do not appear in the study. The mechanism of the reaction of $(NH_4)_2SO_4$ with nitric acid is represented in two schemes: Schemes 1 for the *path A1*, and Scheme 2 for the *path A2*. The energy profile related to Scheme 1 is represented in Figure 13, and the energy profile related to Scheme 2 is reported in Figure 16. The whole reaction mechanism is reported in Scheme 3, while the corresponding energy profile is in Figure 18. The computed energies are also reported in Table 3. Also, the decomposition of the formed aggregates was taken into account: in Figure 14 is represented the decomposition for the aggregates $Aggr_{Aa}^*$, and Figure 17 for the decomposition of the aggregates $Aggr_{Ab}$. Total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.

3.1 Reactions between a molecule of HNO3 to (NH4)2SO4

As a consequence of the symmetry of the ammonium sulfate molecule (Figure 10), the two oxygen atoms number 2 (site a) and number 4 (site b) are equivalents. However, when nitric acid approaches $(NH_4)_2SO_4$, there are two possible types of attacks leading to two different types of aggregates. Therefore, the main reaction path can be divided into PathA1 and PathA2.

3.1.1 Description of the reactions along the PathA1

Once ammonium nitrate has decomposed into NH₃ and HNO₃, the latter can react with ammonium sulfate in the direction of oxygen 2, forming a first aggregate $[(NH_4)_2SO_4...HNO_3]_a$, whose ΔG is equal to 0,6 Kcal/mol. This reaction is immediately followed by another one in which a proton passes from nitric acid to sulfate oxygen 2 through a transition state TS1_{Aa}, which has a barrier of 4.2 Kcal/mol. Once the proton has completely shifted to the sulfate, Aggr_{Aa}^{*} is reached through a slightly exothermic reaction with a ΔG of 4.0 Kcal/mol. Moving from the transition state TS1Aa to the Aggr_{Aa}^{*} aggregate, it is verified that, due to the geometry of the structure, the ammonium molecule (NH₄⁺) closest to the nitrate gives it a proton, leading again to the formation of HNO₃. A study on the decomposition of Aggr_{Aa}^{*} was necessary to analyze whether the decomposition of Aggr_{Aa}^{*} could generate reactive chemical species capable of leading to incompatibilities, thereby destabilizing ammonium nitrate. All the compounds named in this section are reported in Figure 12, the pathway or reaction is in Scheme 1, the table of energies is in Table 1, while the corresponding energy profile is in Figure 13.



Figure 12. Aggregates and transition states s of the reactions of HNO₃ and (NH₄)₂SO₄ for PathA.

Scheme 1. Reaction PathA1 for the interaction between (NH₄)₂SO₄ and HNO₃.

$$NH_4NO_3 \longrightarrow HNO_3 + NH_3$$

$$Path A + (NH_4)_2SO_4$$

$$+ HNO_3 \qquad Path A1$$

$$[(NH_4)_2SO_4 \cdots HNO_3]_a$$

$$\int TS_{1Aa}$$

$$Aggr_{Aa}^*$$

	ΔE	ΔН	ΔG
NH ₄ NO ₃	0	0	0
$HNO_3 + NH_3$	13.5	14.0	5.4
PathA1			
$[(\mathrm{NH}_4)_2\mathrm{SO}_4^{\ldots}\mathrm{HNO}_3]_a$	6.7	-2.5	0.6
TS1 _{Aa}	8.1	-1.1	4.8
Aggr _{Aa} *	9.0	-0.3	4.0

 Table 1 Relative energies (kcal/mol) for the PathA.





Decomposition of $Aggr_{Aa}^{*}$

The theoretical results of the decomposition are presented on Figure 14. $Aggr_{Aa}^{*}$ can undergo eight decompositions, whose reactions are shown below:

(5) $Aggr_{Aa}^* \rightarrow NH_4 \cdots NO_3 + NH_4 + HSO_4$

- (6) $\operatorname{Aggr}_{Aa}^* \rightarrow \operatorname{NH}_4 \operatorname{NO}_3 \operatorname{NH}_4 + \operatorname{HSO}_4$
- (7) $\operatorname{Aggr}_{Aa}^* \rightarrow \operatorname{HNO}_3 \cdots \operatorname{NH}_3 + \operatorname{H}_2 \operatorname{SO}_4$
- (8) $\operatorname{Aggr}_{\operatorname{Aa}}^* \rightarrow \operatorname{HNO}_3 \cdots \operatorname{H}_2 \operatorname{SO4} \cdots \operatorname{NH}_3$

(9) $\operatorname{Aggr}_{\operatorname{Aa}^*} \rightarrow \operatorname{NH}_4\operatorname{NO}_3 \oplus \operatorname{H}_2\operatorname{SO}_4 \rightarrow \operatorname{TS}_{\operatorname{B3}} \rightarrow \operatorname{NH}_3 \oplus \operatorname{HNO}_3 \oplus \operatorname{H}_2\operatorname{SO}_4 \rightarrow \operatorname{NH}_3 + \operatorname{HNO}_3 + \operatorname{H}_2\operatorname{SO}_4 \rightarrow \operatorname{NH}_3 + \operatorname{OH}^* + \operatorname{NO}_2^* + \operatorname{H}_2\operatorname{SO}_4$

- (10) $\operatorname{Aggr}_{Aa}^{*} \rightarrow \operatorname{NH}_{4}^{\cdots}\operatorname{NO}_{3}^{\cdots}\operatorname{HSO}_{4} + \operatorname{NH}_{4} + \operatorname{NH}_{3} \rightarrow \operatorname{NH}_{4}\operatorname{NO}_{3} + \operatorname{HSO}_{4} + \operatorname{NH}_{4} + \operatorname{NH}_{3}$
- (11) $\operatorname{Aggr}_{Aa}^*$ \rightarrow HNO₃ + (NH₄)₂SO₄ \rightarrow OH[•] + NO₂[•] + (NH₄)₂SO₄

(12) $\operatorname{Aggr}_{\operatorname{Aa}^*} \rightarrow \operatorname{HSO}_4 \cdots \operatorname{HNO}_3 + \operatorname{NH}_4 + 2\operatorname{NH}_3 \rightarrow \operatorname{HSO}_4 + \operatorname{HNO}_3 + \operatorname{NH}_4 + 2\operatorname{NH}_3 \rightarrow \operatorname{HSO}_4 + \operatorname{OH}^* + \operatorname{NO}_2^* + \operatorname{NH}_4 + 2\operatorname{NH}_3$



Figure 14. Possible reaction paths for the decomposition of Aggr_{Aa}^{*}.

The reaction number 6 presents a decomposition in which $Aggr_{Aa}^*$ can split into NH_4 ... $NO_3 + NH_4 + HSO_4$, through a reaction that costs 119.5 Kcal/mol and that is not thermodynamically favoured. In decomposition number 6, our aggregates can decompose in chemical species such as NH_4 NO_3 $NH_4 + HSO_4$. This is an expensive reaction, which requires 99.7 Kcal/mol. In the decomposition reaction number 7, Aggr_{Aa}^{*}, through a ΔG of 13.2 Kcal/mol, generates products such as HNO₃ NH₃ + H₂SO₄ with a ΔG of 14.1 Kcal/mol we have the decomposition in HNO₃^{...}H₂SO₄^{...}NH₃, as shown in reaction number 8. Decomposition number 9, is composed of a series of reactions. From the decomposition of Aggr_{Aa}*, sulfuric acid is produced, which induces a new protonation of the nitric acid located within the structure of NH₄NO₃. Once the sulfuric acid has given up its proton, it is returned to it by a molecule of NH_4 , which becomes NH_3 . This reaction starts from NH₄NO₃⁻⁻H₂SO₄ (ΔG=8.6 Kcal/mol), passes through a TS2a (whose barrier is equal to 1.3 Kcal/mol) and ends with the formation of $[NH_3^{"}HNO_3^{"}H_2SO_4]$ ($\Delta G=8.8$ Kcal/mol). HNO₃ once formed, can detach and decompose into radical species OH' and NO2'. Decomposition in the two radicals requires the energy of 58.8 Kcal/mol. In the decomposition reaction number 10, Aggr_{Aa}* decomposes into NH₄...NO₃...HSO₄ + $NH_4 + NH_3$ with a ΔG of 0.7 Kcal/mol. It can further decompose into $NH_4NO_3 + HSO_4 + NH_4 + NH_3$, but through a higher ΔG , equal to 20.6 Kcal/mol. In decomposition 11, Aggr_{Aa}^{*} splits into HNO₃ and (NH₄)₂SO₄, returning to its starting point, i.e., before the nitric acid reacted and protonated the sulfate. This reaction requires a ΔG of 4.9 Kcal/mol, the same energy required by ammonium nitrate to decompose into NH₃ and HNO₃. Nitric acid, at this point, can decompose in the two radicals OH[•] and NO², with a ΔG of 45.6 Kcal/mol, the same barrier as the rate-limiting step of pure ammonium nitrate. The last reaction, the number 12, sees the decomposition of the aggregate in HSO_4 $HNO_3 + NH_4 + 2NH_3$, a spontaneous and slightly exothermic reaction that releases -3.4 Kcal/mol. This aggregate evolves into HSO₄ + HNO₃ + NH₄ + 2NH₃, passing through a necessary ΔG of 20.3 Kcal/mol. Free nitric acid here can decompose in OH[•] and NO₂[•] through a ΔG of 60.5 Kcal/mol. Among all the decomposition reactions shown for Aggr_{Aa}^{*}, the one that presents the most favourable final products following the whole decomposition path is the dissociation of Aggr_{Aa*} in its original components HNO₃ and (NH₄)₂SO₄. This means that the formation of the Aggr_{Aa*} aggregate does not ensure real stabilization of ammonium sulfate against nitric acid. In the previous chapter, it was seen how CaCO₃ and CaSO₄ were able to inactivate HNO₃ through the formation of aggregates thermodynamically much more stable than $Aggr_{Aa}^*$. The decomposition of the $aggregate[(NO_3)_2 CaCO_3H_2]$ into potentially dangerous species required extremely high energies. In the case of Aggr_{Aa}^{*}, the production of nitric acid from its decomposition is easily achieved, so HNO₃ can radicalize in OH[•] and NO₂[•], maintaining the same barrier of 40 Kcal/mol. Therefore, this means that, at least along the PathA1, the aggregate Aggr_{Aa}^{*} appears as an inhibitor not effective in stabilizing HNO₃.

3.1.2 Description of the reactions along the PathA2

In the case of the second reaction path, once the ammonium nitrate has decomposed into NH₃ and HNO₃, the latter reacts with the ammonium sulfate towards oxygen 4, forming a first aggregate $[(NH4)_2SO_4...HNO_3]_b$, whose ΔG is equal to 2.1 Kcal/mol. This reaction is followed immediately by another in which a proton passes from nitric acid to sulfate oxygen 4 through a TS1_{Ab} transition state, which has a barrier of 1.2 Kcal/mol. Once the proton has completely shifted to the sulfate, Aggr_{Ab} is reached through a slightly exothermic reaction with a ΔG of 0.43 Kcal/mol. The geometry of this aggregate does not allow the protonation of nitrate again. As previously done, a study on the decomposition of Aggr_{Ab} was conducted to see if there were any possible decompositions able to destabilize the ammonium nitrate. All the compounds named in this section are reported in Figure 15, the pathway or reaction is in Scheme 2, the table of energies is in Table 2, while the corresponding energy profile is in Figure 16.



Figure 15. Transition states and aggregates of the reactions of HNO3 and (NH4)2SO4.





Table 2 Relative energies	(kcal/mol)	for the PathA2.
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	ΔΕ	ΔН	ΔG
$\rm NH_4 NO_3$	0	0	0
$HNO_3 + NH_3$	13.5	14.0	5.4
PathA2			
$[(\mathrm{NH}_4)_2\mathrm{SO}_4^{\cdots}\mathrm{HNO}_3]_{\mathfrak{b}}$	7.8	-1.4	2.1
TS1 _{Aa}	7.5	-1.7	3.3
Aggr _{Ab}	3.3	-5.9	0.4



Figure 16. Gibbs Free Energy profile for the reaction between AN and (NH₄)₂SO₄ in PathA2.

Theoretical results of the decomposition of the Aggr_{Ab} are presented in Figure 17.

Decomposition of Aggr_{Ab}

As many as 5 decomposition reaction mechanisms have been identified and will be shown below:

- (13) $Aggr_{Ab} \rightarrow HNO_3 H_2SO_4 + NH_3 \rightarrow HNO_3 + H_2SO_4 + NH_3 \rightarrow NH_3 + OH' + NO_2' + H_2SO_4$
- (14) Aggr_{Ab} \rightarrow HNO_3 $\cdot\cdot\cdot$ H_2 SO₄ $\cdot\cdot\cdot$ NH₃ \rightarrow HNO₃ + H₂SO₄ + NH₃ \rightarrow NH₃ + OH[•] + NO₂[•] + H₂SO₄
- (15) $\operatorname{Aggr}_{Ab} \xrightarrow{\bullet} \operatorname{NH}_4\operatorname{NO}_3 \dots \operatorname{H}_2\operatorname{SO}_4 \xrightarrow{\bullet} \operatorname{TS}_{2Aa} \xrightarrow{\bullet} \operatorname{NH}_3 \dots \operatorname{H}_2\operatorname{SO}_4 \xrightarrow{\bullet} \operatorname{NH}_3 + \operatorname{HNO}_3 + \operatorname{H}_2\operatorname{SO}_4 \xrightarrow{\bullet} \operatorname{NH}_3 + \operatorname{OH}^{\bullet} + \operatorname{NO}_2^{\bullet} + \operatorname{H}_2\operatorname{SO}_4$
- (16) $Aggr_{Ab} \rightarrow NH_4NO_3 HSO_4 \rightarrow NH_4NO_3 + HSO_4$
- (17) $Aggr_{Ab} \rightarrow NO_3 \dots NH_4 \dots HSO_4 \rightarrow NH_4 NO_3 + HSO_4$



Figure 17. Possible reaction paths for the decomposition of Aggr_{Ab}.

In reaction 13, Aggr_{Ab} first decomposes into HNO₃"H₂SO₄ + NH₃, with a Δ G of 20.7 Kcal/mol. The decomposition continues with the formation of HNO₃ + H₂SO₄ + NH₃ (Δ G= 18.6 Kcal/mol) which ends with the radicalization of HNO₃ (NH₃ + OH' + NO₂' + H₂SO₄) for which 58.8 Kcal/mol are required. Decomposition number 14 is equal to decomposition number 1, except for the first step where the starting species is HNO₃"H₂SO₄"NH³ (Δ G= 13,1 Kcal/mol). Decomposition number 15 sees the formation of ammonium nitrate in the presence of sulfuric acid H₂SO₄ (Δ G=8.6 Kcal/mol) which, through a transition state TS_{2a} with a barrier of 1.3 Kcal/mol, protons nitrate from NO₃" to HNO₃. At the same time, H₂SO₄ has formed again, due to the transfer of a proton by NH₄, which becomes NH₃, thus resulting in the formation of NH₃"HNO₃"H₂SO₄ (Δ G=18.6 Kcal/mol). The free nitric acid can at this point decompose in NH₃ + OH' + NO2' + H₂SO₄, the Δ G required for this reaction is equal to 58.8 Kcal/mol. Reaction 16 and 17reach the same products as NH₄NO₃ + HSO₄ (Δ G=14.9 Kcal/mol), starting from one of NO₃"NH₄"HSO₄ (Δ G=0.8 Kcal/mol) and the other from NH₄NO₃"HSO₄ (Δ G=1.0 Kcal/mol), which, although similar, have two slightly different spatial geometries. The different geometry of Aggr_{Ab} compared to Aggr_{Aa}^{*} does not allow the reproducibility of nitrate. In the decompositions shown in Figure 17, although there is the possibility of HNO₃ formation during a decomposition reaction, the formation of the two reactive radicals OH' and NO₂'

requires a more energetic path than the reaction that causes $AggrAa^*$ to return to its initial reagents. Therefore, it is possible to say that $Aggr_{Ab}$ is a stabilizer compared to $AggrAa^*$, producing a lower risk of giving rise to unpredictable reactions.

Considerations on the decomposition of Aggr_{Aa}^{*} and Aggr_{Ab}

After the considerations made on the different decompositions of the two aggregates $Aggr_{Aa}^*$ and $Aggr_{Ab}$, returning of the Scheme 1, many considerations are necessary. Looking at the thermodynamic profile proposed in Scheme2 and Scheme3, it is evident that the only one destabilizing reaction for ammonium nitrate is the decomposition number 12 of $Aggr_{Aa}^*$. Starting from here, the formation of free HNO₃ separated by $(NH_4)_2SO_4$, leads to the destabilization of NH₄NO₃. It is possible to affirm that there is, therefore, a reaction route that shows that the intrinsic acidity of the ammonium cation NH₄ does not allow a complete stabilization of AN and that therefore the regenerating HNO₃ can decompose as if there were no interference from the ammonium sulfate inhibitor. Therefore, given the new formation of HNO₃ in the presence of $(NH_4)_2SO_4$, it can decompose in the usual OH[•] + NO2[•] radicals, which start an exothermic and multistep process that sees the final formation of products such as O₂, H₂O, N₂ and OH, following the number 18:

(18) $HNO3 + (NH_4)_2SO_4 \rightarrow OH^* + NO2^* + (NH_4)_2SO_4$

However, other radical reactions by HNO_3 could be tested. Starting from $Aggr_{Aa}^*$, it could decompose into two radicals according to reactions 19 and 20:

(19) $\operatorname{Aggr}_{\operatorname{Aa}}^* \rightarrow \operatorname{OH}^{\bullet} + [\operatorname{NO}_2^{\cdots}(\operatorname{NH}_4)_2 \operatorname{SO}_4]^{\bullet}$

(20) $\operatorname{Aggr}_{\operatorname{Aa}}^* \rightarrow \operatorname{NO}_2^{\cdot} + [OH^{\cdots}(NH_4)_2SO_4]^{\cdot}$

Starting from these decompositions, a possible radical chain could be studied if the barrier of formation of the radicals presented in reactions 19 and 20 is lower than the barrier of decomposition of nitric acid, which is equal to 40 Kcal/mol.

However, from an experimental point of view, after the oxygen formation from AN decomposition,¹³ $(NH_4)_2SO_4$ can be oxidized leading to the formation of N₂, H₂O and H₂SO₄. The theoretical ΔG calculated for the oxidation of $(NH_4)_2SO_4$ (equation 21), is equal to -389 Kcal/mol.

(21) 2 (NH₄)₂SO₄ + 3O₂ \rightarrow 2N₂ + 6H₂O + 2H₂SO₄

The possibility of in oxidation in AS, linked to the Oppau case, has already been hypothesized experimentally by the RARDE experience, and by the EXPLO5 V6.02 software. In the RARDE experiments this oxidation is attributed to the formation of oxygen in the reaction environment coming from AN. The EXPLO5 V6.02 software lists the hypothetical main products of decomposition: N_2 , H_2O , H_2SO_4 . Equation

21, if confirmed by a reaction path that explains the formation of O_2 in the reaction environment, could explain the instauration of un incompatibility between AN and $(NH_4)_2SO_4$.

3.2 Description of the decomposition of (NH4)2SO4 into NH3 and H2SO4 (PathB)

Since the formation of sulfuric acid H_2SO_4 appears to be a key step in the explanation of the hazard associated with ammonium sulfate from an experimental point of view,² a decomposition study of $(NH_4)_2SO_4$ was carried out. The aim was to see if $(NH_4)_2SO_4$ had a greater tendency to react with HNO₃ or to decompose into NH₃ and H₂SO₄. The PathB, shared in Scheme 3, sees the rupture of $(NH_4)_2SO_4$ into two molecules of NH₃ and one molecule of H₂SO₄. This reaction requires a ΔG of 13.2 Kcal/mol. Therefore, this reaction is disadvantaged both with respect to the decomposition of ammonium nitrate into NH₃ and HNO₃ and with respect to PathA. In fact, PathA will be the preferred reaction route, and this means that $(NH_4)_2SO_4$ has the tendencies to react with HNO₃ rather than to decompose.



Figure 18. Gibbs Free Energy profile for the reaction between AN and (NH₄)₂SO₄.


Scheme3. Reaction mechanism between NH₄NO₃ and (NH₄)₂SO₄.

Table 3 Relative energies (kcal/mol) for the decomposition reaction of NH_4NO_3 in the presenceof $(NH_4)_2SO_4$.

	ΔE	ΔН	ΔG
NH ₄ NO ₃	0	0	0
$HNO_3 + NH_3$	13.5	14.0	5.4
PathA1			
$[(\mathrm{NH}_4)_2\mathrm{SO}_4^{\cdots}\mathrm{HNO}_3]_\mathrm{a}$	6.7	-2.5	0.6
TS1 _{Aa}	8.1	-1.1	4.8
Aggr _{Aa} *	9.0	-0.3	4.0
$HNO_3 + (NH_4)_2SO_4$	13.5	14.0	5.4
$OH^{\bullet} + NO_2^{\bullet} + (NH_4)_2 SO_4$	66.1	65.0	45.6
PathA2			
[(NH ₄) ₂ SO ₄ HNO ₃] _b	7.8	-1.4	2.1
TS1 _{Aa}	7.5	-1.7	3.3
Agrr _{Ab}	3.3	-5.9	0.4
PathB			
$\mathrm{HNO}_3 + \mathrm{NH}_3 + 2\mathrm{NH}_3 + \mathrm{H}_2\mathrm{SO}_4$	33.4	31.3	13.2

Conclusion

As far as the reactivity of ammonium sulfate in the presence of ammonium nitrate is concerned, it is possible to affirm that $(NH_4)_2SO_4$ is behaves at the same time as an inhibitor and as a promoter of the decomposition of AN. Making a simple comparison with the two first inhibitors presented in Chapter 3, (CaCO₃ and CaSO₄) it is evident that what made these two species stabilizers for ammonium nitrate was their capability to capture a proton from nitric acid, inactivating HNO₃ with the formation of a very stable aggregate. On the other hand, there was the presence of the calcium cation able to form aggregates with the nitrate ion that physically inhibits it. These two actions carried out together, lead to the formation of aggregates whose stability is demonstrated by the heat released during the formation of the aggregates and by the energy required to break them (see always chapter 3). In the case of the interaction between AS and AN, the energyrelated to $Aggr_{Aa}^*$ and $Aggr_{Ab}$ is not far away from the decomposition product of pure ammonium nitrate. This can be caused by the masked basicity of sulfate anion due to the presence of the acid cation NH₄⁺. Ammonium cation is also not able to create stable interactions as in the case of calcium ion. The result is an inferior stabilization of nitric acid HNO₃. In the case of $Aggr_{Aa}^*$, this is the product of the thermodynamically favoured route (PathA1 in Scheme1). However, this product is less stable than the second Aggr_{Ab}. This one is 3.6 Kcal/mol more stable than $Aggr_{Aa}^*$. The theoretical study conducted on the influence that $(NH_4)_2SO_4$ exerts on NH₄NO₃, is that AS can be considered as a weak inhibitor, which because of the intrinsic acidity of the ammonium cation, and it is unable to stabilize the ammonium nitrate completely. This is especially true for $Aggr_{Aa}^*$, which is not able to deactivate HNO₃ through its deprotonation. This leads to a reaction pathway (PathA1) in which the impossibility to stabilize HNO₃ brings it to a possible radical decomposition. In fact, it has been tested that Aggr_{Aa}^{*} decomposing, presents a favoured reaction which is the one that leads to the liberation of HNO3 and (NH4)2SO4 again. Free nitric acid is then able to decompose. Other possibilities for the Aggr_{Aa}^{*} decompositions are: OH' + $[NO_2^{...}(NH_4)_2SO_4]$, or NO_2 ' + $[OH^{...}(NH_4)_2SO_4]$ '. The formation of these products has not still been tested, but it is in perspective. The barrier of their decomposition will be tested and compared to one of the decompositions of HNO_3 , to see if in the presence of $(NH_4)_2SO_4$ a new radical decomposition and a most-favoured pathway is possible. Another explanation about the problem of the increased explosiveness of ammonium nitrate in the presence of ammonium sulfate is that when AN decomposes, it generates oxygen, and AS can be oxidized by it. The oxidative reaction of AS is much more exothermic than the explosion of AN, and these data are confirmed both by theoretical studies (-165 Kcal/mol for AN, -389 Kcal/mol for AS) and by the experimental ones presented by the RARDE¹⁴ ballistic experiences (27.6 Kcal/mol for AN and 85 Kcal/mol for AS). To evidence an incompatibility reaction between AS and AN, a sufficient amount of oxygen is needed to oxidize AS. The resolution of the Oppau case is very controversial. As mentioned above, ammonium sulfate behaves at the same time as un inhibitor,

i.e., unable to completely stabilize AN, and the promoter of AS only in certain condition, i.e., when the amount of ammonium nitrate exceeds 50% of the composition of the solid mixture. Through the RARDE experiments, it became clear that the oxygen is the cause of the decomposition of the ammonium sulfate, leading to the oxidation of AS. To conclude, about the behaviour of ammonium sulfate in the presence of ammonium nitrate, is that AS is not a good inhibitor of AN, because it does not ensure a stable inactivation of HNO₃. The sensitivity of (NH₄)₂SO₄ to oxidation has been recognized, and it is not negligible, and an environment potentially reach in oxygen represents a danger for the mixture ASN. In the next paragraph, new theoretical work on the reactivity of AN placed in contact with di-ammonium phosphate (DMP), was carried out. DMP presents a similar structure with AS, but it seems that it presents a different behaviour being more stabilizer than AS. These theoretical works aim to determine what is the difference that makes DMP more effective as inhibitor compared to AS.

4 Theoretical study of ammonium nitrate in contact with di-ammonium phosphate (DMP)

The study of the reactivity of ammonium nitrate in the presence of di-ammonium phosphate (DMP or $(NH_4)_2HPO_4$) was carried out due to its structural similarity to ammonium sulfate, which was extensively discussed in this chapter.

4.1 Properties of DMP

From an experimental point of view di-ammonium phosphate salt is classified as compatible with ammonium nitrate, as shown in the Guidance for the compatibility of fertilizer blending materials.²² This is also confirmed by the analysis of the accidentology of ammonium nitrate because no accidents were reported involving the presence of DMP (in Chapter 1 there is an example of a complete accidentology of ammonium nitrate of the last century). Oxley, in his calorimetric experiments,^{18,17} shows that (NH₄)₂HPO₄ when added to ammonium nitrate is able to stabilize it. In this experiment, the Tmax decomposition temperature for pure ammonium nitrate was 326 °C. It has been seen that adding 5 wt% of DMP, results in an increase in Tmax decomposition to 340 °C. Adding 20 wt% the maximum decomposition temperature of nitrate in a mixture with DMP is 364 °C. So, from an experimental point of view, DMP is more stabilizing than AS. The purpose of this study is to determine the reactivity of DMP salt in the presence of AN, and why there is this difference in reactivity with AS, considering that from a structural point of view AS and DMP are similar. They both present two ammonium molecules that potentially this can represent a destabilizing factor, as seen for ASN salt. A first clue could be the basicity of DMP which is equal to 7.4, while AS presents a basicity of 4.8.¹⁷ As affirmed by Oxley in her experimental studies, it seems that the basicity is a very important factor for the AN stabilization.¹⁷

4.2 Theoretical study of ammonium nitrate in contact with DMP

To study the reactivity of DMP, a conformational study to identify the most stable geometry for $(NH_4)_2HPO_4$ molecule, was carried out. It was possible to identify one stable structure that has been subjected to optimization (M06-2X/6-311+G(2d,2p)). The structure is presented in Figure 19. This molecule was adopted as the starting model for the study of reactivity with ammonium nitrate.



Figure 19. Molecule of (NH₄)₂HPO₄.

Taking into account the procedure used previously to study chemical incompatibilities of $AN^{23,24}$ the emphasis of this work was placed on identifying the steps involved in the reaction mechanism between DMP and AN, considering that ammonium nitrate easily decomposes into nitric acid and NH₃ ($\Delta G = 5.4$ Kcal/mol, as discussed in Chapter 1). The reactions of DMP with NH₃ and HNO₃ have been studied through molecular modeling. The reaction between AN and (NH₄)₂HPO₄ was investigated by considering that ammonium phosphate could react with nitric acid, hereafter referred to as *path A*, or decomposing into ammonia and phosphoric acid, *path B*. The reaction between DMP and NH₃, did not present any results and for this reason, these reactions are not reported as in the previous case of ammonium sulfate. The whole reaction mechanism is reported in Scheme 4, while the corresponding energy profile is in Figure 20. The computed energies are also reported in Table 4. Total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.

4.3 Reactions between HNO3 and (NH4)2HPO4

Once ammonium nitrate has decomposed into NH_3 and HNO_3 , nitric acid can react with di-ammonium phosphate in the direction of oxygen 2 (See Figure 19), the unique oxygen free from an atom of hydrogen. After this interaction a first aggregate [HNO₃...(NH₄)₂HPO₄] is formed, whose ΔG is equal to -4.8 Kcal/mol.

Another interaction is still possible and the previous reaction is immediately followed by another one in which a proton passes from nitric acid to sulfate oxygen number 2 (see Figure 19), forming another aggregate called [NO₃...(NH₄)₂H₂PO₄], through a slightly endothermic reaction (ΔG =-2.4 Kcal/mol). Once the proton has completely shifted from HNO₃ on the phosphate to the oxygen in position 2, the proton presented in position number 6 (linked to oxygen 3) can protonate again the aggregate [NO₃...(NH₄)₂H₂PO₄], giving [HNO₃^{...}(NH₄)₂HPO₄]^{*}, which is not equivalent to [HNO₃^{...}(NH₄)₂HPO₄], because the two geometries are quite different. In addition [HNO₃^{...}(NH₄)₂HPO₄]^{*} is more stable than [HNO₃...(NH₄)₂HPO₄], presenting a ΔG is equal to -5.7 Kcal/mol. All the above-mentioned structures are present in Figure 20. In contrast to ammonium sulfate, in the case of (NH₄)₂HPO₄, it is not the ammonium cation that gives a proton back to the nitrate: in this case NO₃⁻⁻ is protonated again by hydrogen coming from the oxygen 3 on the phosphate. Then the aggregate [HNO₃...(NH₄)₂HPO₄]^{*} can decompose into different products that will be presented separately in Path A1, Path A2 and PathA3.



Figure 20. Intermediates of the reactions between HNO₃ and (NH₄)₂HPO₄

Also in the case of the aggregate [HNO₃...(NH₄)₂HPO₄],* its decomposition has been studied. So, it has been tested the elimination of a molecule of NH₃ and decomposition back into HNO₃ and (NH₄)₂HPO₄. Three possible paths were taken into account: PathA1 and PathA2 and PathA3. Following the PathA1 [HNO₃...(NH₄)₂HPO₄]*, by elimination of one molecule of NH₃, it decomposes into NH₄NO₃...H₃PO₄, through a Δ G equal to 1,7 Kcal/mol and a barrier of 7.4 Kcal/mol. In NH₄NO₃...H₃PO₄, the displacement of a proton, generates NH₃...HNO₃...H₃PO₄, with a Δ G=1.6 Kcal/mol. In the PathA2 [HNO₃...(NH₄)₂HPO₄]* by elimination of the other molecule of NH₃, may originate a different aggregate: HNO₃...H₃PO₄...NH₃, with a Δ G of -0.8 Kcal/mol and a barrier of 4.9 Kcal/mol. The structures mentioned in PathA1 and PathA2 are represented in Figure 21. These two mechanisms of reaction are then unified in a single way (See Scheme 4 and Figure 22), giving rise to some common decomposition products: NH₃, HNO₃ and H₃PO₄ (Δ G = 14.1 Kcal/mol). Here, free HNO₃ can decomposes in reactive radicals such as OH* and NO₂*, and the free energy necessary to give rise to the two radicals in this context is 54.2 Kcal/mol, with the same barrier of 40

Kcal/mol of the decomposition of pure ammonium nitrate. So, also in this case the value of the rate-limiting step of the reaction does not change. However, the decomposition into the products NH₃, HNO₃ and H₃PO₄ coming from HNO₃^{...}H₃PO₄^{...}NH₃ (Δ G=-0.8 Kcal/mol) presents a barrier of 14.9 Kcal/mol. Instead starting from NH₄NO₃^{...}H₃PO₄ (Δ G=1.7 Kcal/mol) the barrier is about 12.3 Kcal/mol. For PathA3, the aggregate [HNO₃^{...}(NH₄)₂HPO₄]^{*} decomposes directly into HNO₃ and (NH₄)₂HPO₄ (Δ G=5.4 Kcal/mol), back to the reagents. This reaction presents a barrier of 11.1 Kcal/mol and it is more disadvantaged than the other two decomposition proposed in PathA1 and PathA2.



Figure 21. Intermediates generated by the decomposition of [HNO₃...(NH₄)₂HPO₄]^{*}.



Figure 22. Gibbs Free Energy profile for the reaction between AN and (NH₄)₂HPO₄.



Scheme 4. Reaction mechanism between NH₄NO₃ and (NH₄)₂HPO₄.

Table 4 Relative energies (kcal/mol) for the decomposition reaction of NH_4NO_3 in the presence of $(NH_4)_2HPO_4$.

	ΔΕ	ΔН	ΔG
NH ₄ NO ₃	0	0	0
HNO ₃ +NH ₃	13.5	14.0	5.4
PathA			
[HNO ₃ (NH ₄) ₂ HPO ₄]	-10.1	-8.3	-4.8
[NO ₃ (NH ₄) ₂ H ₂ PO ₄]	-8.4	-6.6	-2.4
[HNO ₃ (NH ₄) ₂ HPO ₄]*	-10.3	-8.5	-5.7
PathA1			
NH ₄ NO ₃ H ₃ PO ₄	1.6	5.8	1,7
NH ₃ HNO ₃ H ₃ PO ₄	2.7	6.9	1.6
NH ₃ + HNO ₃ + H ₃ PO ₄	31.5	40.9	14.1
$NH_3 + OH^{\bullet} + NO_2^{\bullet} + H_3PO_4$	84.1	91.9	54.2
PathA2			
HNO ₃ H ₃ PO ₄ NH ₃	0.9	5.1	-0.8
NH ₃ + HNO ₃ + H ₃ PO ₄	31.5	40.9	14.1
$NH_3 + OH^{\bullet} + NO_2^{\bullet} + H_3PO_4$	84.1	91.9	54.2
PathA3			
$HNO_3 + (NH_4)_2 HPO_4$	13.5	14.0	5.4
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	66.1	65.0	45.6
PathB			
$2NH_3 + H_3PO_4$	22.1	26.9	8.5

4.4 Description of the decomposition of (NH₄)₂HPO₄ into NH₃ and H₃PO₄ (PathB)

The PathB, sees the rupture of $(NH_4)_2HPO_4$ into two molecules of NH_3 and one molecule of H_3PO_4 . This reaction requires a ΔG of 8.5 Kcal/mol, therefore this reaction is disadvantaged both with respect to the decomposition of ammonium nitrate into NH_3 and HNO_3 , and with respect to PathA. In fact, PathA will be the preferred reaction route.

4.5 Conclusion

A possible explanation for the higher stability of the DMP compared to AS may depend on the higher stability of the formed aggregate and the energy barriers of its decomposition, which are shown to be a little more important than the $Aggr_{Aa}^*$ decomposition barrier that would lead to the destabilization of AN.

It seems that DMP does not cause decomposition reactions that could destabilize ammonium nitrate, for the following reasons: although it is able to protonate the nitrate again, leading to the formation of $[HNO_3^{...}(NH_4)_2HPO_4]^*$ (ΔG = -5.7 Kcal/mol), this one is more stable than Aggr_{Aa}^{*} (ΔG = 4.0 Kcal/mol). In addition, the reaction barriers that lead to the decomposition product shared in PAthA1 (NH₄NO₃^{...}H₃PO₄, 7.4 Kcal/mol), PathA2 (HNO₃^{...}H₃PO₄^{...}NH₃, 4.9 Kcal/mol) and PathA3 (HNO₃ + (NH₄)₂HPO₄, 11.1 Kcal/mol) are a little bit bigger than the barrier for Aggr_{Aa}^{*} when it decomposes into HNO₃ and (NH₄)₂SO₄, whose value is about 1.4 Kcal/mol.

As seen in Chapter 3, it seems to emerge that the capability of an additive to stabilize nitric acid seems to be directly linked to the affinity of a substance to accept the proton from HNO_3 . In the case of $(NH_4)_2SO_4$, its lower basicity (pH=4.8) compared to one of $(NH_4)_2HPO_4$ (pH=7.4), makes it less prone to accept a proton from nitric acid. This should confirm the DMP inhibitor character of AN decomposition, compared to behaviour of AS that it seems be at the same time a promoter and an inhibitor of ammonium nitrate.

In the next chapter two studies will be presented: one on the reactivity of the major number of some substances that are generally used to stabilize AN grade fertilizer, trying to understand if these present the same reaction mechanism and if there is a trend between the aggregates that they form with HNO₃ or NH₃ and their reactivity measured experimentally. The other work presents a study on two chlorinated substances, known to be incompatible with AN, namely KCl and CaCl₂, showing their particular mechanism of action that makes them incompatible with ammonium nitrate.

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CHAPTER 5

Theoretical study of the decomposition of ammonium nitrate in presence of two chlorinated salts (CaCl₂ and KCl), and in presence of some oxyanion salts.

This chapter is divided into two parts. In the first one, the reactivity of two inorganic salts in presence of ammonium nitrate will be presented: potassium chloride (KCl) and calcium chloride (CaCl₂). At the beginning, their physico-chemical characteristics will be described, then their reactivity with AN will be introduced from an experimental and theoretical point of view. These substances have been chosen because until now it has not been possible to find a clear explanation at both experimental and theoretical levels about a mechanism that could lead to an incompatibility between AN and these substances. In the second part, the reactivity of ammonium nitrate in contact with same inhibitors and inert salts ((NH₄)₂SO₄, (NH₄)₂HPO₄, NaNO₃, KNO₃, Ca(NO₃)₂, CaCO₃, MgCO₃, Na₂CO₃, KHCO₃, NaHCO₃, CaSO₄, MgSO₄, K₂SO₄, Na₂SO₄, NaHSO₄, KHSO₄, Na₃PO₄, K₃PO₄, Na₂HPO₄, K₂HPO₄, CaHPO₄, NaH₂PO₄, and KH₂PO₄) will be presented. Since all these salts have a similar structure and a stabilizing effect on the decomposition of ammonium nitrate, it was decided to investigate if they reacted with AN through a similar mechanism of reaction.

1. The state of the art of AN decomposition in presence of CaCl2 and KCl

1.1 Physico-chemical properties of CaCl₂

As reported in Ullmann's Encyclopedia of industrial Chemistry¹, calcium chloride is found in seawater and also in many mineral springs. It has been discovered in the 15th century but the first established studies on this salt dates to the 18th century. Since the development of the Solvay-ammonia process, CaCl₂ has started to be produced industrially. This process was originally created for the synthesis of soda ash, (crude sodium carbonate), where CaCl₂ was considered as a waste product. Today, calcium chloride is invaluable for various reasons, as it can be used in processes such as ice and dust control, oil well drilling, refrigeration, coal thawing, and food processing. Figure 1 describes the solubility of pure calcium chloride in water at different temperatures and CaCl₂ concentration. CaCl₂ presents a molecular mass of 110.99 g/mol, it is a white, odorless and extremely water-soluble salt over a wide temperature range, with maximum solubility of approximately 75 % at temperatures above175 °C, as shared in Figure 1. Calcium chloride is a very hygroscopic salt, which is generally encountered as hydrated solid. Its structure can accept a variable number of water molecule: generally, from 0 to 6. The anhydrous form appears at 217 °C.



Figure 1. Solubility of pure calcium chloride in water. From Ullmann's Encyclopedia of Industrial Chemistry, ed. 2012¹

According to the European **harmonized classification and labelling** regulation (CLP), this substance causes serious eye irritation, and the associated hazard identification pictogram (Figure 2) has the signification of "Dangerous for healt".



Figure 2. Pictogram for a substance that is dangerous for health.

1.2 Physico-chemical properties of KCl

Potassium Chloride is a white crystalline and odorless solid. It presents a molar mass of 74.5 g/mol, a density of 1.98 g/cm³, a melting point of 770 °C and a boiling point of 1420 °C. KCl's solubility in water at 0°C is about 217 g/l, at 20°C of 253.9 g/l and at 100°C about 360.5 g/l. Potassium fertilizers are commonly used to overcome plant potassium deficiencies², especially in cases where the soil cannot provide the minimum amount of K necessary for the crops. KCl is the most common substance used to produce potash (a general term used to describe a variety of fertilizers containing K). Potassium chloride is also often referred to as potassium muriate or MOP.² Potassium is found in deep soil deposits, where the dominant mineral is sylvite,

or if KCl is found mixed with sodium chloride (NaCl or halite), forms a mineral called sylvinite. Potassium chloride is a widely used fertilizer due to its low cost and high potassium content. More than 90% of the commercially available KCl is used for plant nutrition.² It dissolves rapidly in the water and the soils where it carries out its maximum fertilizing action are the based-clay solids, where KCl is the best retained. Potassium chloride does not usually have significant impacts on water or air, in fact it is not associated to toxic or environmental risk when it is normally applied: it does not present particular risks, neither at an industrial level nor for the environment.²

1.3 Experimental data about ammonium nitrate in presence of chlorinates substances

According to the study carried out by Horace Leonard Saunders,³ when chlorides are added to an ammonium nitrate formulation, even in a minimum amount of 0.1%, they influence the decomposition of AN. In fact, it has been detected the formation of Cl_2 in the gaseous phase formed during decomposition. The amount of Cl_2 would be proportional to the amount of Cl^- added to the solid mixture. The products found in solution in the reaction are: hydrochloric acid (HCl) and nitric acid (HNO₃). It was also seen that an acid reaction environment, which could be generated by the same formation of HNO₃, due to the simple decomposition of AN, is essential for Cl^- to manifest its characteristic of promoter of the decomposition of ammonium nitrate.³ Studies conducted by Keenan and Dimitriades (1962), also show that when a chloride is placed in contact with AN, the final products of the reaction are Cl_2 , H₂O, HNO₃, N₂ and N₂O.⁴ The products of this reaction would be given by the interaction of the positive ion NO₂⁺, generated by the decomposition of AN, with Cl^- , according to the following scheme:

1) $NO_2^+ + Cl^- \rightarrow NO_2 + Cl^-$

According to the authors, this would be the key step that would lead to the formation of Cl[•], which would give rise to a series of radical reactions, such as:

2) $Cl' + NH_4^+ \rightarrow NH_3^+ + HCl$

 $NH_{3^{+}} + NO_2 \rightarrow [O_2NNH_{3^{+}}] \rightarrow N_2O + H_2O$

3) $Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

 $Cl_2 + NH_3 \rightarrow [NH_2Cl] \rightarrow N_2 + HCl$

4) Cl[•] + NH₃ \rightarrow NH₂ + HCl

 $NH_2 + NO \rightarrow [NH_2NO] \rightarrow N_2 + H_2O$

Sun et al. (2005) proposed a study on the influence of inorganic acids on ammonium nitrate decomposition. The first evidence was that acids such as HCl and H_2SO_4 did not alter the reaction products with AN.⁵ They

simply accelerate their decomposition. They proposed that these inorganic acids had a catalytic role in the decomposition of AN: Cl⁻ ion and the H⁺ would play an activation role on NO₂⁺ and, producing the molecule NO₂Cl, which in turn reacts with the ammonium ion to form a nitramidine ion capable of decomposing into $N_2O + H_3O^+$.

Yu-ichiro Izato and Atsumi Miyake (2015),⁶ presented a more detailed study about the reactivity of chlorinated substances on AN, in particular the reactions between AN and KCl salt. Experimental tests were used to study the thermal properties of reactions, using DSC calorimetry coupled with mass spectrometry (TG-DTA-MS and PDSC-MS).⁶ Through this technique, the following reaction mechanism has been proposed:

5) $NH_4NO_3 \rightarrow NH_3 + HNO_3$

6) $HNO_3 + KCl \rightarrow KNO_3 + HCl$

7) $HNO_3 + HCl \rightarrow [TS] \rightarrow NO_2Cl + H_2O$

8) NO₂Cl \rightarrow NO₂ + Cl[•]

Here, two new reactions have been highlighted: KCl would be able to react firstly with HNO₃, generating HCl. Subsequently, HCl reacting with a second molecule of HNO₃ would generate NO₂Cl. The intermediate NO₂Cl had already been highlighted by other studies, which however justified its production through a mechanism of cationic decomposition of ammonium nitrate. In the case of this study, a transition state between HNO₃ and HCl is presented, from which NO₂Cl and water molecules are obtained.⁶ This experimental study is of fundamental importance because it includes in a more general framework the reactivity of chlorinated substances, especially of KCl salt.⁶ According to the authors, the decomposition of NO₂Cl leads to the formation of the radical species Cl[•] which is able to react, with NH₃, according to the following reaction scheme: ⁶

9) $NH_3 + Cl \rightarrow NH_2 + HCl$

10) $NH_2 + Cl \rightarrow NH_2Cl$

11) $3NH_2Cl \rightarrow N_2 + NH_4 + 3Cl' + 2H^+$

12) $NH_4^+ + Cl^- \rightarrow NH_3^+ + HCl$

1.4 Previous theoretical work on chlorinated substances reactivity with ammonium nitrate

In previous theoretical studies proposed by INERIS in collaboration with Chimie ParisTech, a study was conducted to understand the real mechanism of action of various chlorinated substances in presence of ammonium nitrate.⁷ The substances chosen for this previous study were: Cl₂, HCl, Cl[•], NaCl, LiCl, KCl, OCl[•], HOCl, NaOCl, LiOCl, KOCl. Below, the reactions analyzed by the previous study will be reported.⁷

13) $NH_3 + Cl_2 \rightarrow NH_2Cl + HCl$

14)
$$NH_3 + HCl \rightarrow NH_4Cl$$

- 15) $NH_3 + Cl \rightarrow NH_2 + HCl$
- 16) $NH_3 + NaCl \rightarrow NH_2Cl + NaH$
- 17) $NH_3 + LiCl \rightarrow NH_2Cl + LiH$
- 18) $NH_3 + KCl \rightarrow NH_2Cl + KH$
- 19) $NH_3 + OCl \rightarrow NH_2 + HOCl$
- 20) $NH_3 + HOCl \rightarrow NH_2Cl + H_2O$
- 21) $NH_3 + NaOCl \rightarrow NH_2 + NaOH$
- 22) $NH_3 + LiOCl \rightarrow NH_2 + LiOH$
- 23) $NH_3 + KOC1 \rightarrow NH_2 + KOH$

Considering that ammonium nitrate NH₄NO₃ always decomposes into ammonia and nitric acid, the reactivity of the substances mentioned above has been tested separately in the presence of NH₃ and HNO₃. All the other salts have transition states of the reaction with ammonia that greatly exceeded the value of the rate limiting step (40 Kcal/mol). The tested reactions and the energy diagram of free energy is presented in the thesis of Stefania Cagnina.⁷ As it can be seen in Figure 3, all the three-transition states with KCl, LiCl and NaCl have an energy of activation very close, whatever the cation forming the salt is different. This trend therefore leads to believe that the cation (Na⁺, Li⁺ or K⁺) involved in the mechanism does not have a significant influence on the reaction barrier.⁷ Even the direct reactions between Cl₂ and HOCl are not favored, because they are more endothermic than the decomposition of ammonium nitrate itself. Therefore, the only favored reactions are those generated by the species Cl⁺ and OCl⁺, which are instead competing with the decomposition of AN.⁷



Figure 3. Activation barriers of different reactions involving different chlorinated species with respect to ammonia. Image taken by Stefania Cagnina's thesis.⁷

Direct reactions between these same chlorinated molecules (Cl₂, HCl, Cl^{*}, NaCl, LiCl, KCl, OCl^{*}, HOCl, NaOCl, LiOCl, KOCl.) and nitric acid were studied and the activation barrier of some reactions was also evaluated. A preliminary study was carried out on the reactions between nitric acid and the chlorine radical or alkali metal salts:⁷

- 24) $HNO_3 + Cl \rightarrow HCl + NO_3$
- 25) $HNO_3 + NaCl \rightarrow HCl + NaNO_3$
- 26) $HNO_3 + KCl \rightarrow HCl + KNO_3$
- 27) $HNO_3 + LiCl \rightarrow HCl + LiNO_3$
- 28) $HNO_3 + NaCl \rightarrow HOCl + NaNO_2$

Reactions from 24 to 26 present a barrier in terms of Gibbs' free energy of 17.4 kcal/mol (Cl'), 27.6 kcal/mol and 29.4 kcal/mol (NaCl and KCl).⁷ So, these reactions appear as competitive with the decomposition of pure ammonium nitrate. With regards to reaction 27, the transition state could not be identified and one wonders if it is possible that the cation plays a role in the reaction process, as it is of an alkali metal salt (just like NaCl and KCl).⁷ The last reaction, in which hypochlorous acid and sodium nitrite are produced from nitric acid and sodium chloride, presents a very high barrier with an activation energy of 77.8 kcal/mol.⁷ According to this first theoretical study, due to the limited data available, it seemed complicated to define a

general behavior of chlorinated substances towards nitric acid. Nevertheless, for the energies obtained so far for all the molecules chosen, a reaction between the chlorine radical and ammonia seems to be the most appropriate way to explain the incompatibilities between AN and chlorinated substances characterized in the literature. As a result, a study on the mechanisms and energies involved in the formation of the radical Cl[•] would deserve to be realized.

The current work on chlorinated substances, that will be presented in this chapter, has been limited to two salts: KCl and CaCl₂. The choice of KCl occurred after the results of the experimental study on the chemical incompatibility between potassium chloride and ammonium nitrate performed by Yu-Ichiro Izato,⁶ discussed in the previous paragraph. Instead, the choice of CaCl₂ was made because this substance is of particular interest for studies conducted at INERIS between AN and other incompatible substances.

1.5 Calorimetric data for the interaction between AN + KCl and AN + CaCl₂

The available experimental data about the effect of those contaminants on the decomposition temperature of the ammonium nitrate are reported in the following table for sake of clarity. As we can see from the calorimetric values presented in Table 1, when AN is added with even a small amount of KCl or CaCl₂ the temperature of the mixture decreases significantly compared to the decomposition temperature of pure ammonium nitrate. This confirms that these two chlorinated substances are incompatible with ammonium nitrate and promote its decomposition. However, as already introduced above, there is not yet a clear explanation of the reaction mechanism of these substances in the presence of AN. Therefore, in the next paragraph, a new theoretical work will be introduced, with the aim to explain the nature of such promoters of AN's decomposition.

Authors	Year of Publication	Type of calorimetric test	Tonset or Tmax of pure AN	Tonset or Tmax of AN+KCl or/and AN+CaCl ₂
X.R. Li and H. Koseki ⁸	2005	Modified Closed Pressure Vessel Test (MCPVT)	Tonset: 280°C	Tonset AN+CaCl ₂ (0,1% wt): 226°C Tonset AN+CaCl ₂ (0,5% wt): 220°C Tonset AN+KCl (0,1% wt): 230°C Tonset AN+KCl (0,5% wt): 224°C
J. C. Oxley et al. ⁹	2002	Differential Scanning Calorimetry (DSC)	Tmax: 326 °C	Tmax AN+CaCl ₂ (5% wt): 261°C Tmax AN+CaCl ₂ (10% wt): 262°C Tmax AN+CaCl ₂ (20% wt): 266°C

Table 1. Experimental calorimetric data of AN in presence of KCl and CaCl₂.

				Tmax AN+KCl (5% wt): 256°C Tmax AN+KCl (10% wt): 254°C Tmax AN+KCl (20% wt): 256°C
Z. Han et al. ¹⁰	2015	Reactive Systems Screening Tool (RSST)	Tonset: 200 °C	Tonset AN+KCl (2.78 wt%): 194°C Tonset AN+KCl (5.41 wt%): 196°C Tonset AN+KCl (7.89 wt%): 196°C Tonset AN+KCl (11.39 wt%): 180°C Tonset AN+KCl (12.5wt%): 152°C Tonset AN+KCl (22.22 wt%): 145°C

2. Theoretical study on the decomposition of ammonium nitrate in presence of calcium and potassium chlorides.

2.1 Ammonium nitrate reactivity in presence of KCl

This system has already been studied in the previous Stefania Cagnina's thesis.⁷ Therefore, no new theoretical studies have been conducted. It has been considered that ammonium nitrate decomposes into ammonia and nitric acid, therefore the KCl salt could react with NH_3 and with KNO_3 . The aim was to find a TS or barrier competitive with the rate limiting step of the decomposition of HNO_3 in OH^{\bullet} and NO_2^{\bullet} radicals.

2.1.1 Reaction between KCl and NH₃

The reaction studied in the previous thesis between KCl and NH₃ is as follows:

29) $NH_3 + KCl \rightarrow NH_2Cl + KH$

The formation of the product NH_2Cl and KH passes across a transition state. The TS for chlorinated molecules, such as KCl and NaCl, is similar to the one shown in Figure 4. In fact, the chlorinated salts of the alkaline metals present a similar TS geometry, in which the chlorine attacks the nitrogen in the "anti" position to the hydrogen, which moves towards the alkaline metal atom (sodium or potassium).⁷



Figure 4: Geometry of the transition state of the reaction between ammonia and sodium or potassium chloride

The transition state shown in Figure 4, where a KCl molecule reacts with an NH_3 molecule, requires an activation energy greater than 100 Kcal/mol. Therefore, this TS is not competitive with the reaction barrier of HNO₃ decomposition in OH[•] and NO₂[•] radicals. Thus, this reaction is thermodynamically disadvantaged.⁷

2.1.2 Reaction between KCl and HNO₃

The reaction between HNO_3 and KCl that was always studied in the previous thesis work is represented below:

30) $HNO_3 + KCl \rightarrow HCl + KNO_3$

This barrier, measuring 27.6 Kcal/mol is competitive with the decomposition of HNO₃. Therefore, it means that KCl has a tendency to react with HNO₃ and not with NH₃.⁷ The products generated by this reaction are KNO₃ and HCl. To date, the effect of HCl on the destabilization of ammonium nitrate has never been studied.⁷ In the next paragraph, the reaction path of another chlorinated salt, CaCl₂, will be analyzed, in order to see if there are similarities in the reaction mechanism between calcium chloride and potassium chloride.

2.2 Ammonium nitrate reactivity in presence of CaCl₂

In this section, the new theoretical work about the study of the reactivity of $CaCl_2$ in contact with AN is reported. As we know, NH₄NO₃ tends to decompose into NH₃ and HNO₃. This barrier measures 5.4 Kcal/mol. In the next paragraph, it will be shown how $CaCl_2$ reacts when it enters in contact with HNO₃ and then with NH₃. The energies of the two reactions will be compared to see which reaction path is the most

favorable. Total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.

2.2.1 Reaction between CaCl₂ and HNO₃

When HNO_3 and $CaCl_2$ approach, the calcium atom has the tendencies to form an interaction with the one of the oxygen atoms of nitric acid. This reaction leads to the formation of a first aggregate $[CaCl_2 HNO_3]$, to which corresponds a ΔG equal to -11.7 Kcal/mol. Then, the oxygen atom of HNO₃ on which resides the hydrogen atom, protonates the chlorine atom that comes off as HCl. At the same time, the oxygen atom released by the hydrogen binds to the calcium atom to form an aggregate [CaCl^{...}NO₃]. These two reactions (the protonation of Cl to HCl and the interaction with the second oxygen of Ca) occur at the same time and globally are slightly endothermic. The ΔG associated to the reaction measure -5.3 Kcal/mol, and it presents a barrier with respect to [CaCl₂...HNO₃] of 6.4 Kcal/mol. The [CaCl...NO₃] can accept a second molecule of HNO₃, through a reaction mechanism identical to the previous one: the second HNO₃ gets closer to [CaCl \cdot NO₃], generating the aggregate [HNO₃ \cdot CaCl \cdot NO₃] with a Δ G of -20 Kcal/mol. The oxygen that carries the hydrogen atom protonates the second atom of Cl, leading to the formation of HCl. At the same time, the same oxygen binds to the calcium atom, generating the species $Ca(NO_3)_2$ and a molecule of HCl. Also in this case, the passage of the proton and the simultaneous interaction of NO_3 with the calcium atom is an endothermic process, which presents a barrier equal to 7.4 Kcal/mol. However, this remains a favorable process that leads to the formation of as many as two molecules of HCl and one molecule of $Ca(NO_3)_2$. The images of the compounds mentioned are presented in Figure 5. The energy's values are in Table 2 and the pathway of reaction is presented in Scheme 1. The energetic diagram is in Figure 6.



Figure 5. Aggregates for the reactions of CaCl₂ and HNO₃

Scheme 1. Reaction mechanism between CaCl₂ and HNO₃

$$NH_4NO_3 \longrightarrow HNO_3 + NH_3$$

$$Path A \downarrow + CaCl_2$$

$$[CaCl_2 \cdots HNO_3]$$

$$\downarrow$$

$$[CaCl \cdots NO_3] + HCl$$

$$\downarrow$$

$$[HNO_3 \cdots CaCl \cdots NO_3]$$

$$\downarrow$$

$$Ca(NO_3)_2 + HCl$$

Table 2 Relative energies (kcal/mol) for the decomposition reaction of CaCl₂ in the presence of HNO₃

	ΔЕ	ΔН	ΔG
NH ₄ NO ₃	0	0	0
$NH_3 + HNO_3$	13.5	13.9	5.4
PathA			
[CaCl ₂ ···HNO ₃]	-10.4	-12.7	-11.7
[CaCl···NO ₃] + HCl	4.7	2.9	-5.3
[HNO ₃ ···CaCl···NO ₃]	-18.8	-23.3	-20.6
$Ca(NO_3)_2 + HCl$	-9.4	-7.7	-13.2



Figure 6. Gibbs Free Energy profile for the reaction between CaCl₂ and HNO₃

2.2.2 Reaction between CaCl₂ and NH₃

When a molecule of NH₃ approaches CaCl₂, it rapidly interacts with the calcium atom, generating an aggregate of the type [CaCl₂...NH₃], for which the formation is associated to a Δ G equal to -13.4 Kcal/mol. At this point, the reaction path can go in two directions: it can follow the PathB₁ or the PathB₂. The images of the aggregates and chemical species mentioned are presented in Figure 7. The energy's values are in Table 2 and the pathway of reaction is presented in Scheme 2. The energetic diagram is in Figure 8.

Following the PathB1, the formation of a second aggregate is given with the release of a molecule of HCl, due to the protonation of Cl⁻ by the molecule of NH₃ that once deprotonated becomes NH₂. The new aggregate can be written as [CaCl^{...}NH₂], it requires for its formation a ΔG of 43 Kcal/mol, and the barrier between it and the previous aggregate [CaCl₂^{...}NH₃] is 56.4 Kcal/mol. Therefore, the formation of HCl from CaCl₂ and NH₃ is very disadvantaged, compared to the formation of HCl from CaCl₂ and HNO₃. The species [CaCl^{...}NH₂] can accept a second molecule of NH₃, generating the aggregate [NH₃^{...}CaCl^{...}NH₂], with a ΔG

of 28.8 Kcal/mol. From here, the second molecule of NH₃ has the ability to give a hydrogen to the last Cl⁻, ensuring its exit as HCl, with a Δ G of 86.7 Kcal/mol and a barrier of 57.9 Kcal/mol. Along the PathB₂, there is the formation of a monochloramine NH₂Cl and CaClH through a very endothermic reaction, which requires a Δ G of 107.6 Kcal/mol and a barrier of 121 Kcal/mol compared to [CaCl₂...NH₃]. Therefore, even this reaction, when compared to the reactions that occur between CaCl₂ and HNO₃, are very disadvantaged. The images of the aggregates and chemical species mentioned are presented in Figure 7. The energy's values are in Table 2 and the pathway of reaction is presented in Scheme 2. The energetic diagram is in Figure 8.



Figure 7. Aggregates for the reactions of CaCl₂ and NH₃

Scheme 2. Reaction mechanism between CaCl₂ and NH₃



	ΔΕ	ΔН	ΔG
NH ₄ NO ₃	0	0	0
$NH_3 + HNO_3$	13.5	13.9	5.4
PathB			
[CaCl ₂ …NH ₃]	-9.8	-11.8	-13.4
PathB1			
$[CaCl \cdots NH_2] + HCl$	55.2	53.8	43
[NH ₃ …CaCl…NH ₂]	34.6	30.9	28.8
$Ca(NH_2)_2 + HCl$	100.6	97.4	86.7
PathB2			
CaClH + NH ₂ Cl	117.9	116.5	107.6

Table 3 Relative energies (kcal/mol) for the decomposition reaction of CaCl₂ in the presence of NH₃



Figure 8. Gibbs Free Energy profile for the reaction between CaCl₂ and NH₃

It is possible to affirm that the most favorable reactions of the contaminant $CaCl_2$ placed in contact with NH₃ and HNO₃, are the ones with nitric acid. The final products of the interaction between $CaCl_2$ and HNO₃ are $Ca(NO_3)_2$ and HCl. $Ca(NO_3)_2$ is considered as a compatible additive (inert) of ammonium nitrate⁹, on the contrary the contaminant HCl presents an incompatibility with AN, as just seen in the previous paragraphs. So far, no possible incompatibilities have been highlighted. The only non-compatible species formed is HCl. Therefore, in the next paragraph we will study the reaction mechanism between HCl and NH₄NO₃, trying to understand if there is a possible reaction mechanism between the two that can lead to a chemical incompatibility.

2.2.3 Reactions between NH₄NO₃ and HCl

During the previous theoretical study on chlorinated substances, there had been a stop to the formation of HCl, without going ahead in the study of the interaction between HCl and AN. Thanks to recent experimental studies, new perspectives have opened up about a more consistent reaction mechanism between ammonium nitrate and hydrochloric acid.⁶ Here, a possible pathway between HCl and NH₄NO₃ will be explored; hydrochloric acid would first act as a catalyst for the decomposition of AN, then HCl could be the cause of a reaction that leads in last step to the formation of chloride radicals. Scheme 3 below

represents the possible reaction path for the decomposition of AN in the presence of HCl. NH₄NO₃ can react with hydrochloric acid (PathC) or decompose into nitric acid and ammonia (Path D). The first reaction has a ΔG of 5.4 Kcal/mol. Instead, when HCl reacts with NH₄NO₃, it forms the aggregate [NH₄NO₃...HCl], which is less expensive than the decomposition of ammonium nitrate into NH₃ and HNO₃. In fact, the corresponding ΔG for the formation of [NH₄NO₃...HCl] has a value of -5.1 Kcal/mol. Therefore, the Path C is the preferred reaction path, compared to the Path D. Once the aggregate [NH₄NO₃...HCl] has been formed, ammonium NH₄, which had a hydrogen outstretched towards nitrate (Figure 9), takes the hydrogen on itself and approaching the chloride Cl⁻, obtaining the aggregate [HNO₃...NH₄Cl] (ΔG = -6,3Kcal/mol, Figure 9), passing through a transition state TS_{1C}, (ΔG = -1,3 Kcal/mol, Figure 9), which has a barrier of 4 Kcal/mol.



Figure 9. Transition state and aggregates of the reactions of NH4NO3 and HCl

The aggregate [HNO₃...NH₄Cl] tends to decompose into HNO₃ and NH₄Cl, with a Δ G of -3 Kcal/mol. NH₄Cl then decomposes into NH₃, HCl and HNO₃ with a Δ G of -2.4 Kcal/mol. At this point, the reaction path splits, because HNO₃ can decompose into the two radicals OH[•] and NO₂[•] (PathC₁) with a Δ G of 37.8 Kcal/mol, ever with the same decomposition barrier of 40 Kcal/mol, or pass through a transition state TS_{2C} (Δ G= 41.4 Kcal/mol, PathC₂, Figure 10) with a barrier of 43.8 Kcal/mol, arriving at the formation of NO₂Cl (as hypothesized experimentally) and a molecule of water.⁶ In Figure 10 is represented the transition state TS_{2C}. The energetic diagram is in Figure 11. In Scheme 4 and Figure 12 the reaction pathways A, B, C and D will be taken into account all together.



Figure 10. Transition state TS_{2C} for the reaction between HNO₃ and HCl

Following this reaction path, NO₂Cl could be the cause of the dangerousness of CaCl₂ and KCl, as it decomposes into two radicals NO₂[•] and Cl[•], with a Δ G equal to 24.1 Kcal/mol, by initiating a chain of radical reactions. The tendency towards PathC₁ or PathC₂ depends on the energy gap between the TS_{2B} barrier and the barrier due to the radical rupture of HNO₃ in OH[•] and NO₂[•]. The energy's values of all the species involved in this pathway of reaction are reported in Table 3 while the pathway of the reaction is presented is presented in Scheme 3. In Figure 9 are represented the aggregates and the transition states for the interaction between NH₄NO₃ and HCl.

Scheme 3. Reaction mechanism between NH₄NO₃ and HCl





Figure 11. Gibbs Free Energy profile for the reaction between AN and HCl



Scheme 4. Complete reaction mechanism between NH₄NO₃ and CaCl₂



Figure 12. Gibbs Free Energy profile for the complete reaction pathway between AN and CaCl₂

The role of HCl in these reactions is to convert NH₄NO₃ more quickly to HNO₃ and NH₃, accelerating their decomposition. In fact, once the products HNO₃, NH₃ and HCl are obtained, the latter can interact with HNO₃, passing through a TS_{2C} transition state (Figure 10), whose existence had already been hypothesized experimentally. The incompatibility reaction between HCl and NH₄NO₃ is still under investigation. In fact, once the TS_{2C} transition state has been found, to confirm the incompatibility it is necessary that the TS_{2C} reaction barrier is lower than the HNO₃ decomposition barrier (40 Kcal/mol). Therefore, TS_{2C} presents with 3.8 Kcal/mol more energy than the AN decomposition barrier. In the other cases studied in the previous thesis,^{11,12} the addition of one molecule of water in the reaction mechanism led to excellent results in terms of lowering the reaction barrier, giving rise to the incompatibility that was assumed experimentally. In the previous cited cases, the difference between the two barriers was very large, and with the addition of a molecule of water there was a reduction of up to 25.9 Kcal/mold of the energy associated with TS. This was precisely the example encountered in another chlorinated substance: the SDIC salt.¹¹ Therefore, considering that TS_{2C} is more energetic than the decomposition of HNO₃ by only 3.6 Kcal/mol, we are confident that an approach that considers the intervention of a molecule of water in the transition state geometry can also in

this case lead to positive results, predicting a lower reaction barrier. The product of TS_{2C} decomposition is given by NO₂Cl, which tends to decompose into NO₂• and Cl•. The latter, Cl•, is a very reactive species that can give rise to a series of uncontrolled radical reactions and NH₂Cl, as demonstrated in Stefania Cagnina's thesis⁷ and it is a precursor of trichloramine, which is an extremely explosive chemical compound.

	ΔΕ	ΔН	ΔG
NH ₄ NO ₃	0	0	0
PathD			
NH ₃ + HNO ₃	13.5	13.9	5.4
PathC			
[NH4NO3HCl]	3.5	1	-5.1
TS _{1C}	4.4	1.8	-1.30
[HNO ₃ NH ₄ …Cl]	1.0	-1.6	-6.3
$HNO_3 + NH_4Cl$	11.9	12.0	-3
HNO ₃ + NH ₃ + HCl	17.6	20.2	-2.4
PathC ₁			
$OH^{\bullet} + NO_2^{\bullet} + NH_4Cl$	70.2	71.2	37.8
PathC ₂			
TS _{2C}	54.3	54.1	41.4
$NO_2Cl + H_2O + NH_3$	21.4	21.8	-1.7
$NO_2 + Cl + H_2O + NH_3$	55.3	56.3	24.1

Table 4 Relative energies (kcal/mol) for the decomposition reaction of NH₄NO₃ in the presence of HCl

3. Conclusion

The two chlorinated salts KCl and CaCl₂ show different mechanisms about reactions with NH₃ and HNO₃. However, for both, reactions with NH₃ are strongly disadvantaged compared to reactions with HNO₃. For CaCl₂, the reactions with nitric acid are much more favorable than the same reactions in the case of KCl. This can be explained by the tendency of $CaCl_2$ to form aggregates through spontaneous and slightly exothermic reactions. So, the presence of calcium positively affects the interaction with HNO₃, much more than what potassium cation can do. The interesting point is that both salts (CaCl₂ and KCl) preferentially generate a molecule of nitrate (Ca(NO₃)₂ or KNO₃) and a molecule of hydrochloric acid HCl. From this point their reaction path, shown in Scheme 3 and in Figure 11, is identical for both salts and leads to the same reaction products. Particularly interesting is the TS_{2C} transition state, which appears could be competitive with the decomposition of nitric acid HNO₃ in OH[•] and NO₂[•]. However, the difference in energy between TS_{2C} and the decomposition barrier of HNO₃ is 3.6 Kcal/mol, so the transition state is just a few more energetic than the decomposition barrier of HNO₃. As it was done for other incompatible substances during previous studies conducted at INERIS on ammonium nitrate (SDIC and NaNO₂ salts),^{11,12} in order to decrease the barrier and see if the most favorable reaction is actually the decomposition of TS_{2C} , the influence of a molecule of water on the geometry of the transition state could be studied, looking at the effect on the barrier of reaction. If through the presence of a molecule of water the lowering of the reaction barrier is confirmed, so much so that TS_{2C} becomes competitive with respect to the decomposition of HNO₃, the problem related to the incompatibility between CaCl₂ and AN would be solved.

In the next section it will be introduced a study about the possible interactions between inhibitory and inert substances and AN, which experimentally show a stabilization of ammonium nitrate. The interest of this study is to investigate the mechanism of action of these compounds and if there is a link between the structural similarity of these salts, their ability to stabilize AN by increasing the temperature of decomposition and a possible identical mechanism of action.

4. Other substances stabilizing ammonium nitrate: selected oxyanion salts

In this section will be discussed the reactivity of ammonium nitrate in presence of some selected and compatible substances: the oxyanion salts. The aim of this study is to analyze the behavior of a series of structurally similar inorganic substances that exert a stabilizing effect on AN. The final goal is to demonstrate if a structural similarity and a common experimental behavior can indicate an identical mechanism of reaction for the substances here presented. The other goal is a tentative to correlate the obtained theoretical reactivity of the oxyanion salts with the experimental data obtained by DSC tests.

4.1 Experimental behavior of inhibitors and inerts of ammonium nitrate

As already introduced in the first chapter, the inhibitors and inert substances of ammonium nitrate decomposition can be identified through calorimetric experiments, taking as a reference parameter the variation of the decomposition temperature of AN mixed with these additives compared to the decomposition temperature of pure AN.¹³ In fact, the decomposition temperature of AN in presence of inhibitors is higher than the decomposition temperature of AN in its pure state. On the other hand, inert substances do not cause temperature changes when added in a mixture with AN, but they stabilize AN with a dilution effect absorbing the heat generated during the decomposition reaction. Experimentally, some oxyanions $(A_x O_y^{z})$ such as sulfates, carbonates, phosphates of sodium, potassium, ammonium and calcium, raise the peak of exothermic AN decomposition obtained by DSC experiments.⁹ As shared in Figure 13. most oxyanion salts increase the temperature of the exothermic maxima (represented by Tmax) of AN and it seems to be a certain correlation between their and their ability to inhibit the AN decomposition. At the same time, by varying the cation between Na⁺, K⁺, Mg⁺, NH₄⁺ and Ca²⁺, it appears that there are no major differences in the position of the exothermic peak.⁹ So it seems that cations does not exert an important role in AN stabilization. But experimentally it has been seen that Na⁺ cation can be considered as an inert counter ion, because it is considered that it does not take apart in the reaction. As introduced in Oxley in DSC studies, oxyanions with an inion more basic than nitrate tend to stabilize AN.^{9,14} For substances such as (NH₄)₂SO₄, NaHCO₃ and K₂CO₃, some RSST experiments are also available.^{15,10} These values are in line with previous DSC trends. Looking at Figure 13, oxyanions such as CO₃²⁻, HCO₃⁻ and HPO₄²⁻ maintain a pH range of 7.4-8.3, DSC experiments show that they improve the exothermic maximal peak of AN (Tmax) by 40-60 °C higher than pure AN. Other anions such as SO₄²⁻ and H₂PO₄⁻, with a pH value of 4-5, increase the maximum value by 10-20 °C. For oxyanions such as Ca(NO₃)₂, KNO₃ and NaNO₃ that have the same nitrate anion like AN (i.e. that have the same basicity) report a shift of the Tmax of 1 or 2 degrees °C with respect to the Tmax of AN.9


Figure 13: Oxyanions's pH versus Tmax decomposition temperature of AN placed in contact with compatible substances (inorganic inerts and inhibitors), data extracted by the Oxley's article (2002).

In the next paragraph it will be introduce a theoretical study to better understand the reactivity of ammonium nitrate in the presence of the inhibitors and inerts substances such as: (NH₄)₂SO₄, (NH₄)₂HPO₄, NaNO₃, KNO₃, Ca(NO₃)₂, CaCO₃, MgCO₃, Na₂CO₃, KHCO₃, NaHCO₃, CaSO₄, MgSO₄, K₂SO₄, Na₂SO₄, NaHSO₄, KHSO₄, Na₃PO₄, K₃PO₄, Na₂HPO₄, K₂HPO₄, CaHPO₄, NaH₂PO₄, and KH₂PO₄, in order to clarify their mechanism of reaction with the aim of find a possible relationship that links their experimental behavior to the theoretical data obtained.

4.2. Theoretical study on the reactivity of oxyanion salts with ammonia and nitric acid

As has already been introduced, ammonium nitrate easily decomposes into nitric acid and ammonia ($\Delta G = 5.4 \text{ kcal/mol}$) and it is through interaction with HNO₃ and NH₃ that a substance can develop an incompatibility or stabilization reaction with ammonium nitrate. In this chapter it will be proposed an analysis of the reactivity of the substances that are experimentally used to improve the thermal stability of ammonium nitrate, limited to the interaction with ammonia and nitric acid. The idea is to determine the possibility of defining a common behavior for all these molecules that are inside on chosen set: it is intended

to assess a preferential reactivity with ammonia or nitric acid, trying to find a general mechanism of reaction that expresses the compatibility between the selected substances and ammonium nitrate. A second objective is to verify that the reactivity obtained at the theoretical level is in line with the reactivity detected experimentally. Finally, the aim is to analyze whether what has been predicted by the theoretical calculations is consistent with the calorimetry data presented in the literature. It is important to underline that for each of the oxyanion salt taken into account, a modeling study was carried out with the aim of identifying the most symmetrical and stable geometry. In structures such as KHSO₄, NaHSO₄, KH₂PO₄, NaH₂PO₄, Na₂HPO₄, K₂HPO₄, where different sites of anion protonation could exist, all possible geometries were carried out, choosing the most energetically stable. For the reactions total energies, enthalpies, and Gibbs free energies were computed for all of the identified intermediates and products at 25 °C and 1 atm, but only Gibbs free energies will be discussed in detail.

4.2.1 Reactions between oxyanion salts and nitric acid

Direct reactions between the selected molecules and nitric acid were studied, looking for a possible energy barrier activation. Each reaction was evaluated in the gas phase (at standard temperatures and pressures) using as always, the theoretical level M06-2X/6-311+G(2d,2p). Among the reactions reported below there are some already studied, as in the case of CaCO₃, CaSO₄, (NH₄)₂SO₄ and (NH₄)₂HPO₄, therefore it will be simply report the values shown in the previous chapters. For most of the substances presented in the list of reactions below, experimental data are available. However, for a small number of them, no experimental data exist. This second group includes substances such as MgSO₄, Na₃PO₄, NaHCO₃, K₂SO₄, NaHSO₄. The study was also conducted on salts for which no experimental data were available in order to complete the series of carbonates/sulfates/phosphates/ with the cations of NH₄, Na, K, Ca, Mg. The aim was to test whether it was possible to predict experimental behavior even in the case of those substances for which no detailed experimental information were available. All reactions between HNO₃ and the various oxyanion salts will be reported below. They will be written in descending order of Gibbs free energy with respect to the aggregates formed as products, during the interaction between salts and HNO₃. The Gibbs free energy profile for this substances is reported in Figure 14 and in Table 5 are reported the relative energies for the decomposition reaction for inhibitors and inerts substances in presence of HNO₃.

31) $(NH_4)_2SO_4 + HNO_3 \rightarrow [NO_3...(NH_4)_2SO_4H]1$

32) $(NH_4)_2SO_4 + HNO_3 \rightarrow [NO_3...(NH_4)_2SO_4H]_2$

33) Ca(NO₃)₂ + HNO₃ \rightarrow [HNO₃...Ca(NO₃)₂]

34) (NH₄)₂HPO₄ +HNO₃ \rightarrow [NO₃...(NH₄)₂HPO₄H]

35) KHSO₄ + HNO₃ \rightarrow [HNO₃...KHSO₄]

- 36) NaNO₃ + HNO₃ \rightarrow [NO₃...NaNO₃H]
- 37) NaHSO₄ + HNO₃ \rightarrow TS_[NO3..H..NaHSO4] \rightarrow [HNO₃...NaHSO₄]
- 38) $\text{KNO}_3 + \text{HNO}_3 \rightarrow [\text{NO}_3...\text{KNO}_3\text{H}]$
- 39) NaHCO₃ + HNO₃ \rightarrow [NO₃...NaHCO₃H]
- 40) KHCO₃ + HNO₃ \rightarrow [NO₃...KHCO₃H]
- 41) $KH_2PO_4 + HNO_3 \rightarrow [NO_3...KH_2PO4H]$
- 42) $NaH_2PO_4 + HNO_3 \rightarrow [NO_3...NaH_2PO_4H]$
- 43) $Na_2SO_4 + HNO_3 \rightarrow [NO_3...Na_2SO_4H]$
- 44) Na₂CO₃ + HNO₃ \rightarrow [NO₃...Na₂CO₃H]
- 45) $K_2HPO_4 + HNO_3 \rightarrow [NO_3...K_2HPO_4H]$
- 46) $K_2SO_4 + HNO_3 \rightarrow [NO_3...K_2SO_4H]$
- 47) Na₂HPO₄ + HNO₃ \rightarrow [NO₃...Na₂HPO₄H]
- 48) $K_2CO_3 + HNO_3 \rightarrow [NO_3...K_2CO_3H]$
- 49) Na₃PO₄ + HNO₃ \rightarrow [NO₃...Na₃PO₄H]
- 50) K₃PO₄ + HNO₃ → [NO₃...K₃PO₄H]
- 51) CaHPO₄ + HNO₃ \rightarrow [NO₃...CaHPO₄H]
- 52) $CaSO_4 + HNO_3 \rightarrow [NO_3...CaSO_4H]$
- 53) $CaCO_3 + HNO_3 \rightarrow [NO_3...CaCO_3H]$
- 54) MgSO₄ + HNO₃ \rightarrow [NO₃...MgSO₄H]
- 55) $MgCO_3 + HNO_3 \rightarrow [NO_3...MgCO_3H]$



Figure 14. Gibbs Free Energy profile for the reaction between inhibitors and inerts substances and HNO3

		-	
	ΔE	ΔΗ	ΔG
NH ₄ NO ₃	0	0	0
$NH_3 + HNO_3$	13.5	13.9	5.4
[NO ₃ (NH ₄) ₂ SO ₄ H]1	9	-0.2	4.1
[NO ₃ (NH ₄) ₂ SO ₄ H]2	3.3	-5.9	0.4
[HNO3Ca(NO3)2]	1.2	-1.1	0.1
[NO ₃ (NH₄) ₂ HPO₄H]	-10.3	-8.5	-5.7
[HNO3KHSO4]	-6.3	-8.6	-6.9
[HNO ₃ NaNO ₃]	-6.6	-8.9	-7.1
[HNO3NaHSO4]1	-15.8	-18.5	-7.0
TS _{INO3HNaHSO41}	-15.2	-18.0	-4.4
[HNO ₃ NaHSO ₄]2	-18.5	-21.3	-9.1
[NO ₃ KNO ₃ H]	-6.7	-9.1	-7.4
[NO3NaHCO3H]	-7.5	-13.0	-11.0
[NO ₃ KHCO ₃ H]	-13.7	-13.2	-11.4
[NO ₃ KH ₂ PO4H]	-23.6	-18.6	-16.0
[NO3NaH2PO4H]	-19.0	-18.4	-17.1
[NO ₃ Na ₂ SO ₄ H]	-17.2	-19.6	-17.8
[NO ₃ Na ₂ CO ₃ H]	-26.4	-25.9	-24.1
[NO ₃ K ₂ HPO₄H]	-33.4	-27.5	-25.1
[NO ₃ K ₂ SO ₄ H]	-31.7	-34.0	-30.6
[NO3Na2HPO4H]	-45.8	-40.3	-36.9
[NO ₃ K ₂ CO ₃ H]	-49.8	-52.1	-50.2
[NO ₃ Na ₃ PO ₄ H]	-57.3	-56.9	-53.5
[NO ₃ K ₃ PO ₄ H]	-63.0	-56.4	-53.3
[NO3CaHPO4H]	-54.2	-56.6	-55.7
[NO ₃ CaSO₄H]	-58.6	-57.6	-56.8
[NO ₃ CaCO ₃ H]	-69.4	-68.5	-67.1
[NO3MgSO4H]	-73.5	-75.8	-75.4
[NO ₃ MgCO ₃ H]	-90.4	-92.7	-90.7

Table 5. Relative energies (kcal/mol) for the decomposition reaction for inhibitors and inerts substances

in presence of HNO₃

As already seen for the cases previously studied (CaCO₃, CaSO₄, (NH₄)₂SO₄) also in the case of these other salt, there is the formation of aggregates, where the nitric acid gives its proton to the anion of the salt with which it interacts. Then there is the formation of an interaction between the nitrate resulting from HNO₃ and the cation of the salt with which it has reacted. The theoretical study shows that these aggregates have different stability, which could be related to the capacity of the salt to receive the proton from HNO₃ and to the interaction that NO₃ establishes with the cation. These two combined effects would make the resulting aggregate more or less stable. The order of stability of the aggregates is as follows, and increasing Gibbs free energy has been taken as a reference: [NO₃...MgCO₃H] > [NO₃...MgSO₄H] > [NO₃...CaCO₃H] > [NO₃...CaCO₃H] > [NO₃...K₂CO₃H] > [NO₃...K₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₂CO₃H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄CO₃H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄CO₃H] > [NO₃...R₄CO₃H] > [NO₃...R₄CO₃H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄CO₃H] > [NO₃...R₄CO₃H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄CO₃H] > [NO₃...R₄(NO₃H] > [NO₃...R₄PO₄H] > [NO₃...R₄PO₄H] > [NO₃...R₄(NO₃H] > [NO₃...R₄(NO₃H]

As regards ammonium sulfate, the two aggregates presented here in this study [NO₃...(NH₄)₂SO₄H]1 and [NO₃...(NH₄)₂SO₄H]2 are equivalent to Aggr_{Aa}* and Aggr_{Ab} presented in chapter 4. In the case of NaHSO₄ and KHSO₄ bisulfates presents a different behavior than other oxyanions. As Oxley has already shown,⁹ bisulfates do not play a role as good stabilizers of ammonium nitrate, although they are commonly used as inhibitors in AN formulations. The theoretical study has in fact shown that NaHSO₄ and KHSO₄ are able to form an aggregate with HNO₃, but not to ensure the deprotonation of nitric acid. In the case of the aggregate [HNO₃^{...}KHSO₄], nitric acid physically interacts with the cation potassium, thus remaining bound in the aggregate. On the contrary, in the case of NaHSO₄, nitric acid only approaches salt but does not remain in interaction with the sodium cation due to a different geometry than KHSO₄.



Figure 15. Images relative to the salt NaHSO₄ and its interaction with HNO₃.

As we can see from Figure 15, HNO_3 interacts with $NaHSO_4$, but there is no interaction with the Na cation. Through the transition state TS [$NO_3...H...NaHSO_4$], a simultaneous protonation of the sulfate anion by HNO_3 and the restitution of a proton from the sulfate on NO_3 has been evidenced, generating again HNO_3 . Therefore, this confirms the experimental behavior of sodium bisulfate $NaHSO_4$, which due to their acidity cannot fully stabilize ammonium nitrate.



Figure 16. Images relative to the salt KHSO₄ and its interaction with HNO₃.

For KHSO₄ is valid what is has been said about NaHSO₄: the deprotonation of HNO₃ does not exist, as shown in Figure 16. The difference with sodium bisulfate is that given the geometry of KHSO₄ there is interaction between HNO₃ and cation K, given the higher tendency of potassium cation to form aggregates.

4.2.2 Reactions between oxyanion salts and ammonia

Also the interaction reactions between oxyanion salts and an ammonia molecule have been theoretically studied. The reactions studied are the following (they are ordered according to a decreasing Gibbs free energy). Their Gibbs free energy profile is reported in Figure 17 and in Table 6 the relative energy for the decomposition reaction in presence of NH_3 are presented.

- 56) KHSO₄ + NH₃ → [NH₃^{...}KHSO₄]
- 57) KH₂PO₄ + NH₃ → [NH₃...KH₂PO₄]
- 58) $K_2CO_3 + NH_3 \rightarrow [NH_3 \therefore K_2CO_3]$
- 59) KNO₃ + NH₃ → [NH₃...KNO₃]
- 60) NaHSO₄ + NH₃ \rightarrow [NH₃...NaHSO₄]
- 61) KHCO₃ + NH₃ \rightarrow [NH₃^{...}KHCO₃]
- 62) $K_2HPO_4 + NH_3 \rightarrow [NH_3 K_2HPO_4]$
- 63) $K_2SO_4 + NH_3 \rightarrow [NH_3 K_2SO_4]$
- 64) $Na_2CO_3 + NH_3 \rightarrow [NH_3 Na_2CO_3]$
- 65) NaHCO₃ + NH₃ \rightarrow [NH₃...NaHCO₃]
- 66) $K_3PO_4 + NH_3 \rightarrow [NH_3 K_3PO_4]$
- 67) Na₂HPO₄ + NH₃ \rightarrow [NH₃...Na₂HPO₄]
- 68) NaNO₃ + NH₃ \rightarrow [NH₃...NaNO₃]
- 69) NaHPO₄ + NH₃ → [NH₃···NaHPO₄H]
- 70) Na2SO4 + NH₃ \rightarrow [NH₃...Na₂SO₄]
- 71) Na3PO4 + NH₃ \rightarrow [NH₃···Na₃PO₄]
- 72) CaHPO₄ + NH₃ \rightarrow [NH₂···CaHPO₄H]
- 73) $Ca(NO_3)_2 + NH_3 \rightarrow [NH_3 Ca(NO_3)_2]$
- 74) $CaCO_3 + NH_3 \rightarrow [NH_3 CaCO_3] \rightarrow TS_{[NH_3 CaCO_3]} \rightarrow [NH_2 CaCO_3H]$

75) $CaSO_4 + NH_3 \rightarrow [NH_3 - CaSO_4]$

76) $MgCO_3 + NH_3 \rightarrow [NH_3 - MgCO_3] \rightarrow TS_{[NH_3 - MgCO_3]} \rightarrow [NH_2 - MgCO_3H]$

77) $MgSO_4 + NH_3 \rightarrow [NH_3 MgSO_4] \rightarrow TS_{[NH3...MgSO4]} \rightarrow [NH_2 MgSO_4H]$



Figure 17. Gibbs Free Energy profile for the reaction between inhibitors and inerts substances and NH₃

		-	
	ΔE	ΔΗ	ΔG
NH₄NO3	0	0	0
$NH_3 + HNO_3$	13.5	13.9	5.4
[NO ₃ (NH ₄) ₂ SO ₄ H]1	9	-0,2	4,1
[NO ₃ (NH ₄) ₂ SO ₄ H]2	3,3	-5,9	0,4
[HNO ₃ Ca(NO ₃) ₂]	1,2	-1,1	0,1
[NO ₃ (NH ₄) ₂ HPO ₄ H]	-10,3	-8,5	-5,7
[HNO3KHSO4]	-6,3	-8,6	-6,9
[HNO ₃ NaNO ₃]	-6,6	-8,9	-7,1
[HNO3NaHSO4]1	-15,8	-18,5	-7,0
TS _{INO3HNaHSO41}	-15,2	-18,0	-4,4
[HNO ₃ NaHSO ₄]2	-18,5	-21,3	-9,1
[NO ₃ KNO ₃ H]	-6,7	-9,1	-7,4
[NO3NaHCO3H]	-7,5	-13,0	-11,0
[NO ₃ KHCO ₃ H]	-13,7	-13,2	-11,4
[NO ₃ KH ₂ PO4H]	-23,6	-18,6	-16,0
[NO3NaH2PO4H]	-19,0	-18,4	-17,1
[NO ₃ Na ₂ SO₄H]	-17,2	-19,6	-17,8
[NO ₃ Na ₂ CO ₃ H]	-26,4	-25,9	-24,1
[NO ₃ K ₂ HPO₄H]	-33,4	-27,5	-25,1
[NO ₃ K ₂ SO ₄ H]	-31,7	-34,0	-30,6
[NO ₃ Na ₂ HPO ₄ H]	-45,8	-40,3	-36,9
[NO ₃ K ₂ CO ₃ H]	-49,8	-52,1	-50,2
[NO ₃ Na ₃ PO ₄ H]	-57,3	-56,9	-53,5
[NO ₃ K ₃ PO ₄ H]	-63,0	-56,4	-53,3
[NO ₃ CaHPO₄H]	-54,2	-56,6	-55,7
[NO3CaSO4H]	-58,6	-57,6	-56,8
[NO ₃ CaCO ₃ H]	-69,4	-68,5	-67,1
[NO ₃ MgSO ₄ H]	-73,5	-75,8	-75,4
[NO ₃ MgCO ₃ H]	-90,4	-92,7	-90,7

Table 6. Relative energy (kcal/mol) for the decomposition reaction for inhibitors and inerts substances in

presence of NH₃

Looking at the list of reactions above, it is evident that when an ammonia molecule encounters one of the salts, it generally forms an aggregate in which the NH₃ molecule is bound to the salt cation. Only in few cases, in addition to the formation of the bond between NH₃ and the cation, also the transfer of an ammonia proton to the salt happens. This type of reactivity is represented by reactions number 72, 74, 76, 77. In fact, in all these cases there is the displacement of a proton on the anion of the salt, reaching the formation of aggregates [NH₂...CaHPO₄H], [NH₂...CaCO₃H], [NH₂...MgCO₃H], [NH₂...MgSO₄H]. In the case of the reactions 74, 76, 77, transition state were isolated (TS [NH₃...CaCO₃], TS [NH₃...MgSO₄]), in which

the movement of the proton from NH_3 towards the anion of the salt with which the ammonia forms the aggregate has been seen. The images of the transition states are reported in Figure 18.

Figure 18. Transition state for the reaction between CaCO₃, MgCO₃ and MgSO₄ and a molecule of ammonia

4.2.3 Comparison between the reaction energies of oxyanion salts in the presence of HNO₃ or NH₃

In this paragraph it is illustrated and summarized all the reactions seen previously for the oxyanion salts. In particular, the focus will be on the higher tendency of these salts to react with HNO₃ or with NH₃. Table 7 summarizes for each salt the separate contributions of energy ΔE , ΔH , ΔG when they react with HNO₃ (left column in blue) and when they react with NH₃ (right column in red). Comparing the free energy values of the reactions of the salts studied with HNO₃ and then with NH₃, it is immediately evident that for all the salts the most favored reactions from the thermodynamic point of view are those with HNO₃. On the contrary, reactions with NH₃, although spontaneous and favored, have a lower tendency to occur. This trend is confirmed by Table 7, which introduces a direct comparison between what happens in the presence of nitric acid and in the presence of animonia. As we can see, reactions with ammonia are disadvantaged compared to reactions in the presence of nitric acid, confirming once again that the stabilization of ammonium nitrate with these salts passes through the inactivation of nitric cacid as a fundamental step. HNO₃, as already mentioned in the case of CaCO₃ and CaSO₄ in the third chapter, generally becomes part of an aggregate with the oxyanion. This mechanism is confirmed by the theoretical data reported in Table7. The only exception is represented for a substance considered inert as Ca(NO₃)₂, which reacts more easily with NH₃ (ΔG =-9.9 Kcal/mol) compared to HNO₃ (ΔG =0.1 Kcal/mol).

	ΔΕ	ΔН	ΔG		ΔΕ	ΔН	ΔG
NH ₄ NO ₃	0	0	0	NH4NO3	0	0	0
NH ₃ + HNO ₃	13.5	13.9	5.4	NH ₃ + HNO ₃	13.5	13.9	5.4
[NO ₃ (NH ₄) ₂ SO ₄ H]1	9	-0.2	4.1				
[NO ₃ (NH ₄) ₂ SO ₄ H]2	3.3	-5.9	0.4				
[HNO ₃ Ca(NO ₃) ₂]	1.2	-1.1	0.1	[NH ₃ Ca(NO ₃) ₂]	-7.8	-9.8	-9.9
[NO ₃ (NH ₄) ₂ HPO ₄ H]	-10.3	-8.5	-5.7				
[HNO3KHSO4]	-6.3	-8.6	-6.9	[NH ₃ KHSO ₄]	8.5	6,5	7.1
[HNO3NaNO3]	-6.6	-8.9	-7.1	[NH ₃ NaNO ₃]	0.1	-1.8	-2.4
[HNO3NaHSO4]1	-15.8	-18.5	-7.0	[NH ₃ NaHSO ₄]	2.5	0.5	1.9
TS _[NO3HNaHSO4]	-15.2	-18.0	-4.4				
[HNO3NaHSO4]2	-18.5	-21.3	-9.1				
[NO ₃ KNO ₃ H]	-6.7	-9.1	-7.4	[NH ₃ KNO ₃]	3.5	1.5	2.8
[NO3NaHCO3H]	-7.5	-13.0	-11.0	[NH ₃ NaHCO ₃]	2.8	-2.3	-0.8
[NO3KHCO3H]	-13.7	-13.2	-11.4	[NH ₃ KHCO ₃]	6.7	1.5	1.5
[NO ₃ KH ₂ PO4H]	-23.6	-18.6	-16.0	[NH ₃ ···KH ₂ PO ₄]	5.5	3.6	4.4
[NO ₃ NaH ₂ PO ₄ H]	-19.0	-18.4	-17.1	[NH ₃ ···NaH ₂ PO ₄]	3.1	-3.2	-3.6
[NO3Na2SO4H]	-17.2	-19.6	-17.8	[NH ₃ Na ₂ SO ₄]	-1.5	-3.5	-3.9
[NO ₃ Na ₂ CO ₃ H]	-26.4	-25.9	-24.1	[NH ₃ ···Na ₂ CO ₃]	6.6	0.8	0.4
[NO ₃ K ₂ HPO ₄ H]	-33.4	-27.5	-25.1	[NH ₃ …K ₂ HPO ₄]	2.9	0.9	1.3
[NO ₃ K ₂ SO ₄ H]	-31.7	-34.0	-30.6	[NH ₃ K ₂ SO ₄]	0.8	-1.1	1.1
[NO3Na2HPO4H]	-45.8	-40.3	-36.9	[NH3 ··· Na2HPO4]	0.1	-1.9	-2.0
[NO ₃ K ₂ CO ₃ H]	-49.8	-52.1	-50.2	[NH ₃ ···K ₂ CO ₃]	5.6	3.6	3.6
[NO ₃ Na ₃ PO ₄ H]	-57.3	-56.9	-53.5	[NH ₃ Na ₃ PO ₄]	4.0	-3.8	-2.4
[NO3K3PO4H]	-63.0	-56.4	-53.3	[NH ₃ ···K ₃ PO ₄]	-0.5	-2.5	-1.5
[NO ₃ CaHPO₄H]	-54.2	-56.6	-55.7	[NH₂…CaHPO₄H]	-5.4	-7.3	-7.8
[NO3CaSO4H]	-58.6	-57.6	-56.8	[NH3 ··· CaSO4]	-14.9	-15.2	-14.0
NO3CaCO3H	-69.4	-68.5	-67.1	[NH3 CaCO3]	-12.8	- 12.8	- 12.4
				TS _[NH3···CaCO3]	- 0.9	- 1.5	0.7
				[NH2 CaCO3H]	- 17.7	-17.2	-18.3
NO3MgSO4H	-73.5	-75.8	-75.4	[NH3"MgSO4]	-28.0	-30.0	-29.6
				TS [NH3····MgSO4]	-25.3	-27.3	-24.2
				[NH ₂ MgSO₄H]	-31.5	-33.4	-34.6
NO ₃ MgCO ₃ H	-90.4	-92.7	-90.7	[NH ₃ ···MgCO ₃]	-24.7	-26.6	-28.8
				TS _{[NH3} ····MgCO3]	-11.6	-13.6	-11.1
				[NH ₂ MgCO ₃ H]	-38.8	-40.7	-40.6

Table 7. Comparative table of relative energies (Kcal/mol) generated during the reactions of inhibitors and inert substances, in presence of HNO₃ (on the left in blue) and NH₃ (on the right in red).

The Δ Gs here calculated represents the index of stability of these aggregates. with the experimental reactivity expressed as the maximal peak of decomposition temperature (Tmax). It has been therefore tried to correlate the stabilization of these aggregates with the maximum decomposition temperature of AN (Tmax). Below, in Figure 19, a graph where the Tmax of decomposition of AN is correlated to the DG of formation of each aggregate is presented.

															∆G (Kcal/mol)	Tmax
	388 –									₩		[/	10 ₃ (NH	$\sum_{4} SO_4 H]1$	4,1	348
	384 -											[]	10 ₃ (NH	$\int_{4^2} SO_4 H]2$	0,4	348
	380 -					₩							INO3Ca	$(NO_3)_2]$	0,1	328
	376 -							₩				[N	103(N H .	() ₂ HPO ₄ H]	-5,7	364
Ő	3/2 -			4								[]	INO3Na	NO ₃]	-7,1	328
, ر	364				♥		₽					[N	103KNC	<i>]</i> ₃ <i>H</i>]	-7,4	323
lior	360]		4	۲		₩			₽			[]	/ <i>O</i> 5 <i>KH</i> C	CO_3H	-11,4	372
isit	356 -											[]	O_3KH_2	P <i>O4H]</i>	-16	348
dr	352 -											[]	103Na H	$_2PO_4H]$	-17,1	366
00	348 -	₩ ₩			\$							[]	O_3Na_2S	$O_4H]$	-17,8	349
de	344 -											[N	103Na2 C	CO_3H	-24,1	381
of	340 -											[N	103K2H	PO₄H]	-25,1	364
X	336 -]								*			[]	O_3Na_2H	HPO₄H]	-36,9	366
Ĕ	332 -								¥			[]	103K2 C ($O_3H]$	-50,2	374
F	328 -	4	•	₩								[]	103K3 P 0	$O_4H]$	-53,3	362
	324 -			♥								[]	103CaH	$PO_4H]$	-55,7	337
	320 -											[/	103CaS	$O_4H]$	-56,8	334
	310 -											[] []	103CaC 103. MaC	O₃H] '○₅H1	-67,1	389
	³¹² +				· - 1				, ,		·	· · · ·		<u> </u>	-90,7	378
	10	0)	-10	-2	0 -3 Gibb	s Fre	10 -50 e Energ	-60 gy (Ko	-70 al/mol)	-80	-90	-100			

Figure 19: Oxyanions's ΔG versus Tmax decomposition temperature of AN placed in contact with compatible substances (inorganic inerts and inhibitors).

However, looking at Figure 19, it was not possible to correlate the Δ Gs with the experimental reactivity expressed as the maximal peak of decomposition temperature (Tmax). From a qualitative point of view, this lack of correlation could be due to a slight overestimation of the stabilizing effect that the cation exerts on AN. An excellent example is the case of [NO₃...MgCO₃], for which looking at its Δ G, is more stable than the aggregate [NO₃...CaCO₃]. But, from an experimental point of view, it is CaCO₃ to have a more stabilizing effect that MgCO₃. In fact, experimental data tell us that CaCO₃ stabilizes ammonium nitrate better than MgCO₃ with a Tmax of 389 °C, compared to the presence of AN Tmax of MgCO₃ which is about 378 °C.⁹ Instead, the theoretical values tell us that the Δ G of formation of the aggregate [NO₃...CaCO₃H] is equal to

-67.1 Kcal/mol, lower than the Δ G of formation of the aggregate [NO_{3...}MgCO₃H] that is -90.7 Kcal/mol, the exact opposite results compared then on decomposition temperature of ammonium nitrate, expressed ad Tmax. Therefore, in order to circumvent this possible obstacle presented by the cation, a correlation has been sought between the proton affinity linked to each salt and the Tmax presented experimentally. This work is presented in the Annexe II, at the end of this manuscript.

4.3 Conclusion

This study confirms that the oxyanion salts presented in this chapter all show the same mechanism of action with AN, namely that they all preferentially react with HNO_3 . The only exception is $Ca(NO_3)_2$ which seems to interact with NH₃ instead of HNO₃. The ability of these salts to stabilise nitric acid may determine their inhibitory character. Each oxyanion salt presented in this study has a different tendency (different values of ΔG) to stabilize HNO₃. However, looking at the relative trends of ΔG s resulting from the formation of aggregates, it does not give us a measure of the experimental reactivity of each salt. This means that the ΔG of formation of each aggregate are not directly correlated with the real reactivity in the presence of ammonium nitrate, which is generally expressed in term of the decomposition temperature. A good example of the problem is the reactivity of CaCO₃ compared to the reactivity of MgCO₃. Other experimental works confirming the better stabilization of calcium carbonate compared to magnesium carbonate are the ones of Poplawski¹⁶ and a work of Rudkiak¹⁷ in which was evidenced see that calcium carbonate is a better stabilizer than magnesium carbonate. The other cases studied are inert substances such as NaNO₃ (Tmax=328 °C) and KNO₃ (Tmax=323 °C), which as inert it was expected that they should generate a lower stabilization than the real inhibitors. Instead, the theoretical reactivity of NaNO₃ and KNO₃ would seem comparable to that of other oxyanion salts such as (NH₄)₂HPO₄ (Tmax=364 °C) and (NH₄)₂SO₄ (Tmax=348 °C), which have a decomposition temperature higher than the decomposition temperature of NaNO₃ and KNO₃. It could lead to the conclusion of an overestimation of the effect of the cation on the stabilisation of the nitrate. For this reason it was performed a study that did not take into account the effect of the cation but only the ability of oxyanion salts to accept a proton from HNO₃. In fact, in Annex II, a work is presented in which the proton affinity was correlated with the experimental reactivity of ammonium nitrate, with the aim to try to eliminate the obstacle presented by the cation of oxyanion salts in attempt to seek a better correlation.

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Conclusion

This study aims to better understand by molecular modelling the phenomena behind the reactivity of ammonium nitrate in the presence of additives and contaminants. Ammonium nitrate (NH₄NO₃, AN) is an inorganic compound classified as an oxidizing agent according to the UN Recommendations on the Transport of Dangerous Goods (UN, 2015) and extensively used in the industry as fertilizer and propellant due to its nature of oxidizer. AN is usually stable, and its thermolysis depends on various factors such as the presence of contaminants, confinement, humidity, pressure, and temperature. The presence of impurities during manufacturing, storage, transport and use processes such as acids, chlorides, fuels, metals can destabilize the AN formulation. AN also presents a long list of incompatible substances such as dichloroisocyanurate (SDIC), organic compounds, nitrites (e.g. NaNO₂) just to mention few. The catalytic effect of the contaminant can lead to an unexpected and sometimes dangerous reaction, i.e. like self-ignition and explosion on the decomposition of ammonium nitrate. In the industrial context, identify and prevent the incompatibility phenomena represents a challenge to improve safety and security. Control of chemical risk in the industrial environment requires quick and accurate screening. In order to evaluate the incompatibility of chemicals with other materials, tools have been proposed for this purpose. These tools exist to facilitate the information sharing about the reactivity of substances, their physico-chemical properties and, most importantly, their incompatibilities. Currently, the tools available for the recognition of chemical incompatibilities are labelling system (Safety Data Sheets (SDS), Chemical incompatibility tables), software (CAMEO, WISER, Chemical Reactivity Worksheet), experimental tools (differential scanning calorimetry, differential thermal analysis, Isothermal calorimetry C80).

Despite the existence of all these instruments used for the prevention of the chemical risk related to ammonium nitrate, safety issues related to the use of AN is far from being achieved: insufficient knowledge is still available about the interaction mechanisms of ammonium nitrate with contaminants. INERIS, in collaboration with Chimie ParisTech, has led to the development of a molecular modelling approach to complete and improve experimental knowledge about chemical incompatibilities with ammonium nitrate. The previous theoretical works were based on Density Functional Theory (DFT) calculations, and they were intended to provide information in terms of energetics and products formed by the interaction between ammonium nitrate and some AN's contaminants (SDIC salt, NaNO₂ and NaNO₃). The previous computational studies helped to face some difficulties by clarifying the reaction mechanisms of the previous chemicals when they interacted with AN.

The aim of this thesis was to improve and increase the theoretical knowledge about ammonium nitrate reactivity and to investigate and predict the effect of the different types of AN's additives and contaminants that can be found in AN's formulations. In general, AN is used in formulations mixed with additives. These

additives can be added to improve the efficiency of the formulation (as in fertilizers) or to improve explosion effect in explosive applications. Some additives are also used as a stabilizer (like carbonates, sulfates, phosphate of sodium, potassium, calcium) to avoid the decomposition during transport and storage. Preliminary extended bibliographic work allowed the identification of three systems representing the different behaviours when substances are placed in contact with AN, namely inerts, promoters and inhibitors.

The purpose of this thesis was to investigate what is meant by compatibility between an additive and ammonium nitrate in the case of fertilizers, and to investigate a particular case of incompatibility for which until today it has not been possible to find a coherent explanation both from an experimental and a theoretical point of view. This is the case of chlorinated substances, in particular for CaCl₂.

More in general, it has been tried to define the key characteristics of inhibitors, promoters and inert substances of decomposition with ammonium nitrate.

Through the study of the first system, CaCO₃, known and used as an inhibitor of the decomposition of AN, it was seen that the stabilization of AN was due to the inactivation of HNO₃ (coming from the decomposition of AN into HNO₃ and NH₃). Indeed, HNO₃, by forming a stable aggregate with CaCO₃, was unable to decompose in the two radicals that were at the basis of the AN destabilization. Moreover, the reactions between HNO₃ and CaCO₃ did not present a barrier, but they proved to be spontaneous and highly favourable reactions. The same mechanism of action presented by CaCO₃ was confirmed in the case of CaSO₄, although the latter was experimentally seen to be less effective than calcium carbonate, and theoretical calculations have confirmed and given a possible explanation about the lower reactivity of CaSO₄ compared to CaCO₃. After the investigation of the first two systems just described, a clearer idea of the microscopic mechanism of action of the inhibitors began to emerge.

The study continued with the exploration of a borderline case, such as the one of ammonium sulfate $(NH_4)_2SO_4$, which is used as an inhibitor of AN in fertilizer context. DSC experiences showed its effectiveness in raising the temperature of AN decomposition, while ballistic mortar experiments indicated its dangerousness when the concentration of AN exceeds 50%. Moreover $(NH_4)_2SO_4$ was involved in a serious accident of the chemical industry: the accident of Oppau on 21 September 1921. The theoretical study indicated the formation of two possible aggregates: $Aggr_{Ab}$ ($[NO_3^{...}(NH_4)_2SO_4H]_{Ab}$) and $Aggr_{Aa}^*$ ($[HNO_3^{...}(NH_4)_2SO_4]_{Aa}^*$). The previous structures, shown in round brackets, differ not only in the protonation of the sulfate anion present in AggrAb and absent in AggrAa^{*}, but also in their overall structural geometry. It has been seen that $Aggr_{Aa}^*$ can easily decompose into its components, namely $HNO_3 + (NH_4)_2SO_4$, which have energy close to that of the decomposition of AN into HNO₃ and NH₃. This suggested

that $(NH_4)_2SO_4$ was a mild AN inhibitor, due to its inability to completely stabilize HNO₃, compared to what it has seen in the two previous cases of CaCO₃ and CaSO₄. Experimentally it was also hypothesized that the danger of $(NH_4)_2SO_4$ lies in the possibility of oxidation of the ammonium cation, NH_4^+ , whose reaction in the presence of oxygen is much more exothermic than the one of pure NH_4NO_3 . However, the mechanism of oxidation of $(NH_4)_2SO_4$ remains to be clarified in order to have a complete picture of this incompatibility that occurs after an incomplete inhibition.

Next, the study of diammonium sulfate ($(NH_4)_2HPO_4$, DMP) was performed to clarify how this substance, with a structure similar to $(NH_4)_2SO_4$, is experimentally a more effective inhibitor. From the theoretical study emerged that DMP leads to more stable HNO₃ aggregates than those formed by $(NH_4)_2SO_4$. Although DMP does not easily lead to HNO₃ deprotonation, it does stabilize it.

In these four compatibility cases studied, the key element is, therefore, the ability to stabilize HNO₃, preventing its decomposition, through the formation of aggregates. This hypothesis was then verified on other systems classified as inert, including KNO₃, NaNO₃, Ca(NO₃)₂ and also to other systems classified as inhibitors (MgCO₃, Na₂CO₃, KHCO₃, NaHCO₃, MgSO₄, K₂SO₄, Na₂SO₄, NaHSO₄, KHSO₄, Na₃PO₄, K₃PO₄, Na₂HPO₄, K₂HPO₄, CaHPO₄, NaH₂PO₄, and KH₂PO₄). For all these substances, it was found that they all had the same mechanism of action, namely that they reacted with HNO₃, ensuring all a certain stabilization. However, it was not possible to correlate the Δ Gs, index of stability of these aggregates, with the experimental reactivity expressed as the maximal peak of decomposition temperature (Tmax). From a qualitative point of view, this lack of correlation could be due to a slight overestimation of the stabilizing effect that the cation exerts on AN: an excellent example is the case of MgCO₃, which is more stabilizing than CaCO₃, even if the experimental reactivity indicates the exact opposite. Therefore, in order to circumvent this obstacle, a correlation has been sought between the proton affinity linked to each salt and the Tmax presented experimentally. In this case, there is an improvement of the tendency even if, however, there is no real relation between Tmax and proton affinity.

The last chapter deals with the interaction of AN with chlorinated substances. In particular, the focus was on the reaction mechanism of CaCl₂, but the same mechanism seems to be applicable also to KCl. It has been seen that the formation of HCl, coming from the reaction between HNO₃ and CaCl₂ or KCl, is able to destabilize AN, leading to the formation of NO₂Cl that is able to decompose in the two radicals NO₂[•] and Cl[•]. These latter can generate a cascade of reactions able to strongly destabilizing AN. However, the difference in energy between TS_{2C} that led to the formation of NO₂Cl, and the decomposition barrier of HNO₃ is 3.6 Kcal/mol, so the transition state is just a few more energetic than the decomposition of HNO₃. As it was done for other incompatible substances during previous studies conducted at INERIS on ammonium nitrate (SDIC and NaNO₂ salts), to decrease the barrier and see if the most favourable reaction

is actually the decomposition of TS_{2C} , the influence of a molecule of water on the geometry of the transition state could be studied, looking at the effect on the barrier of reaction. This study can be considered explorative research of the incompatibility of chlorinated substances, using molecular modelling.

In an attempt to give a systematic definition to the terms of inhibitors, inert and promoter of ammonium nitrate decomposition, the following definitions can be derived from our results:

- An inhibitor is a substance that is able to inactivate HNO_3 radical decomposition through the creation of stable aggregates whose formation is generally spontaneous and does not present energetic barriers to a reaction. The macroscopic effect of this microscopic mechanism of action is an increase in the temperature of decomposition of the mixture between AN and the inhibitor.

- A promoter can react either with HNO₃ or with NH₃, give chemical species that are more reactive than the original ones. From a microscopic point of view, this incompatibility is generally established because the reaction barrier between the incompatible substance and AN presents a lower energetic barrier than that of the decomposition of HNO₃ in OH[•] and NO₂[•]. However, it may happen, as in the case of chlorinated salts such as KCl and CaCl₂, that the chemical species causing the incompatibility are not directly the starting species but also a substance that is formed during the course of complex reactions.

-A definition of inert is still under study. Experimentally, inert substances used in AN grade fertilizer are NaNO₃, Ca(NO₃)₂, KNO₃. They do not alter the thermochemistry of the decomposition of AN; in fact, the temperature of decomposition measured with DSC is not affected by their presence in the mixture. It is commonly accepted that inerts act as diluent of the heat generated from AN decomposition. From a theoretical point of view, it was studied that AN did not interact with NaNO₃, due to a higher reaction barrier than the barrier of the decomposition of HNO₃. Looking at the new theoretical results, it seems that NaNO₃, Ca(NO₃)₂, KNO₃ could react as the other tested inhibitors, forming quite stable aggregates and inactivating HNO₃. With regards to the proton affinity, an inert has a lower capability to capture the proton from HNO₃, so they present a lower proton affinity than the other inhibitor substances. This means that as far as inerts are concerned, a more in-depth study deserves to be carried out, to see if, in addition to the reactions studied up to now, there may be other specifics of this category.

Computational chemistry approach allowed to identify the reactivity with AN of most of the substances explored in this study, by describing both the thermodynamic profile and the reaction path. Thanks to molecular modelling, it has been possible to predict the inhibitor and promoter behaviour of the substances taken into account, with a good agreement with experimental studies. Even if a great effort was made in order to understand the behaviour of AN in the presence of additives and contaminants, still some points remain unexplored. In particular, the predictive part of the study did not bring the expected results. In fact,

the attempt to extrapolate one or more predictive physico-chemical parameters linked to the reaction mechanism of these substances did not lead to the desired results. It could, therefore, be interesting and fruitful to conduct a purely relational-structure-reactivity QSPR study, to see if this approach can be more exhaustive and trying to find more satisfactory relationships between the numerous types of existing descriptors and the reactivity of AN in the presence of inhibitors, inerts and promoters of its decomposition.

Annexe I

ADR incompatibility table, Recommendation for the segregation of dangerous substances

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Annexe II

Attempt to build a predictive tool on ammonium nitrate reactivity in the presence of additives and contaminants

I. Research of predictive physico-chemical descriptor of the influence of additives on the thermal stability of ammonium nitrate.

I.I Proton Affinity

In chapter 5, salts of oxyanions were identified to show the same reaction mechanism when they react with AN. The explanation of their reactivity has been assigned to the fact that they can form stable aggregates with HNO₃ and prevent the latter from decomposing into OH[•] and NO₂[•].

Ideally, the formation of these aggregates can be imagined as the sum of two different actions that co-occur for most of the salts taken into account:

1) Interaction by HNO₃ with the salt's cation

2) the deprotonation of HNO₃ to NO₃⁻ caused by the salt of oxyanion which can capture a proton

The experimental reactivity of these stabilizing salts has been attributed to their pH and therefore to their basic nature.^{1,2} For this reason, it was then decided to investigate how high was their tendency in capturing the proton of HNO₃, without considering the influence of their cation. Once nitric acid has become NO_3^- , it no longer decomposes into OH and NO_2^- .

So it was thought that the essential condition for HNO_3 to be inactivated by various oxyanions was at least their ability to capture a proton. It was therefore thought to study the proton affinity of each oxyanion salt, just seen in the previous chapter, in capturing a proton coming from HNO_3 , which became NO_3^- .

The proton affinity (Pa or Epa) of an anion or a neutral molecule is defined as the negative of the variation of enthalpy between the species shown below, calculated in the gas phase:³

$A^- + H^+ \rightarrow HA$

Concerning our case of study, all reactions between the various oxyanion salts and HNO₃ were considered as follows:

 $HNO_3 + MA_xO_y^z \rightarrow NO_3^- + (MHA_xO_y^z)^+$

Where M is the cation of the oxyanion. The various proton affinity values have been calculated for all salts for which the experimental decomposition temperature was available, i.e. the Tmax provided by Oxley's article (2002).¹ In Figure 1, the species whose proton affinity was investigated are presented:



Figure 1: Energetic diagram of the Tmax of the decomposition of AN associated to proton affinity of each salt for a proton coming from a molecule of HNO₃.

Since at an experimental level a key role was attributed to basicity expressed as pH, a parameter was searched that could reflect the tendency of these types of salts to take on themselves a proton from HNO₃. Looking at the energetic diagram in Figure 1, a linear correlation or a certain proportionality between the protonic affinity and the Tmax does not appear. The unique quite interest information is that the inert substances such as Ca(NO₃)₂, NaNO₃, KNO₃ and CaSO₄, they are the ones with the lower proton affinity. A low tendency to capture the proton of HNO₃, could confirm their inert behavior. Also CaHPO₄ is experimentally considered as an inert,¹ but it presents a proton affinity higher than the rest of inert substances. Therefore, also proton affinity cannot accurately predict the behaviour of AN in contact with this type of additive.

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Résumé de Thèse

Introduction

Le nitrate d'ammonium (NA) a été impliqué dans un certain nombre d'accidents majeurs au cours du siècle dernier. Les questions de sécurité liées à l'utilisation du nitrate d'ammonium sont loin d'être résolues : les connaissances sur les mécanismes d'interaction du nitrate d'ammonium avec les contaminants sont encore insuffisantes malgré des efforts importants. Le présent document propose d'étudier les contaminants du nitrate d'ammonium, qui peuvent être regroupés en trois catégories selon leur action lorsqu'ils sont en contact avec le nitrate d'ammonium : les promoteurs, les inhibiteurs et les inertes. Le but de cette étude est d'identifier les voies de réaction communes possibles à l'intérieur de chaque catégorie pour finalement construire un outil prédictif capable de déterminer si un contaminant peut impliquer une incompatibilité chimique avec NA ou non, à l'aide de la chimie computationnelle. Le nitrate d'ammonium est largement utilisé dans l'industrie comme engrais et propulseur en raison de sa nature d'oxydant. Il est classé comme agent oxydant selon les Recommandations relatives au transport des marchandises dangereuses de l'ONU (ONU, 2015). Le nitrate d'ammonium est incompatible avec un large éventail de substances telles que les chlorures comme le dichloroisocyanurate (DCCNa), les composés organiques, les nitrites (p. ex. NaNO₂), pour n'en citer que quelques-uns. Par ailleurs, l'identification et la prévention des problèmes d'incompatibilité représentent un défi de sécurité important dans le contexte industriel. La maîtrise du risque chimique dans l'environnement industriel nécessite un contrôle rapide et précis. Actuellement, cette information est principalement fournie par les tests de calorimétrie différentielle à balayage (DSC). La limitation de cette approche repose sur le fait qu'il n'est pas possible d'identifier et de comprendre le mécanisme détaillé impliqué dans les réactions entre deux ou plusieurs substances. Au cours des dernières années, l'INERIS, en collaboration avec Chimie ParisTech, a développé une approche de modélisation moléculaire pour compléter et améliorer les connaissances expérimentales sur les incompatibilités chimiques avec le nitrate d'ammonium. Ce travail théorique, basé sur les calculs de la théorie fonctionnelle de la densité (DFT), visait à fournir un aperçu des voies de réaction possibles, en termes d'énergie et de produits formés par interaction entre le nitrate d'ammonium et les contaminants du NA. Dans une première étape, le mécanisme de décomposition du nitrate d'ammonium pur en phase gazeuse a été caractérisé.¹ Ensuite, la réactivité en contact avec SDIC a été étudiée en raison de son rôle possible dans l'accident survenu à l'usine AZF en 2001 à Toulouse. Le mécanisme caractérisé implique la réaction directe du SDIC avec le NH₃ en présence d'eau qui a joué un rôle catalytique dans la réaction.² La même approche théorique a également été utilisée avec succès pour les sels de sodium en contact avec NA, démontrant la capacité de l'approche théorique à prédire a priori si un contaminant est expérimentalement compatible ou non.³ Ces résultats théoriques ont été validés par comparaison avec des essais expérimentaux réalisés par les outils calorimétriques du CERL (Laboratoire canadien de recherche sur les explosifs).³ Cette étude informatique a permis de faire face à certaines difficultés en clarifiant les mécanismes de réaction impliqués dans ces incompatibilités chimiques et d'identifier les produits dangereux générés. Les travaux en cours visent maintenant à étendre l'utilisation de cette approche de chimie computationnelle pour étudier et prédire de façon plus générale l'effet des différents types de contaminants AN que l'on retrouve dans les formulations du NA : inhibiteurs, inertes et promoteurs. Dans ce but, de nouveaux contaminants ont été étudiés en vue du développement futur d'un outil simplifié de prédiction du comportement des contaminants dans les formulations du NA.

Contaminants du nitrate d'ammonium

En général, le nitrate d'ammonium est utilisé dans des formulations mélangées avec des additifs ou des contaminants. Les additifs sont ajoutés aux formulations pour améliorer l'efficacité de la formulation (comme dans les engrais) ou pour améliorer l'effet d'explosion dans les applications explosives. Certains additifs sont également utilisés comme stabilisants (comme les carbonates, sulfates, phosphate de sodium, potassium, calcium) pour éviter la décomposition pendant le transport et le stockage. De plus, les formulations de nitrate d'ammonium pourraient également être accidentellement soumises à une contamination par des impuretés : les contaminants peuvent diminuer la stabilité thermique du NA et favoriser l'auto-inflammation et les explosions, causées par leurs effets catalytiques sur la décomposition du NA. En outre, le tableau 1 énumère une série de catastrophes majeures causées par le nitrate d'ammonium au cours des cent dernières années. La plupart des accidents ont été causés par l'incompatibilité avec des substances avec lesquelles le nitrate d'ammonium est entré en contact.

Année, Lieu	Substances en cause	Effets
1921, Oppau-Allemagne	$(NH_4)_2SO_4/NH_4NO_3$	Feu
1947, Canada	NH ₄ NO ₃	Explosion
1947, Texas City- États-Unis	NH ₄ NO ₃ (pure)-NH ₄ NO ₃ -sulfure	Explosion
1954, Finlande (navire)	NH4NO3/ papetière / acétoarsénite de	Incendie suivi d'une
	cuivre	explosion
1994, Sergent Bluff_États-	NH ₄ NO ₃	Explosion
Unis		
2000, Aunay-Sous-Crecy-	NH ₄ NO ₃ / matières organiques	Décomposition du NA
France		
2001, Toulouse- France	NH4NO3/ sel de sodium de l'acide	Explosion
	dichloroisocyanurique (DCCNa) ?	
2013, Texas Ouest États-Unis	NH ₄ NO ₃	Explosion

 Tableau 1 : Quelques accidents majeurs du NA

Idéalement, les substances avec lesquelles le nitrate d'ammonium peut entrer en contact peuvent être divisées en trois grandes catégories : les promoteurs, les inhibiteurs et les inertes. Ils seront expliqués plus en détail ci-dessous.

Promoteurs

Un promoteur (ou une substance incompatible) est un contaminant qui favorise la décomposition du nitrate d'ammonium, abaissant la température de décomposition par rapport au NA pur. Ceci est notamment introduit dans la formulation NA à cet effet. Pour démontrer ce comportement, des expériences calorimétriques telles que la calorimétrie différentielle à balayage (DSC) ou le Reactive System Screening Tool (RSST) peuvent être réalisées sur du nitrate d'ammonium pur, sur les substances incompatibles suspectes et sur leur mélange. Dans le cas d'un promoteur, la température de décomposition du mélange est inférieure à celle du NA pur et la chaleur dégagée peut être supérieure. Les promoteurs sont nombreux parmi les contaminants du nitrate d'ammonium. À l'intérieur de cette catégorie, on retrouve divers types de produits chimiques tels que les carburants, les sels d'halogénures,⁴ les nitrates et les sulfates de chrome, fer, cuivre, aluminium et oxyde de chrome⁵. Les expériences DSC et RSST menées sur une grande série de contaminants ont clairement démontré l'effet déstabilisateur de ces contaminants incompatibles en abaissant la température de décomposition (Tmax et Tonset) par rapport au nitrate d'ammonium pur^{6,7,8}. Le tableau 2 présente quelques-uns des promoteurs les plus courants.

Combustible	Sels halogénés	Nitrates	Sulfates
carbone, huile	KCl, NH ₄ Cl, CaCl ₂ ,	Nitrates de chrome(III),	Sulfates de chrome(III),
minérale, diesel, sucre,	NaCl,	d'aluminium(III) et de	d'aluminium(III), de
nitrobenzène,	KBr, KI, KF	cuivre(II)	fer(II), de fer(III) et de
nitrométhane,			cuivre(II)
nitrométhane,			
aluminium			
sulfure			

Tableau 2 : Exemples de promoteurs de la décomposition du nitrate d'ammonium, données extraitespar Oxley (2002), données extraites par Oxley (1992), (Han et al., 2015 ; 2016).4-8

Inertes

Les inertes de NA se comportent selon un effet de dilution sur NA. Ils ne modifient pas la réaction chimique elle-même, mais les conditions de réaction dues à son incorporation dans le mélange, ce qui réduit la probabilité d'une explosion du NA.⁴ Les matériaux inertes (NaNO₃, KNO₃ et Ca(NO₃)₂)

ne semblent pas affecter la stabilité thermique du NA⁴. Ces contaminants sont donc utilisés comme diluant et non comme stabilisants.

Inhibiteurs

Les inhibiteurs du NA peuvent être identifiés dans les expériences calorimétriques, lorsque la température de décomposition du NA mélangé au contaminant est supérieure à la température de décomposition du NA pur.⁸ Cependant, la chaleur dégagée pendant la réaction est inférieure à celle de la décomposition du nitrate d'ammonium pur. Les inhibiteurs ont la capacité de rendre le nitrate d'ammonium plus stable. Expérimentalement, la plupart des oxyanions (comme les sulfates, carbonates ou phosphates de sodium, potassium, ammonium et calcium $A_x O_y^{z-}$) augmentent le pic exothermique de décomposition du NA obtenu par les expériences DSC⁴. Comme le montre la figure 1, la plupart des oxyanions augmentent la température exothermique du NA et il semble exister une certaine corrélation entre le pH des oxyanions et leur capacité à inhiber la décomposition et les réactions dangereuses du nitrate d'ammonium (représenté par Tmax). Lorsque l'on fait varier le cation entre Na⁺, K⁺, NH₄⁺ et Ca²⁺, il n'y a pas de grandes différences dans la position du pic exothermique.⁴ Pour des substances comme (NH₄)₂SO₄, NaHCO₃ et K₂CO₃, certaines expériences RSST sont également disponibles.^{6,7} Ces valeurs sont en accord avec les tendances DSC précédentes. En regardant la figure 1, les oxyanions comme CO₃^{2-,} HCO₃⁻ et HPO₄²⁻ maintiennent un pH compris entre 7,4 et 8,3. Les expériences DSC montrent qu'elles augmentent les pics exothermiques de l'AN de 40 à 60 °C supérieurs à ceux du NA pur. Les contaminants comme le SO₄²⁻ et le H₂PO₄⁻, avec un pH de 4-5, augmentent le maximum de 10-20 °C. AN +pН Tmax



Figure 1 : pH des oxyanions en fonction de la température de décomposition du Tmax de l'AN, données extraites par Oxley (2002).

Modélisation moléculaire appliquée à l'incompatibilité chimique

Jusqu'à présent, les seuls outils consacrés à l'étude et à la prévention des phénomènes d'incompatibilité chimique sont les essais calorimétriques, les tableaux d'incompatibilités, les fiches de données de sécurité, l'analyse de l'accidentologie et les informations issues des réglementations chimiques telles que CLP. Ces outils, malgré leur importance incontestée, ne fournissent que des informations incomplètes. La difficulté d'étudier les incompatibilités chimiques réside principalement dans la complexité des voies de réaction générées en présence d'intermédiaires dont la caractérisation expérimentale est parfois difficile. Pour surmonter ce problème, des études de modélisation moléculaire ont été effectuées sur NA. Comme pour les expériences calorimétriques, le mécanisme de décomposition NA pur a d'abord été étudié. Des essais successifs ont été effectués entre NA et d'autres contaminants pour voir si la réaction préférée était celle du NA pur ou du NA avec la substance. Le chemin de réaction, le profil énergétique et tous les intermédiaires de réaction possibles ont été déterminés. Ce travail théorique, basé sur les calculs de la théorie fonctionnelle de la densité (DFT) (M06-2X fonctionnel) et le logiciel Gaussian09, donne un aperçu des voies de réaction possibles en termes d'énergie et de produits formés par la réaction d'incompatibilité entre nitrate d'ammonium et contaminants.

Décomposition du nitrate d'ammonium

Dans un premier temps, le mécanisme de décomposition du nitrate d'ammonium pur a été étudié,¹ dans le but de définir toutes les étapes et tous les intermédiaires impliqués.

La décomposition du nitrate d'ammonium pur commence par un transfert de protons en anion nitrate pour donner NH_3 et HNO_3 (eq.1). Ensuite, l'acide nitrique se décompose en deux radicaux qui génèrent une chaîne radicale séquentielle (eq.2). La dissociation de l'acide nitrique est l'étape limitant :

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$
(1)
$$HNO_3 \rightarrow OH' + NO_2$$
(2)

Sur la base de ce mécanisme, une méthodologie a été appliquée pour étudier l'incompatibilité du NA. Elle consiste à rechercher les réactions entre une substance et NH₃ ou HNO₃, générées par la décomposition de l'AN. En cas de contaminants non compatibles avec NA, ils peuvent réagir avec NH₃ et/ou HNO₃ dans une réaction plus favorable que l'AN pur générant des produits instables (dangereux). Au contraire, ils peuvent réagir avec NH₃ ou HNO₃ toujours dans une réaction plus favorable que le AN pur mais générant des produits stables.

Effets des contaminants et additives

Certains contaminants et additives ont été étudiés pour couvrir un large éventail d'espèces chimiques que l'on trouve dans les formulations du nitrate d'ammonium, à savoir :

1) CaCO₃ qui est normalement utilisé comme inhibiteur de décomposition du nitrate d'ammonium,

2) CaSO₄ qui est normalement utilisé comme inerte (cela signifie qu'il ne réagit pas avec NA) et qui a une action diluant,

3) (NH₄)₂SO₄ qui a un profil promoteur de la décomposition du NA.

4) CaCl₂ qui a un profil promoteur de la décomposition du NA.

5) Etude de la réactivité du nitrate d'ammonium en présence des substances compatibles et recherche de paramètres physico-chimiques prédictifs

$AN + CaCO_3$

Pendant le transport et le stockage, le carbonate de calcium est utilisé comme inhibiteur de la décomposition du nitrate d'ammonium, c'est-à-dire non seulement compatible mais aussi stabilisant les formulations de nitrate d'ammonium. Ce système a déjà été étudié expérimentalement et les produits de la réaction sont : nitrate de calcium, dioxyde de carbone, ammoniac et eau ^{9,10} Cela a conduit à la réaction suivante :

$2 \text{ NH}_4\text{NO}_3 + \text{CaCO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2 \text{ NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (3)$

L'étude du mécanisme de décomposition entre NA et le carbonate de calcium a été réalisée par calculs DFT. Une bonne concordance a été obtenue entre les calculs et les résultats expérimentaux. En fait, en appliquant la méthodologie expliquée précédemment, les produits obtenus expérimentalement ont été identifiés (eq.3). Nos calculs DFT indiquent que le carbonate de calcium intervient après la première étape de la décomposition du nitrate d'ammonium en NH₃ et HNO₃. Comme le montre la figure 2, le carbonate de calcium peut réagir avec l'ammoniac, formant l'agrégat [NH₃CaCO₃], ou avec l'acide nitrique, pour former l'agrégat [NO₃...CaCO₃H]. Dans les deux cas, nous avons deux réactions favorables et spontanées. Celui avec HNO₃ est plus favorable que celui avec NH₃. À la fin de la voie de réaction complète, un agrégat de calcium inerte stable [(NO₃)₂---CaCOH₂] est formé (voir figure 3(a)). Il se décompose facilement en donnant les produits identifiés au niveau expérimental. Ceci confirme que cette méthodologie décrit bien le comportement du nitrate d'ammonium.



Figure 2. Energie libre de Gibbs pour le système NA+ CaCO₃

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Schéma 1. Chemin des réactions entre le nitrate d'ammonium et le CaCO<sub>3</sub>
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$$NH_4NO_3 \longrightarrow HNO_3 + NH_3$$

$$Path A + CaCO_3 Path B$$

$$[NO_3 \cdots CaCO_3H] \qquad [NH_3 \cdots CaCO_3]$$

$$\downarrow + HNO_3 \qquad \downarrow TS_{1B}$$

$$[NO_3 \cdots CaCO_3H_2 \cdots NO_3] \qquad [NH_2 \cdots CaCO_3H]$$

$$\downarrow + NH_3$$

$$Ca(NO_3)_2 + H_2CO_3 \qquad [NH_2 \cdots CaCO_3H \cdots NH_3]$$

$$+ NH_4NO_3 \qquad \downarrow + NH_3$$

$$[NH_4NO_3 \cdots H_2CO_3] \qquad H_2O + CO_2$$

$$\downarrow TS_{3A}$$

$$[NH_3 \cdots HNO_3 \cdots H_2CO_3]$$

$$\downarrow$$

$$NH_3 + HNO_3 + H_2CO_3$$

$NA + CaSO_4$

Le sulfate de calcium est compatible avec NA mais, malgré les similitudes structurelles avec le CaCO₃, il semble plus être un matériau inerte qu'un inhibiteur. Comme il existe moins de données expérimentales dans ce cas, d'autres études expérimentales ont été réalisées au CERL, afin d'obtenir plus d'informations, en particulier sur les produits de réaction qui se forment au cours de la décomposition en présence de CaSO₄. Cependant, la température de décomposition de NA+CaSO₄ n'est pas influencée par la concentration de sulfate de calcium. L'ajout d'une plus grande quantité de CaSO₄ n'affecte pas de façon constante le déplacement de Tmax.⁴

L'étude du système NA + CaSO₄ a été menée par similarité avec le système NA+ CaCO₃. Comme dans le système précédent, le nitrate d'ammonium se décompose en ammoniac et en acide nitrique, qui réagit avec CaSO₄ par deux voies de réaction différentes. Le canal de réaction privilégié passe par la réaction avec HNO₃, formant des complexes finaux cationiques comme [NO₃...CaSO₄H₂...NO₃] (Figure 3(b)). L'analyse suggère que la nature des produits formés lors de la décomposition peut expliquer pourquoi CaSO₄ présente un comportement inerte plutôt qu'inhibiteur (comme CaCO₃).



Figure 3. Energie libre de Gibbs pour le système NA + CaSO₄



Figure 3(a). Image de l'agrégat [(NO₃)₂---CaCO₃H₂]. Figure 3(b). Image de l'agrégat [NO₃---CaSO₄H₂---NO₃].




$NA + (NH_4)_2SO_4$

L'étude d'un autre système, $NA + (NH_4)_2SO_4$ impliqué dans l'accident d'Oppau (Allemagne 1921). L'usine chimique d'Oppau était un centre industriel de la BASF (à l'origine : Badische Anilin- & Soda-Fabrik). Dans cette usine, les engrais azotés ont été produits selon une nouvelle méthode innovante, qui a permis la synthèse à haute pression de l'ammoniac. Le site de production de BASF était situé près du Rhin, près du village d'Oppau. Le mercredi 21 septembre 1921, à 07:32:14 heure locale, l'usine d'Oppau fut semi-détruite par deux explosions apocalyptiques à quatre secondes l'une de l'autre (la deuxième explosion eut lieu à 07:32:18 heure locale). La deuxième explosion était la plus dévastatrice. Le nombre de décès enregistrés, selon les enquêtes officielles, était d'environ 559, 1977 blessés et 1870 sans-abrit. L'usine d'Oppau a été gravement endommagée, et au centre de l'explosion, un énorme cratère de forme circulaire a été formé : 96 mètres de large, 165 mètres de long, avec une profondeur de 18,5 mètres. Le comportement du nitrate d'ammonium en présence de sulfate d'ammonium présente un réel défi puisque la capacité déstabilisatrice du (NH₄)₂SO₄ semble dépendre de sa concentration (Kristensen 2016).¹¹ Les résultats du DFT semblent montrer une faible capacité du mélange à stabiliser le nitrate d'ammonium du fait de (1) à la protonation de l'anion NO₃ en HNO₃ par une molécule de NH₄⁺, 2) la formation d'un acide fort dans l'environnement, H_2SO_4 , qui peut déstabiliser NA et 3) la forte acidité du sulfate d'ammonium lui-même.¹² En fait, il a été démontré expérimentalement qu'un mélange de 1:1 du NA/AS n'est pas détonable, mais qu'il le devient lorsque la concentration du NA est supérieure à 55%.^{13,11} En appliquant l'approche théorique de la DFT, on a mis en évidence une nouvelle voie possiblement incompatible qui pourrait justifier le comportement des certains mélanges NA/AS.



Figure 4. Energie libre de Gibbs pour le système $NA + (NH_4)_2SO_4$

Scheme3. Reaction mechanism between NH₄NO₃ and (NH₄)₂SO₄



AN + DMP

D'un point de vue expérimental, ce sel est considéré comme compatible avec le nitrate d'ammonium dans la table de Fertilizer Europe, et aussi les données expérimentales de calorimétrie vont également dans ce sens.^{5,4} Aucun accident impliquant la présence du DMP n'est signalé dans l'accidentologie du chapitre 1. Oxley, dans ses expériences calorimétriques,^{5,4} montre que le (NH₄)₂HPO₄ ajouté au nitrate d'ammonium peut le stabiliser. Dans ces expériences, la température de décomposition du Tmax pour le nitrate d'ammonium pur était de 326 °C. On a constaté que l'ajout de 5 % en poids de DMP entraîne une augmentation de la décomposition du Tmax à 340 °C. En ajoutant 20 % en poids, la température maximale de décomposition du nitrate dans un mélange avec du DMP est de 364 °C. D'un point de vue expérimental, le DMP est donc plus stabilisateur que l'AS. Le but de cette étude est de déterminer quelle est la réactivité du sel DMP en présence d'AN, et pourquoi il y a cette différence de réactivité avec AS, considérant que d'un point de vue structurel AS et DMP sont similaires. Ils présentent tous les deux molécules d'ammonium qui peuvent potentiellement représenter un facteur de déstabilisation, comme dans le cas du sel ASN. Un premier indice pourrait

être la basicité du DMP qui est égale à 7,4, alors que l'AS présente une basicité de 4,8.⁴ Comme Oxley l'affirme dans ses études expérimentales, il semble que la basicité soit un facteur très important pour la stabilisation du AN. En ce qui concerne le phosphate de di-ammonium, contrairement au sulfate d'ammonium, il ne provoque a priori pas de réaction de décomposition qui pourraient déstabiliser le nitrate d'ammonium, pour les raisons suivantes : la barrière associée à la décomposition d'AggrAa* dans HNO₃ + (NH₄)₂SO₄ était égale à 1,4 Kcal/mol tandis que la barrière associée à la décomposition de [HNO₃···(NH₄)₂HPO₄]* dans HNO₃ + NH₃ + H₃PO₄ est égale à 14,9 Kcal/mol. Cela signifie que la décomposition de [HNO₃···(NH₄)₂HPO₄]* dans ses principaux composants conduisant à la libération de HNO₃ capable de générer une déstabilisation est beaucoup plus difficile à faire, confirmant qu'effectivement le (NH₄)₂HPO₄ a un comportement plus compatible avec AN en raison de la stabilité plus élevée de l'agrégat [HNO₃···(NH₄)₂HPO₄]*. Toutefois, dans le cas du AS. Cepen



Figure 5. Energie libre de Gibbs pour le système NA + (NH₄)₂HPO₄



Schéma 4. Reaction mechanism between NH₄NO₃ and (NH₄)₂HPO₄

$AN + CaCl_2$

Les substances chlorées, ainsi que le CaCl₂, sont des substances incompatibles avec le NA qui diminuent sa température de décomposition. L'incompatibilité chimique possible du CaCl₂ réside dans sa transformation en HCl par réaction avec deux molécules de HNO₃, ce qui conduit à la formation du produit Ca(NO₃)₂ et HCl. L'acide chlorhydrique, en tant qu'acide inorganique incompatible avec NA,¹² d'une part catalyse la réaction de décomposition de NH₄NO₃ en NH₃ + HNO₃, et ensuite il peut réagir avec la nouvelle molécule de HNO₃ obtenue par la décomposition du NA, en conduisant à la formation de NO₂Cl, par un état de transition TS_{2C} qui présente un Δ G de 41,4 Kcal/mol. Cependant, HNO₃ peut aussi se décomposer en radicaux OH[•] et NO₂[•] avec Δ G=37,8 Kcal/mol. Le NO₂Cl se décompose en NO₂' et Cl', ce dernier étant un radical très réactif qui peut réagir avec le NH₃, ce qui conduit à la formation de NH₂Cl, un précurseur de NCl₃ (trichloramine) qui est notamment une substance explosive. La différence d'énergie entre le TS_{2C} et la barrière de décomposition du HNO₃ est de 3,6 Kcal/mol, donc l'état de transition est juste un peu plus énergétique que la décomposition du HNO₃. Comme cela a été fait pour d'autres substances incompatibles lors d'études antérieures menées à l'INERIS sur le nitrate d'ammonium (sels DCCNa et NaNO₂)^{15,3} pour diminuer la barrière et voir si la réaction la plus favorable est bien la décomposition du TS_{2C}, l'influence d'une molécule d'eau sur la thermochimie de l'état de transition pourrait être étudiée en regard de son effet sur la barrière de réaction. Le diagramme relatif de Gibbs de la réaction de CaCl₂ avec NH₄NO₃ est présenté en Figure 6, et le Schème 5 présente le chemin réactionnel.



Figure 6. Profil d'énergie libre de Gibbs pour l'ensemble de la voie de réaction entre le NA and CaCl₂



Schème 5. Mécanisme de réaction complet entre NH₄NO₃ et CaCl₂

Etude de la réactivité du nitrate d'ammonium en présence des substances compatibles et recherche de paramètres physico-chimiques prédictifs

Ce travail tente de décrire la réactivité du nitrate d'ammonium en présence de substances sélectionnées et compatibles : les sels d'oxyanion.⁴ Le but de cette étude est d'analyser le comportement d'une série de substances inorganiques structurellement similaires qui exercent un effet stabilisant sur le NA. L'objectif final est de démontrer si une similarité structurelle et un comportement expérimental commun peuvent indiquer un mécanisme de réaction identique pour les substances présentées ici. L'autre objectif est d'essayer de corréler la réactivité théorique obtenue des sels d'oxyanion (exprimée comme variation de l'énergie libre ou de l'enthalpie de réaction) avec les données expérimentales obtenues par les expériences DSC. Une étude théorique a été réalisée pour mieux comprendre la réactivité du nitrate d'ammonium en présence d'inhibiteurs et des substances inertes telles que : (NH4)2SO4, (NH4)2HPO4, NaNO3, KNO3, Ca(NO3)2, CaCO3, MgCO3, Na2CO3, KHCO3, NaHCO3, CaSO4, MgSO4, K2SO4, Na2SO4, NaHSO4, KHSO4, Na3PO4, K3PO4, Na2HPO4, K₂HPO₄, CaHPO₄, NaH₂PO₄, and KH₂PO₄, afin de clarifier leur mécanisme d'action dans le but de trouver une relation possible qui lie leur comportement expérimental aux données théoriques obtenues. Après une étude théorique des substances présentées mises en contact avec le nitrate d'ammonium, la conclusion est que cette étude confirme le mécanisme de réaction des inhibiteurs avec l'acide nitrique afin de le désactiver. Chaque sel d'oxyanion présenté dans cette étude a une tendance différente (différentes valeurs de ΔG) à stabiliser le HNO₃. La tendance de chaque sel à stabiliser le HNO₃ d'une manière différente dépend de divers facteurs, tels que la façon dont l'anion est lié au proton de l'acide nitrique et la capacité du cation à stabiliser l'agrégat contenant le nitrate. Cependant, si nous regardons les tendances relatives de Δ Gs résultant de la formation d'agrégats, cela ne nous donne pas une mesure de la réactivité expérimentale de chaque sel. Cela signifie que les ΔG de formation de chaque agrégat ne sont pas directement corrélés avec la réactivité réelle en présence de nitrate d'ammonium, qui est généralement exprimée par la température de décomposition du 'AN en présence d'autres substances. Il semble que cette tendance différente puisse être due à une surestimation de l'effet général du cation sur la stabilisation du nitrate. Pour cette raison, une étude a été réalisée sans tenir compte de l'effet du cation, mais seulement de la capacité des sels d'oxyanion à accepter un proton du HNO₃. En fait, l'annexe I présente un travail dans lequel l'affinité des protons et la basicité en phase gazeuse ont été corrélées avec la réactivité expérimentale du nitrate d'ammonium, afin d'éliminer l'obstacle que représente le cation des sels d'oxyanion pour tenter d'obtenir une meilleure corrélation.

Conclusion et perspectives

L'approche de chimie computationnelle a permis d'identifier la réactivité du carbonate et du sulfate de calcium, du sulfate d'ammonium, du phosphate de di ammonium, du CaCl₂ et un large nombre des substances compatibles avec NA en décrivant le mécanisme détaillé de la réaction de réaction. Il semble possible de prédire si une substance agit comme promoteur, inhibiteur ou inerte sur le NA à l'aide de la modélisation moléculaire. Par conséquent, compte tenu de l'impossibilité de tester un nombre infini de substances et de déterminer pour chacune d'elles le mécanisme d'action avec le nitrate d'ammonium, une approche simplifiée a été également recherchée. Grâce à la polyvalence de la méthodologie DFT, des paramètres physico-chimiques ont été recherchés dans l'espoir d'associer un descripteur théorique au type de réaction qu'un contaminant peut avoir avec NA. L'objectif était de démontrer que les promoteurs, les inhibiteurs et les inertes ont une façon particulière de réagir avec le nitrate d'ammonium.

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RÉSUMÉ

Le nitrate d'ammonium (NA) est un composé largement utilisé comme propulseur dans l'industrie chimique et comme engrais dans l'environnement agricole. Il est connu pour sa longue liste d'incompatibilités et souvent impliqué dans des accidents majeurs. L'approche de modélisation moléculaire (DFT, Density Functional Theory) a été appliquée avec succès, lors d'études antérieures à l'INERIS, pour décrire la décomposition du nitrate d'ammonium pur et la réactivité du nitrate d'ammonium en mélange avec le dichloroisocyanurate de sodium (DCCNa). La même approche théorique a été utilisée pour d'autres incompatibilités chimiques pour les systèmes à base de nitrate d'ammonium (NaNO₂, NaNO₃), en se concentrant sur l'étude des étapes limites des mécanismes, pour tester le potentiel de l'approche théorique comme outil de prévision a priori pour les processus d'incompatibilité. Le but de cette thèse est de mieux comprendre la réactivité du nitrate d'ammonium, lorsqu'il est mis en contact avec différents types de substances. Après une étude bibliographique approfondie, trois systèmes présentant des comportements différents en contact avec le NA (inertes, promoteurs, inhibiteurs) ont été sélectionnés : AN+CaCO₃, AN+(NH₄)₂SO₄, AN+CaSO₄. Le système AN+CaCO₃, présente un chemin de décomposition différent de la décomposition de NA pur. En fait, les produits de décomposition ne sont pas dangereux et le chemin de réaction est moins exothermique que la décomposition de NA en absence du carbonate de calcium. Dans un premier temps, le nitrate d'ammonium se décompose en ammoniac et en acide nitrique. NH3 et HNO3 réagissent avec CaCO3 par deux voies de réaction différentes, formant dans les deux cas des agrégés de calcium cationiques : [NH3 ·· CaCO3], [NH2 ·· CaCO3H·· NH3], [NO3 ·· CaCO3H] et [(NO3)2 ·· CaCO3H2]. NA réagit préférentiellement avec HNO3 car la voie thermodynamique réactionnelle est beaucoup plus exothermique et sans barrière. Elle conduit à la formation de produits identifiés par des tests expérimentaux (Ca(NO₃)₂, NH₃, H₂O, CO₂). Pour le deuxième système, AN+CaSO₄ un comportement similaire a été constaté. En fait, l'étude DFT a clarifié le mécanisme par lequel CaCO3 et CaSO4 stabilisent NA : ceci est dû à la formation d'agrégés stables et non dangereux capables de stabiliser HNO3 en évitant la formation des deux radicaux OH* et NO2*. Le système NA+(NH4)2SO4 (NA/AS) présente un intérêt particulier, car il a été impliqué dans un accident industriel important, survenu à Oppau (Allemagne) en 1921. Les résultats de la DFT ont montré que la faible capacité du mélange à stabiliser le nitrate d'ammonium pourrait être due à : 1) l'absence de stabilisation complète du HNO3 due à l'acidité excessive de l'environnement à cause de l'excès de cations NH4+2) l'oxydation du cation NH4+ en présence de l'oxygène. En utilisant l'approche théorique DFT, une voie de réaction a été mise en évidence qui pourrait justifier le comportement particulier du mélange NA/AS, qui peut également agir comme promoteur de la décomposition du nitrate d'ammonium. Finalement, grâce à l'utilisation de la DFT, il a été possible d'expliquer l'effet d'additifs dits inhibiteur (CaCO3), inerte (CaSO₄) et, dans le cas particulier du (NH₄)₂SO₄, inhibiteur et en même temp promoteur de la décomposition du nitrate d'ammonium en fonction de la concentration (en AS). L'étude de ces cas confirme que l'approche théorique utilisée décrit bien la réactivité du nitrate d'ammonium, tant en ce qui concerne la compatibilité que les réactions d'incompatibilité.

MOTS CLÉS

Propriétés physico-chimiques dangereuses, DFT, nitrate d'ammonium, modélisation moléculaire

ABSTRACT

Ammonium nitrate (AN) is a widely used compound in the chemical industry and in agriculture. It is known for its long list of incompatibilities with other chemicals and it was often involved in major accidents. As for others chemical compounds, the knowledge of AN hazards is essentially based on the feedback on the past accidents and on experimental studies, mainly calorimetric and kinetic studies. If these latter provide valuable information on the global effect of additives on the thermal stability of AN, they do not allow to identify and understand the detailed reaction mechanism involved in the decomposition of AN in contact with other substances. In order to bring some insights on these problems molecular modeling approaches, based on Density Functional Theory (DFT) were used during previous studies at INERIS to describe the decomposition of pure ammonium nitrate and its reactivity of incompatible substances, such as sodium dichloroisocyanurate (SDIC) and nitrates compounds (NaNO2, NaNO3). The purpose of this thesis is to better understand the reactivity of ammonium nitrate when it is placed in contact with different types of substances. Preliminary extended bibliographic work allowed the identification of 3 systems representing the different behaviors when they are placed in contact with AN, namely inerts, promoters and inhibitors. These systems are: CaCO₃, (NH₄)₂SO₄, and CaSO₄. As mentioned before, the microscopic reaction mechanism of the AN decomposition in presence of these three molecules, was investigated at DFT level. The system AN+CaCO₃ follows a different decomposition path from that identified for pure AN. Indeed, NH₃ and HNO₃, produced during the first simple step of AN decomposition, react with CaCO₃, through two different reaction pathways, forming non-reactive cationic calcium aggregates: [NH₃-CaCO₃], [NH₂---CaCO₃H---NH₃], [NO₃---CaCO₃H], [(NO₃)₂--CaCO₃H₂]. In such a way, the production of highly reactive species is avoided, and the decomposition products are not reactive. Furthermore, the reaction path is less exothermic than the AN decomposition in the absence of contaminants. The thermodynamically favored path with HNO3 leads to the formation of products identified by experimental tests (Ca(NO₃)₂, NH₃, H₂O, CO₂). For the second case, AN+CaSO₄, a similar global behavior was found. In fact, the DFT study clarified the mechanism by which CaCO₃ and CaSO₄ stabilize AN: it's due to the formation of stable and non-hazardous aggregates capable of stabilizing HNO₃ by avoiding the formation of OH' and NO₂' radicals. The system AN + (NH₄)₂SO₄ is of particular interest, since it was involved in an important industrial accident, that happens in Oppau (Germany) in 1921. DFT results evidenced that the small capability of the mixture to stabilize AN could be due to:1) the absence of complete stabilization of HNO3 for the excessive acidity of the environment given by the excess of NH_4^+ cations 2) the oxidation of the NH_4^+ in the presence of oxygen. Using the DFT theoretical approach, a reaction pathway was identified that could justify the behavior of the NA/AS mixture, which can also act as a promoter of ammonium nitrate decomposition. Finally, thanks to the use of DFT, it was possible to explain the effect of additives known as inhibitors (CaCO₃), inert additives (CaSO₄) and, in the particular case of (NH₄)₂SO₄, inhibitor and at the same time promoter of the decomposition of ammonium nitrate according to concentration (in AS). The study of these cases confirms that the theoretical approach used describes the reactivity of ammonium nitrate, both in terms of compatibility and incompatibility reactions.

KEYWORDS

Hazardous physico-chemical properties, DFT, ammonium nitrate, molecular modelling