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Preface

As the first book on *Liquid Explosives*, this book, covering part of the author's achievements on energetic materials in the past about half a century, presents the results of a wide range of research fields with abundant information and valuable practicality. It also reviews the development of liquid explosives for the first time over the world and focuses on the latest research findings of the explosion mechanism, properties, and preparation process of liquid explosives. Different from the detonation of condensed explosives, liquid explosives show distinct features to easily form under-compressed detonation. The charging and application of liquid explosives are not influenced by geographical conditions, local topographic feature, and land features. Thus, the application range of liquid explosives is considerably wide.

The first word that pops up in the mind would be war, or national-defense, while talking about liquid explosives. The truth is that military use accounts for only a small part. Liquid explosives have been widely used in aerospace, sounding rockets, communications satellites, transportation, mining, construction, seismic prospecting, mineral exploration, channelization, underground blasting, underwater bursting, and channel development. The propellant is the main component of liquid explosives that mainly consist of nitrate ester, perchlorates, hydrazines, or hydrogen peroxide. To understand the basic properties of these materials is important to optimize the performances of liquid energetic materials, including energy levels, combustion behavior, detonation characteristics, stability, processing characteristics, service characteristics, and prolonging storage period. The materials to prepare liquid explosives are well known. Thus, by using the information of technique process, the formulation of liquid explosives can be precisely adjusted to achieve optimized explosion strength and performance. Further improvement of charging conditions and application range would maximize the energy of liquid explosives.

The book is organized into seven chapters. The first chapter, Introduction, contains the concept of liquid explosive and its development direction. In Chap. 2, the detonation mechanism of liquid explosive is reviewed. The liquid explosive exhibits the essential property of explosives. However, its detonation characteristics are different from the common explosives. The general detonation theory cannot

completely explain the detonation behaviors and characteristics of liquid explosives, such as under-compressed detonation. In an infinite free space, the short-distance over-compression of explosion for liquid explosives is not as high as condensed explosives, but the pulse width of its shock wave is much larger than condensed explosives. The positive pressure lasts a long time, thus the total corresponding work is high. Particularly in a semi-closed room, accompanied by the release of large amounts of gas, oxygen surrounding the explosion is involved in the detonation reaction, so-called as oxygen uptake characteristic, which is not observed for common condensed explosives. It is intended to guide researchers to gain primary understanding on the detonation characteristics of liquid explosive, so as to provide supports to applications of liquid explosives. In Chap. 3, the formulating of liquid explosive recipe is presented and the relationship among energy, detonation parameters, and performance of liquid explosives with different structures is systematically discussed. Chapters 4–6 contain the property and preparation technology of typical liquid explosives of nitroalkanes, nitrate esters, and azides. New findings in nitrate ester liquid explosives in our work have been addressed based on previous work. For example, the issue that nitroglycerine is sensitive to be exploded even under a slight shake has been solved using modern technology. We also improved the preparation technology of nitrate esters to implement pollution-free green process of nitrification. Great amounts of azide energetic materials, developed in the past decade, have come to light for the first time in this book. Chapter 7 contains seven types of liquid explosive mixtures and their composition, property, preparation process, and performance.

Besides the author's achievements, the book also contains the scientific views and theoretical knowledge for the research and development of liquid explosives over the world. The main aims of the book are to review the current status of liquid explosive research and development, to provide instruction for studying liquid explosives, and to enlighten researchers of energetic materials. Through reviewing the current application level of liquid explosives, the book, basically, has been designed to address the needs of scientists, researchers, and engineers, who are interested in the composition, preparation, property, application, and performance of energetic materials.

The author is grateful to Ms. Wenxia Qi for her long-standing assistance in preparing and editing the manuscript, and to the editors at Springer Link for their exceptional patience and efforts.

Any suggestions to the book on both academic and expression grounds are welcome, due to the limitations of the author.

Beijing, China, August 2014   Jiping Liu

Contents

Chapter 1
Introduction

1.1 Liquid Explosives

A liquid explosive is a fluxible compound or mixture that suddenly releases energies under certain conditions.

Liquid explosives can be simply clarified to single compound explosives (composed of one liquid molecule such as nitroglycerine, xylitol nitrate, nitromethane, and other azide mitrates) and liquid explosive mixtures (consist of two or more compounds, such as a mixture of a combustible agent and an oxidizer). At least one of the nonexplosive components should be a liquid. The liquid explosive mixtures are of liquid solution, or of colloidal solution or suspension. Combustible agents include nitric acids, nitrogen oxides, and tetranitromethane. Oxidizers are of liquid, including benzene, toluene, ethanol, and hydrazine, while combustible agents could be either liquid or solid nitro compounds. The major purpose of the makeup of liquid explosive mixture is to minimize risks in the process of transportation and operation. The explosive components are separately charged and, at the time before use, mixed together. Liquid explosive mixtures are applied in military affairs and commercial blasting [1]. The components in the formulation contain nitric acid and nitrogen oxide with features of high volatility and strong corrosivity that raise challenges in storage and refill.

Since it was first synthesized in 1847 [2], nitroglycerin as a main component in liquid explosives, has been tremendously investigated and widely used in mining and other industrial blasting, as well as in military, such as propellant powers. Later, a series of liquid explosives of nitrate ester, such as dinitrate esters, with better explosive property and safety were developed [3–5]. In recent years, the United States has launched studies of high power and low characteristic signal propellants to continuously expand the application range of liquid nitrate esters [6].

The development and application of liquid explosives are limited because of stability and energy issues. In order to solve the problems, recently, a great deal of effort has been made to develop considerable alkyl azide compounds and azide

nitrate compounds worldwide [7, 8]. The energetic compounds of nitroalcohol, alcohol with azido- and nitro- groups, and amines have been also extensively studied [9]. The performance of these energetic liquid explosives offsets the shortcoming of low energy density of single compound liquid explosives.

In the 1960s, Astrolite, a new family of high liquid explosive mixture based on hydrazine nitrate was developed by the Atlas Powder Company, USA. It has a maximum detonation velocity of 8,600 m/s and twice the explosion strength to TNT [10]. Since its inception, this explosive has been extensively studied, manufactured, and used in many countries because of its advantages of high energy, excellent performance, and wide application. In 1978, a composite liquid explosive of nitromethane and ammonium nitrate was discovered in the USA. The explosive has extremely low freezing point. Thus, it exhibits great detonation property even at low temperature [11].

In 1966, an explosion bulge test of new liquid explosives was successfully performed in Japan [12]. The binary liquid explosives composed of oxidizer and combustible agent reportedly have high improved reliability and safety. The combustible agent is aromatic sulfonic acid and the oxidizer is hydrogen peroxide. They are stored separately unless in use. The advantages of the explosives, such as easy-obtaining raw materials, powerful explosive effect, good safety, easy operation, make them widely applied in many fields. In 1981, a composite liquid explosive, which was mixed with nitric acids, aminomethane, and an oxidizer [13], with denotation velocity of 8,400 m/s was developed and used in water in Japan. The Government Chemical Industrial Research Institute, Tokyo, developed high liquid explosives with density of more than 1.5 g/cm^3 and denotation velocity of 7,600–8,200 m/s. The explosives were made from tri(trinitroethyl)orthoformate, tetra(trinitroethyl)orthocarbonate, bis(trinitroethyl)carbonate, and nitro alkanes, such as nitromethane and nitroethane, and featured as small critical diameter, good safety, and shock insensitive [14].

In 1974, high powerful liquid/solid explosives with 75 % gasoline and 25 % carbon stone were developed in France. When the projectile contacts with an objective, acetylene gas is formed. Under function of an ignition tube, a massive blast takes place. The blast would not only destroy the objective, but also cause extensive burns [15].

In 1984, China developed a liquid explosive of ammonium nitrate hydrazine hydrate [16] with detonation velocity of 8,300 m/s.

In the past two decades, it the study of high energy density materials over the world has attracted considerable attention and a series of liquid explosives of azide ammonium nitrate and azide nitrate have been developed [9, 17, 18]. In recent years, liquid explosives of azide alkanes and nitrate esters have been also developed to break the limit of application conditions and make product serialization [19].

Overall, the developed countries lead the development and application of liquid explosives [7, 17]. Asian countries involve in the area positively.

The following features of liquid explosive mixture, in comparison with solid explosives, are the main reason to attract widespread attention.

(1) Better explosive property

The molecules of a composite liquid explosive are fully mixed and evenly dispersed. Thus, its detonation velocity is almost the same as a single compound liquid explosive. It is also not difficult to prepare an explosive with zero oxygen balance to make the utmost out of energy. For example, the explosion heat of hydrazine nitrate and hydrazine composite is up to 6.688 MJ/kg, while the value for octogen (HMX) is only 5.668 MJ/kg. The volume energy for the hydrazine nitrate and hydrazine composite and HMX is 10.62 and 10.5 kJ/cm^3, respectively, and the maximum detonation velocity is 8,600 m/s (ρ = 1.33 g/cm^3) and 8,900 m/s (ρ = 1.91 g/cm^3), respectively. Hence, liquid explosives have superior explosive property.

(2) Good flowability

Because of its good flowability, the propelling charge operation seems to be simple and suitable for any shape of container; transport can be done, if necessary, by a pump or spraying up. The convenience of charge is beneficial for loading of large explosives such as torpedoes, mine fuses, and bombs, and special engineering project. Some liquid explosives are able to be directly poured on the ground for a large area of blasting. The liquid explosives percolate through the soil and the rock crevices and keep their explosion performance. Thus, they are a good choice to be applied in channel operations and bunker mining.

(3) High detonation sensitivity and good detonating property

The detonation sensitivity of liquid explosives is usually relatively high. Explosion could be safely detonated by using No. 6 or 8 detonators with small limiting diameter. For examples, the liquid explosive of sensitized nitromethane can be detonated in a tube with diameter of 0.8 mm. A nylon webbing dipped by the liquid explosive of hydrazine nitrate and hydrazine composite can be of complete detonation after explosive generation at one end. The thickness of its critical liquid layer for denotation is less than 1 mm. Most liquid explosives have excellent detonating and transmitted detonation properties. Thus, generally, it is not necessary to set up a complex and unwieldy detonating device, easy to be used.

(4) Simple and safe manufacturing process

The manufacturing process of liquid explosive mixture is usually simple. The components for many liquid explosives can be mixed together on-site, for examples, liquid explosives of nitric acid-nitro compounds or nitric acid-nitromethane, and a liquid explosive of hydrazine–hydrazine nitrate obtained by pouring hydrazine into hydrazine nitrate. Therefore, the corresponding production cost is very low. Some of explosives are transported and stored, usually, by separated chemical compounds. Those compounds would be mixed together to be an explosive just before use. Such manufacturing process significantly improves the safety of explosives in storage and use.

(5) Extensive sources of raw materials with low price

Most of raw materials of liquid explosives are of common chemicals with wide sources, simple production, and low price.

The obvious disadvantages of some liquid explosives include long-term storage impossible, poor stability, easy volatilization, serious corrosivity, and toxicity. That limits, somehow, their application. Nevertheless, their prominent advantages encourage people to overcome those shortcomings and maximize their strengths in use.

1.2 Composition and Classification of Liquid Explosives

It has developed a series of liquid explosives with multispecies since first synthesis. According to their reaction characteristics, liquid explosives are classified into single compound liquid explosives and liquid explosive mixture. Single compound liquid explosives, such as nitrate esters, nitro alkanes, azide esters, azide alkanes, and azide nitro alcohol, consist of a single explosive liquid compound. Without any other additions, a single compound liquid explosive can be directly initiated by a detonator or flame. Its explosion strength is, sometimes, over TNT energy.

Generally, liquid explosive mixture divides two groups. The first group of liquid explosives is composed of oxidizers and combustible agents (explosive materials or nonexplosive materials), such as hydrazine–hydrazine nitrate composite, nitric acid-nitro toluene composite, perchloric acid-dimethyl ether-water solution composite, and hydrogen peroxide-ethanol composite. The structure of the second group of liquid explosive mixture is that one liquid compound is considered as main explosive component mixing with other additions of explosive or nonexplosive compounds, such as additions of RDX and others sensitizers, which are added into nitromethane, nitroglycerin/nitromethane, nitroalcohol/ammonium nitrate.

According to their physical state, liquid explosives can be divided into pure liquid, condensed state, and paste state. According to their functional groups, liquid explosives can be divided into nitric acid group, hydrazine nitrate group, nitro alkane group, azide group, and perchloric acid urea group. It must note that those classifications are done based on one of aspects of liquid explosives. There is no strict discrimination. The classification chart of liquid explosives is shown in Fig. 1.1.

To simplify the studies on the composition and detonation properties of liquid explosives, their components will be divided into elements, oxidizers, combustible agents, and additives for composition description in this book. However, when detonation properties are discussed, the classification method will be based on their characteristics.

1.3 Raw Materials and Formulation of Liquid Explosives

Many materials can be used to synthesize liquid explosives. In summary, those materials include oxidizers, combustible agents, additives, and processing additives.
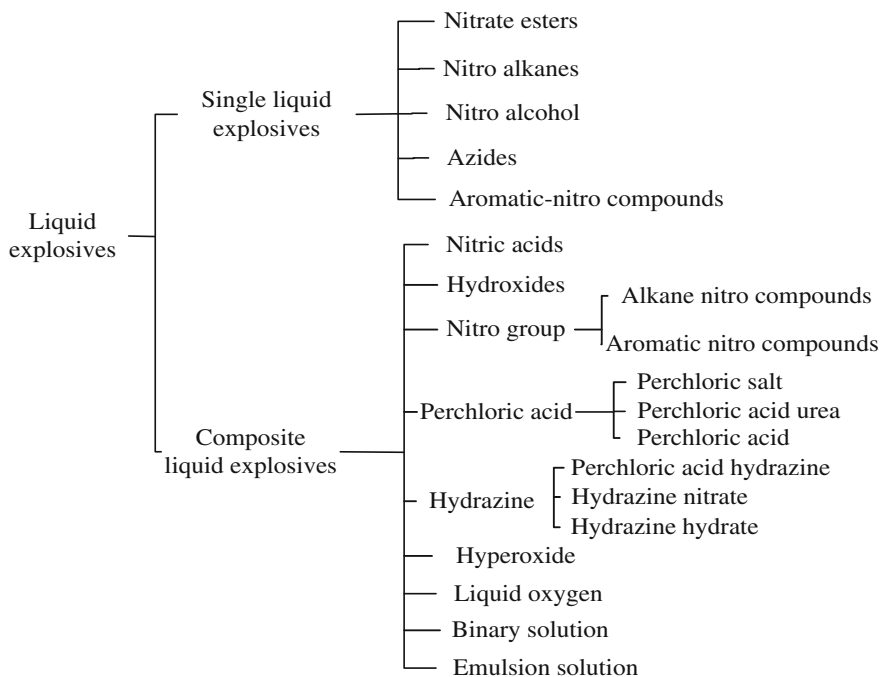
Fig. 1.1   Classification chart of liquid explosives

1.3.1 Oxidizers

The oxidizer component in liquid explosives is referred to as the materials that can provide oxygen in a detonation reaction, commonly including dinitrogen tetroxide, nitric acid, nitrogen dioxide, tetranitromethane, hydrogen peroxide, hydrazine nitrate, hydrazine perchlorate, and nitrate esters. The typical raw materials of oxidizers include tris-(2,2,2-trinitroethyl) orthoformate (TNEOF), tetra-(2,2,2-trinitroethyl) orthocarbonate (TNEOC), urea perchlorate, nitro alcohol, and azido nitrate. The typical oxidizers are listed in Table 1.1.

Except for the well-known chemicals of condensed nitric acid, nitrogen dioxide, tetranitromethane, nitrate ester, azide nitrate, and hydrogen peroxide, the synthesis method and properties of oxidizers, including hydrazine nitrate, dinitrogen tetroxide, urea perchlorate, glycol dinitrate, TNEOF, and ENEOC, will be introduced.

(1) Hydrazine nitrate

Hydrazine nitrate was first synthesized by Germans in 1989. Hydrazine nitrate, in general, refers to hydrazine mononitrate with molecular formula of $N_2H_5NO_3$. There is a similar compound of hydrazine dinitrate, which is very unstable, thus that it would be involved in this section [1].

Table 1.1 Typical oxidizers of liquid explosives [1]

Compounds	M_t	θ_m/°C	θ_b/°C	ρ (20 °C)/ g cm^{-3}	$OB \times 100$	$\Delta H_{f,m}$/ kJ mol^{-1}
Condensed nitric acid (95 %)	63.01	−4	86	1.5027	63.5	−173.0
Dinitrogen tetroxide	92.0	−10.2	21	1.49	69.6	−9.8 (gas)
Tetranitromethane	196.04	14.2	126	1.638	49.0	36.8
Hydrogen peroxide	34.02	−0.41	150	1.39	47.1	−188.8
Hydrazine nitrate	95.1	70.7		1.64	8.6	−250.0
Hydrazine perchlorate	132.5	144		1.83	24.1	−176.4
Urea perchlorate	160.5	83		1.623	9.9	
TNEOF	552.2	128		1.80	10	−630.7
TNEOC	732.4	161		1.84	13	−500.9

There are two crystalline types for hydrazine nitrate, stable α type and unstable β type. The former is usually used in explosives. Its solubility is small in alcohols but large in water and hydrazine. It has strong hygroscopicity, only slightly lower than ammonium nitrate.

Hydrazine nitrate has a good thermal stability. Its weight loss rate at 100 °C is slower than that of ammonium nitrate [20]. Its explosion point is 307 °C (50 % detonation) and explosion heat is about 3.829 MJ/kg. Because of no carbon elements, the detonation products are not solid and their average molecular weight is small.

Hydrazine nitrate was synthesized by neutralization reaction between nitric acid and hydrazine. In early years, anhydrous hydrazine was used to dissolve into methanol. The solution was cooled down to approximately −20 °C, and then slowly added to diluted nitric acid (70 %) with temperature of −20 °C till pH of 5.5. The temperature should keep under 0 °C in the whole reaction process. The precipitates of hydrazine nitrate were successively treated by filtration, recrystallization, and drying to obtain final products.

The method was improved later to reduce the production cost. In the new synthesis process, hydrazine hydrate with concentration of 80 % and nitric acid of 80 % were adopted as raw materials and ethanol (95 %) was used as a inert medium and precipitant. At the condition of the precipitation temperature at 0 °C and time over 30 min, the precipitation ratio can be up to 90 % with the product purity of up to 99 %.

(2) Dinitrogen tetroxide

Dinitrogen tetroxide (N_2O_4) forms an equilibrium mixture with nitrogen dioxide. The molecule is relatively stable because of its symmetric structure. It has strong oxidizability, high toxicity, and strong corrosivity. It is usually used as an oxidizer in propellants. Under standard atmospheric pressure, its boiling point is 21.2 °C, its melting point is −11.2 °C, and its density (20 °C) is 1.446 g/cm^3. The appearance

whatever in solid, liquid, or gas phase is colorless. However, the color would turn to brown to red with increasing temperature because of nitrogen dioxide. Dinitrogen tetroxide can dissolve into water and carbon disulfide, though that it is partially miscible with water. N_2O_4 easily reacts with water to produce equimolar nitric acid and nitrous acid mixture. The nitrous acid, as a strong oxidizer, would decompose into nitric acid and nitrogen oxide at high temperature. The mixture of N_2O_4 and ammonium would be exploded even at low temperature. Molecular adducts would be formed between N_2O_4 and many organic solvents, such as esters, ethers, ketones, and nitriles. Liquid N_2O_4 can corrode some metals, such alkali metals, alkali earth metals, zinc, cadmium, and mercury, to form metal salts and release nitrogen monoxide.

The typical preparation method of N_2O_4 is distillation. The crude liquid dinitrogen tetroxide obtained from the process of concentrated nitric acid production by direct method was used as raw materials. After distillation and condensation, pure liquid dinitrogen tetroxide can be obtained.

(3) Urea perchlorate

Urea perchlorate, with molecular formula of $CO(NH_2)_2 \cdot HClO_4$, is of sheet-shaped crystallite with melting point of 83 °C. It has good chemical stability and strong hygroscopicity. The solubility in water is large. At 20 °C, 958 parts of urea perchlorate can be dissolved into 100 parts of water with a density of 1.6226 g/cm^3.

The synthesis method of urea perchlorate is to gradually add urea into a perchloric acid solution. A urea perchlorate aqueous solution with concentration of 80 % can be obtained by solving all added urea. The main reaction equation is:

$$CO(NH_2)_2 + HClO_4 \rightarrow CO(NH_2)_2 \cdot HClO_4$$
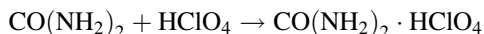
Urea perchlorate also can be synthesized by adding urea to hydrochloric acid solution with concentration of 35 %. After dissolution, a sodium perchlorate aqueous solution with concentration of 51 % was added the solution. The final solution was stood for 10 min for reaction and then cooled down to 20 °C. The precipitate of sodium chloride was removed by filtration. The filtrate was vacuum concentrated under 80 °C and cooled down. By repeating the concentration-cooling-filtration procedure several times, a high concentration urea perchlorate solution can be obtained. The main reaction equation is:

$$NaClO_4 \cdot H_2O + CO(NH_2)_2 + HCl \rightarrow CO(NH_2)_2 \cdot HClO_4 + NaCl + H_2O$$
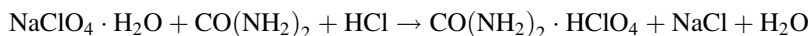
(4) Glycol dinitrate

The molecular formula of glycol dinitrate is $C_2H_4N_2O_6$. It is a colorless liquid with density of 1.4918 g/cm^3 and boiling point of 197 ± 3 °C. As a strong explosion strength liquid explosive, its chemical properties and explosive property are similar with nitroglycerine. It can be used to prepare low-freezing mining explosives because of its melting point as low as -22.8 °C. The synthesis method is to nitrify glycol by an acid mixture of nitric acid and sulphuric acid under 15 °C. It can be obtained after stabilization treatment.

(5) TNEOF and TNEOC

Both TNEOF and TNEOC have extremely excellent chemical stability. Even in the air for a long time, they would be neither deteriorated, nor decomposed. It does not have hygroscopicity, not dissolve into water, and not react with acids. It would not be decomposed in dilute hydrochloric acid and sulphuric acid, but it is decomposed in NaOH aqueous solution to release formaldehyde odor.

The explosion point of TNEOF is 229 °C. At 190 °C, it begins to be decomposed. Its explosion heat is 6.3076 J/g and specific volume is 682 L/kg. The explosion point of TNEOC is 238 °C. It begins to be decomposed at 200 °C. Its explosion heat is 5.797 J/g and specific volume is 694 L/kg. Both compounds are susceptible to be initiated by the 6th detonator.

In the synthesis of TNEOF and TNFOC, trinitroethanol reacts with chloroform or carbon tetrachloride under a catalyst of $FeCl_3$. The synthesis mechanism can be expressed as following equations [21, 22]:

$$CHCl_3 + 3HOCH_2C(NO_2)_3 \xrightarrow{FeCl_3} TNEOF + 3HCl$$

$$CCl_4 + 4HOCH_2C(NO_2)_3 \xrightarrow{FeCl_3} TNEOC + 4HCl$$
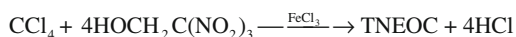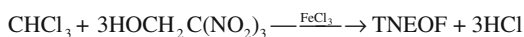
The procedure of TNEOF and TNEOC synthesis are described as follows:

Dry trinitroethanol of 100 g, chloroform of 220 mL, and anhydrous ferric chloride of 15 g are added to a 500 mL three-necked flask equipped with a condenser. The mixture would be refluxed on a water bath for 12 h and then cooled down. Diethyl ether of 1,500 mL is added to the reaction solution. The diethyl ether is then removed by a separatory funnel. The remaining is washed by water and then vacuum distilled to remove more diethyl ether. The obtained crude TNEOF is dissolved into benzene. The solution is recrystallized from n-hexane solution. Colorless crystals of pure TNEOF of 83 g with melting point of 128 °C can be obtained. The final yield is about 77 %.

Similar with the above procedure for TNEOC synthesis, dry trinitroethanol of 50 g, carbon tetrachloride of 110 mL, and anhydrous ferric chloride of 4 g are in reaction for 8 h. After cooling, the remaining carbon tetrachloride is removed by filtration. The solid is vacuum dried at 60 °C and then put in dilute hydrochloric acid to gradually remove ferric chloride. Colorless crystals of pure TNEOF of 46.2 g with melting point of 161 °C can be obtained after purification by chloroform. The final yield is about 92.4 %.

1.3.2 Combustible Agents

The combustible agents of liquid explosive mixture include hydrocarbons, nitro compounds, hydrazine, and aluminum. The combustible agents used in condensed composite explosives can be used as combustible agents of liquid explosives.

Table 1.2 Properties of common combustible agents [1]

Compounds	M_t	$\theta_m/°C$	$\theta_b/°C$	$\rho/\text{g cm}^{-3}$	$OB \times 100$	$\Delta H_{f,m}/\text{kJ mol}^{-1}$
Nitromethane	61.04	101.2	−28.6	1.14	−39.3	−113.1
Nitroethane	75.07	114.0	−90	1.05	−95.9	−134.7
Nitropropane	89.09	131.6	−108	1.03	−134.8	−167.6
Toluene	92.3	110.6	−90	0.866	−313.0	12.0
Nitrotoluene (industry)	137.1	220–240	−10.5	1.16	−180.9	−25.1
2,4-dinitrotoluene	182.1	304	71	1.33	−114.4	−68.23
2,6-dinitrotoluene	182.1	290	65.5	1.33	−114.4	−43.92
Hydrazine	32.05	113.5	1.54	1.004	−99.9	50.42
Hydrazine hydrate	50.05	118.5	−40	1.048	−64	−242.5

To form a relative stable homogeneous system with nitric acid is the primary requirement to prepare combustible agents of nitric acid-based liquid explosives. There is a great deal of combustible agents meeting the requirement. Performance tests of nitric acid mixture with one or more of those combustible agents, including nitrobenzene, ortho-nitroethylbenzene, para-nitrochlorobenzene, gasoline, diesel, aviation kerosene, toluene, xylene, methanol, pyridine, and ethylene dichloride, were carried out. Most of liquid explosives prepared by nitric acid and those combustible agents mixed based on oxygen balance exhibited a certain explosive property, especially for those liquid explosives prepared from nitro compounds. After comprehensive consideration about all aspects of detonation property, raw material resources, economical efficiency, and performance stability, toluene is chosen as the combustible material by many people.

The molecular weight of toluene ($C_6H_5CH_3$) is 92. Its melting point is −95 °C and boiling point is 110.8 °C. It occurs as a volatile and sweet odorous liquid that is insoluble in water and soluble in ethanol, diethyl ether, and acetone. The specific gravity for toluene is 0.866, the formation heat is −12.01 kJ/mol, and the oxygen balance is −3.13 g/g. The chemical property of toluene is similar with benzene. The mixture of toluene vapor and air is explosive with explosion limit of 1.2–7.0 % (v/v). Based on its sources, toluene can be divided into coal-based toluene, petroleum-based toluene, and synthesized toluene. The first two sources, which are of industrial grade with toluene content of over 98 %, are usually used to prepare liquid explosives. The common combustible agents for liquid explosives are listed in Table 1.2.

1.3.3 Additives

Under the different requirements of denotation performance, additives are used to modify liquid explosives. Additives mainly include sensitizers to improve initiation

sensitivity [17], desensitizers to reduce risk sensitivity, cryoprotectants to lower the freezing point, gelling agents to raise consistency in gelatinization process, and others to achieve complete explosion and improve the explosion work. The typical thickening method [23] of nitric acid based liquid explosives is to stably disperse carbon-white particles into liquid explosives. When the amount of the solid particles reaches a certain proportion, the fluxility of liquid explosives would be decreased to be of paste because of the continuous decrease of liquid phase and the alteration of interfacial force. Such thickened liquid explosives exhibit excellent waterproof effect. A descent of only 1.0 cm was found after contact with water for 53 h. The transmitted detonation property is exceedingly good and the sensitivity is reduced. When the liquid explosives are stored in plastic tubes with different diameters for 180 d, the plastic tubes would become harder and the detonation velocity would be slightly increased.

For nitric acid-based liquid explosives, macromolecule monomers, which would be cross-linked to form network structure, are used in thickening methods [24]. The initiator should be capable of generating free radicals at low temperatures in the course of the reaction. Ammonium peroxydisulfate is able to be an initiator. The initial radial reaction is given as:

$$H_4NO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-ONH_4 \longrightarrow 2H_4NO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O$$
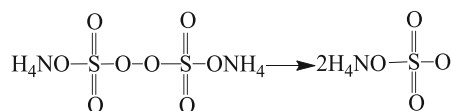
The generated radicals could be involved in a cross-linking polymerization reaction. Acrylamide and N,N'-methylene bisacrylamide would be adopted in the formulation to play roles of adjusting oxygen balance and lowering acidity, and thus to increase the storage period.

1.4 Applications of Liquid Explosives

1.4.1 Mining and Industrial Applications

(1) Mining

In mining, a liquid explosive can be injected directly into boreholes and detonated by a detonator inserted at the center of the liquid explosive. If a detonating cord is used for detonating, it should be buttered and the explosive should be waterproofed to ensure the reliability of explosive initiation [25, 26].

Most of liquid explosives, in practice, can be successfully detonated in mining operations, whatever in hard rocks or water holes, with a favorable detonation property. In comparison with condensed explosives, liquid explosives have distinct advantages to be used in the bursting of extremely hard rocks and multi-waterholes.

Meanwhile, liquid explosives improve the safety and reliability of detonation operation, save the labors of explosive preparation and detonation, and lower the cost of 22–30 %.

(2) Cutting

Low detonation velocity of approximate 2,000 m/s is required for explosives used in explosion working. Thus, liquid explosives with low detonation velocity are suitable for explosion working [27, 28]. Gathering energy effect (Munroe effect) is the enhancement of partial destruction by a hollow charge at the end of explosives. In order to improve the Munroe effect, a copper shaped charge liner is used on the hollow or void surface with geometrical shapes. The explosion energy would be converted to the kinetic energy of metals. A bunch or a sheet of high-velocity jet with high temperature, high pressure, and high density would be projected at the symmetric axis or symmetric plane of the liner. The jet would "puncture" or "cut" steel plates.

The cutting effect for a linear shaped charge cutter depends on the liner width, the liner apex angle, the liner thickness, the charge height, and the burst height. Table 1.3 lists the optimum size and application conditions of the linear shaped charge cutter of liquid explosives based on a rich supply of experimental data.

(3) Exploration of coal or oil field distribution and structure as an artificial hypocenter

The surrounding medium would be of permanent deformation and elastic deformation with explosion underground. The seismic wave would be rippled outwards from the explosion center and reflected when it contacts with some heterogeneous medium interfaces. The information of reflection and refraction could be achieved and recorded by specialized instrumentation to be used for the analysis of geological structure and mineral distribution [29].

High explosives are required to be used as hypocenter sources in exploration. The amplitude and the signal-to-noise ratio of the seismic waves are still high even after deep reflection. Thus, the interference for detection is small and the corresponding resolution is high. Hydrazine nitrate liquid explosives with different charges of 100, 500, 1000, and 2000 g were used to be hypocenter sources in comparison with ammonium nitrate explosives and deactivation RDX. The results indicated that liquid explosives have stronger excitation waves, higher signal-to-noise ratio, more convenient charge, no site-specific constraints, being uninflammable, and high safety and reliability without corrosion and pollution.

Table 1.3 Cutting parameters of the shaped charge cutter of hydrazine nitrate liquid explosives

No.	Target materials	Target thickness (mm)	Jet numbers	Unit charge weight	Puncture depth (mm)
1	A-3 steel	25	4	0.705	24 ± 1.0
2	$45^{\#}$ steel	25	4	0.874	25 ± 0
3	Alloy steel	20	4	0.874	20 ± 0

Note The apex angle of the copper shaped charge liner α 90°, the width: 100 mm, and the burst height: 18 mm

(4) Detonation underwater

Obstacle clearance operations underwater take place often in marine development and bridge constructions [30]. However, it is difficult and dangerous to charge powders and set up detonation device in water for solid explosives. Especially, the removal of residual powders of squibs could endanger operator's life. The specific gravity of both liquid explosives and inert solution is larger than water. If the charge to a borehole is carried out successively with liquid explosives and inert solution, a layer of inert fluid should be formed above the liquid explosives. Thus, the liquid explosives in the hole could be completely separated from water, as shown in Fig. 1.2, the detonation could be operated safely [17].

In procedure, a borehole (2) is drilled first on the obstacle (1) in water by a drilling machine, as shown in Fig. 1.2. Two tubes are inserted into the borehole and the inert liquid (B) is pressure-injected through one of the tubes. Because the specific gravity of the inert liquid (B) is bigger than that of water (A), the inert liquid would drive the water out of the borehole. A liquid explosive (C), which is heavier and insoluble to the inert liquid (B) (usually solubility of 0.1/100 g or less), is then pressure-injected into the inert liquid (B). The inert liquid (B) would move forward to separate the liquid explosive from water. In order to make the water at opening nonflowable, the specific gravity of the inert liquid (B) is best in the range of 1–1.3. A mixture of silicone oil and carbon tetrachloride with specific gravity of 1.1–1.3 could be chosen as an inert liquid.

Fig. 1.2 Schematic diagram of underwater detonation device *1* obstacle, *2* borehole, *3* wiring, *4* detonator, *5* wiring terminal, *6* leading wire, *7* cover, *8* floating body
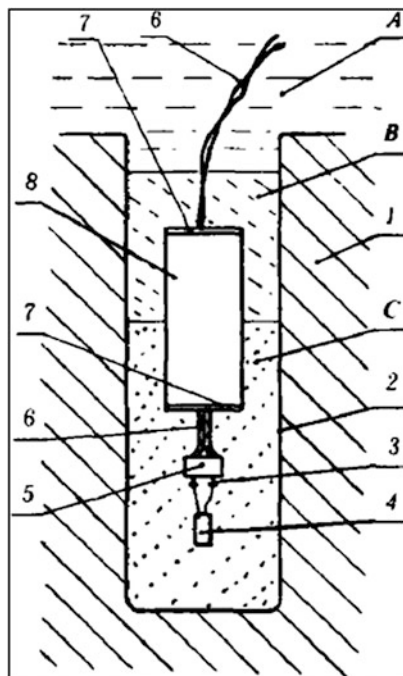
Table 1.4 Specific gravity of liquid explosives used in underwater detonation

Components	Fraction	Specific gravity
Nitromethane/urea perchlorate	80/20	1.24
Nitromethane/urea perchlorate	30/70	1.40
Nitromethane/urea perchlorate	20/78/2	1.51
Hydrazine nitrate/amino alcohol/water	80/15/4	1.42
Hydrazine nitrate/ethylene diamin/water	80/16/4	1.41
Hydrazine nitrate/aminomethane/hydrazine dyrate/water	75/6/4/15	1.40
Hydrazine perchlorate/hydrazine/water	67.7/10.4/21.9	1.45
Hydrazine perchlorate/hydrazine/amino alcohol/water	60.2/9.3/10.0/20.5	1.38
Hydrazine perchlorate/sodium nitrate/hydrazine/water	52.3/10.0/8.1/29.6	1.40

The specific gravity of liquid explosives must be greater than 1.2, so that the treatment after failure detonation could be facilely finished and the water solubility is also good. The specific gravities of liquid explosives with main oxidizers of urea perchlorate, hydrazine nitrate, and hydrazine perchlorate are listed in Table 1.4. Metal perchlorates are also main components for liquid explosives [31, 32].

Because of the filling method of liquid explosives through tubes, there are not dangers in the process. The liquid explosives can be safely released in case of failure detonation.

(5) Explosive lens

A plane shock wave generating apparatus consists of a hanging cone, in which a low detonation velocity explosive of nitromethane or nitromethane mixture is filled, and an encapulsated space outside the cone, in which a ternary high detonation velocity liquid explosives of hydrazine nitrate/hydrazine/water is filled [33, 34].

1.4.2 Military Applications

(1) Rapid excavation of fortifications

In the extreme conditions of hard rock or permafrost, liquid explosives, because of the features of high speed and high efficiency, have been widely used to build fortifications, such as antitank ditches, trenches, communications trenches, foxholes, tank pits, and personal bunkers [35]. For example, to build a personal bunker needs to excavate the soil layer by a knife first. A liquid explosive of approximate 0.5 kg is then poured in the apertures of soil layer and detonated by a detonator. A personal bunker with a diameter of 1.2 m and depth of 1 m could be formed in 1 min. In application, the explosive containers could be put in a charge room in a straight row or column in advance and connected one another by tubes. Liquid explosives, such as tetranitromethane/toluene (85/15, detonation velocity of

8,100 m/s), could be filled into the containers through the tubes with transparent parts till the position of detonators. After confirmation of the charge, the liquid explosive could be detonated.

The Large Caliber Weapon Systems Laboratory at the United States Army Armament Research, Development and Engineering Center uses liquid explosives of nitromethane/nitroethane/RDX to excavate personal hunkers [11].

For simply constructed works, the tubes can be exposed on ground other than underground. The tubes are used not only as charge channels but also as a detonating route. This approach is also suitable for other detonations.

(2) Charges of mines, bombs, and torpedoes [36]

The charges with liquid explosives for various bombs are very convenient, better than condensed explosives, during wars. In France, liquid explosives of nitrogen dioxide and gasoline mixture are adopted to charge bombs. In the World War II, the liquid explosive, called as Dithekite-13 with compositions of 62.6 % nitric acid, 24.4 % nitrobenzene, and 13 % water, was used to charge mines.

In addition, liquid explosives can be used to charge special ammunition and special anti-tank mines, clear mines, remove obstacles, and operate in-fracture explosive in wells. Even electric power generation by liquid explosives has been considered.

(3) Road open-up and military blasting

Some liquid explosives can be easily absorbed by the soil capable of detonation property. They have high stability to the mechanical shock, vibration, and adiabatic compression of impact waves. Thus, the liquid explosives used to be laid by manual, vehicles, and planes, so-called as liquid mines, in the United States. The liquid explosives can be used to destroy armored vehicles and other chariots. They can be also used in mine clearance, battlefield clearance, road open-up, and various military blasting works.

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Chapter 2
Explosion Features of Liquid Explosive Materials

As everyone knows that the explosion characteristics of explosive materials have close relationship with their packed density and structures. Liquid explosive materials are noncompressible. One of the notable characteristics is that its excellent detonation is not influenced by its phase, shape, and geophysical environment. Its application is much broader than the condensed explosive materials. When a liquid explosive material explodes in unlimited free spaces, though the super pressure is lower than that of condensed explosive materials, the shock pulse is broader and positive action lasts longer. Its performance is better. Especially in semiconfined spaces, a liquid explosive material releases gas materials and the nearby oxygen (gas) also takes part in the detonation reaction. This oxygen absorption reaction is an excellent characteristic, which is not indicated by general condensed explosive materials. Liquid explosive materials follow the explosion factors, and have their special detonation reactions, which are different from the general explosive materials. The detonation processes have close relationship with their low-pressure denotation. This chapter studies the detonation mechanism of liquid explosive materials, and discusses their explosion characters, lets detonation characteristics understood, and supplies technical support for the applications.

2.1 Explosion Phenomena and Key Factors of Liquid Explosive Materials

Explosion is a phenomenon of physical or chemical changes within extreme short time. In the changing processes, the energy inside the explosive materials changes from one form to another, such as from reactant to production, or from chemical energy to the compression energy or kinetic energy of their media. One of the key features is that huge amount of energy is released or transformed within certain space. The energy accumulation within extreme time and limited space leads to a high-temperature and high-pressure condition. This nontraditional environment with rapid pressure rise followed complex movement resulting in abnormal shift or mechanical damage. The most external/obvious feature of explosions is that the media give the audible effect after a shake. In general, explosion has two stages.

First, the energy with certain form transforms to the compressing energy of products. Then the compressed materials expand rapidly, while the compressing energy changes into mechanical energy, which leads to the shape change, damage, or shift of the around media. Physical change leads to physical explosion, while chemical change results in chemical explosion.

In our daily life, the most common physical explosion is lightning. It is a spark discharge. Within the discharge space, the energy density and temperature of the media raise to an unbelievable high condition (e.g., several ten kilo degrees Celsius) within extreme short time. This leads to the fast pressure increase of the discharged air and explosion. All explosions from high-pressure cookers, steam boiler, high-pressure compressed gas cylinders, and earthquakes are physical ones.

Explosions from liquefied gas pipes, gasoline tanks, chemical processes of industry, gas inside mines, coal dust, and all explosive materials are chemical explosions. The explosion caused by mixtures of inflammable liquid leakage and air is also chemical one. All staffs, which can have chemical explosions, are named explosives. If the used staff is in liquid or sol-gel, this is the explosion from liquid explosive materials. This chapter studies the explosion variation law and features of liquid explosive materials.

The explosive abilities are determined by the exothermicity, rapidity, and gas production of explosion reaction.

2.1.1 Heat/Energy Releasing of Liquid Explosive Explosion

All explosion reactions are exothermic with the formation of new molecules. Considering the decomposition of a compound, certain amount of energy must be supplied to activate the molecules or break the chemical bonds, which subsequently generate new compound and release heat. If the released heat cannot activate the subsequent reactions, the chemical reactions will terminate automatically. To maintain such a reaction, energy has to be supplied from the environment. Obviously, these materials are not explosives. If the energy released from the initial explosive reaction activates the unreacted molecules, and the explosive reaction propagates continually until all reactants are consumed.

Explosion is a process in which energy transforms rapidly. Explosion produces stable compounds by transforming chemical energy into heat. The heat is then transformed into the mechanical work of media. Endothermic reactions or exothermic reactions with less heat released are not explosion. For example,

$$(NH_3)_2C_2O_2 = 2NH_3 + H_2O + CO + CO_2 \qquad -263.6\,kJ$$
$$ZnC_2O_4 = Zn + 2\,CO_2 \qquad -205.4\,kJ$$
$$PbC_2O_4 = Pb + CO_2 \qquad -69.87\,kJ$$
$$CuC_2O_4 = Cu + CO_2 \qquad +23.85\,kJ$$
$$HgC_2O_4 = Hg + 2\,CO_2 \qquad +47.28\,kJ$$
$$AgC_2O_4 = 2Ag + 2\,CO_2 \qquad +123.43\,kJ$$
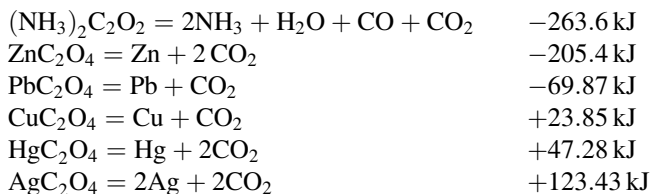
Table 2.1 Released energy comparisons of various fuels

Materials	Explosion heat (kJ/kg)	Mixtures with air (kJ/kg)	Mixtures with air (kJ/L)
Wood	18,828	7,950	19.7
Coal	33,472	9,205	17.99
Gasoline	41,840	9,623	17.6
Black powder	2,929	2,929	2,803
Nitrotoluene (TNT)	4,184	4,184	6,485
Nitroglycerine (NG)	6,276	6,276	10,042
Octogen (HMX)	5,530	5,530	10562.3
Hexanitrohexaazaisowurtzitane (CL-20)	6,028	6,028	12319.4

All above reactions are the decomposition of citrates and have similar products. In decomposition processes, their exothermicities are different. All citrates with endothermic decomposition reaction are not explosive materials. Only silver citrate and mercury citrates with exothermic decomposition reaction are explosive. Although copper citrate has exothermic decomposition reaction, the heat is too less compared to the general explosive materials. Copper citrate can cause explosion, but a weak explosion. However, the heat released in explosion from explosive materials is probably not much. If counted in unit weight, this heat is probably lower than fuels. Why explosive materials can have violent explosion? Because explosive materials release more energy in unit volume, and the energy density is very high. Table 2.1 shows the comparison of released energy by different materials.

Table 2.1 indicates that the energy/heat released by explosive materials per unit kilogram is much lower than that by fuels, just part of the energy/heat that fuels release in combustion. The density of air is very low compared to fuels and explosive materials. But the energy/heat of explosive materials is about 130–600 times that of fuels. The energy of explosive materials is concentrated, and energy density is higher.

2.1.2 Rapid Reaction of Liquid Explosive Materials

The second necessary condition of explosions is the rapidity of reactions, which differentiates the general chemical reactions and explosions. Explosive materials per unit weight have less energy than fuels. However, the combustion of general fuels per unit weight has more energy/heat than explosive materials. These combustion reactions plod slowly. The energy aggregation and release conduct in a rapid speed. Rapidity of energy release is one of the most obvious features of explosion. Per kilogram coal releases 25,940 kJ after complete combustion. While per kilogram nitroglycerine only has 6213.2 kJ. The energy from per kilogram coal is about 4.175 times than that of nitroglycerine. The complete combustion of 1-kg coal needs

several to more than 10 min. However, the explosion of nitroglycerine finishes within 1/100–1/1000000 s. Explosion reaction is about 100–1,000 times faster than the combustion of general fuels. Both explosion and combustion reactions release a lot of heat and large volume of stable gas finally. Combustion reacts slowly. There is enough time for gas transportation, and no high-pressure space forms. While the rapidity of explosion limits the expansion of gas products, the energy is confined to the original volume of explosive materials, and the energy density is extremely high. The as-prepared high-temperature and high-pressure gas products let explosion powerful and damaging. For example, the energy released by one-kilogram explosive materials equals the electricity that a 1,000 W motor needs to work for an hour.

$$C + O_2 = CO_2 + 394.55\,kJ$$

This reaction is familiar for most of us. The combustion of coal in air releases large amount of heat and gas production. But coal combustion is not explosion. Only when oxygen diffuses onto the surface of coal, combustion reacts. This process is very slow. And the produced energy and gas diffuse into the atmosphere gradually. The space of energy is open. Neither high temperature nor high pressure is created. There is no mechanical interaction with the environment. If coal powders with ~ 200 nm diameters are obtained by grinding, and suspended in the air, violent explosion takes place after a flash. Explosive power increases following that the diameters of powders become smaller. The main reason is that the dramatic increase in surface area per unit weight and complete contact of surface with oxygen results in rapid combustion reaction.

2.1.3 Gas Products in Explosion of Liquid Explosives

Explosions of liquid explosives affect the nearby media using the speedy expansion of high-temperature and high-pressure gases. Immediate release of large amount of gas is one of the key features in explosion reactions. Explosion of nitromethane (1 L, 1,140 g) produces $\sim 1,464$ L (std) gas and explosion of isopropyl nitrate (1 L, 1,040 g) generates $\sim 1,551$ L gases. While in explosion, TNT (1 L, 1,600 g) begets 1,656 L gas production. Because of exothermic and rapid reactions of explosions, huge amount of gas production limited in the original little space is heated to extreme high temperature. High-temperature and high-pressure gases violently affect the environment in mechanical work.

There are other materials, whose reactions are rapid and release a lot of energy/ heat at the same time. However, the reactions do not generate gas productions. These materials are not explosives. Take thermite reaction as an example,

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + 828.4\,kJ$$
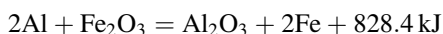
The heat released in this reaction is enough to raise the temperature of products at 3,000 °C while Fe and Al_2O_3 are liquids now. No gas is produced in this reaction, and it is nonexplosive.

In certain conditions, rapid and exothermic reactions without gas production also lead to explosion. E.g., reactions of well-grounded thermite reactants in the air make the nearby air heated and expand, and then explode. This explosion comes from the heated air, not the reaction of thermites. Sometimes the amount of gases reduces rather than increase, especially the explosive reaction of gas reactants. The explosion of detonation gas is listed below.

$$2H_2 + O_2 = 2H_2O + 481.68\,kJ$$
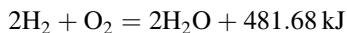
In above reaction, 1/3 amount of gases is cut off. The rapidity and exothermicity make up the reduction of gas amount. The volume of gases increases rapidly under high temperature. If the volume is maintained, the pressure reaches more than 10 atm within an extreme short time. This is the key feature of detonation gases.

In summary, exothermicity, rapidity, and gas productions are key features of explosive reactions. Exothermicity of reactions supplies the initiating energy for explosion. Rapidity is the must condition which helps to confine the limited energy into small space, while produced gases are media of energy conversion. Explosion power has close relationship with exothermicity, rapidity, and gas productions. Exothermicity helps heat explosive to a relative high temperature, which increases the reaction speed and makes the reaction reach rapidity. In addition, the released energy dramatically increases the temperature and promotes the conversion of reaction products into gas state.

The chemical structures and physical states of explosive determine whether they explode or not. But, to some degree, different explosives are different in amount of released energy, reaction speeds, and gas productions. In general, explosion reactions must have the three key features: exothermicity, rapidity, and gas productions. This is applied for all explosions.

2.2 The Explosion Changing of Liquid Explosive Materials

Liquid explosives are noncompressible, and are different from condensed explosives. In the explosion, liquid explosives should be gasified first, later ignited. Once this abnormal combustion reaction becomes normal one, self-sustaining spread detonation follows. The explosion changes of liquid explosives have two classic forms: combustion and detonation.

2.2.1 Combustion of Liquid Explosives

Combustion reaction of explosives is deflagration, which is another classic form. Deflagration is different from general combustion. Explosives have oxidants and combustible materials. Combustion of explosives does not need the oxygen in air, and it spreads smoothly. For propellants and pyrotechnics, combustion is the basic form of explosion. Some primary explosives work through combustion or combustion–detonation. Here in all, study of the general rules of liquid explosives and the basic conditions of combustion-to-detonation are of great importance for the safety productions and applications of liquid explosives.

2.2.1.1 General Features of Combustion of Liquid Explosives

Combustion is very common, e.g., combustion of wood, coal, etc. The chemical reactions with light and heat released are combustion. The space with light and high temperature of chemical reaction is named as flame. The geometric surface of separating burning layer from nonreaction zone is the flame front.

The combustion of liquid explosives leads to violent chemical reactions, which spread themselves. It is different from the combustion of general fuels. The combustion of liquid explosives can be isolated from air, and the oxidations depend on the oxygen of the explosive. This combustion is also deflagration. The processes of explosive combustion are the processes in which flame fronts spread themselves [1]. Spreading of flames is determined mainly by conduction of heat and diffusion of combustion productions [2].

Combustion of liquid explosives is different from that of condensed ones. Liquid explosives are noncompressible, and have fixed density, and their combustion spreading is continuous and fast. There are two stages for the combustion process of liquid explosives. First, the surfaces of liquid explosives flame. Then, the flame spreads into the inside of the liquid explosives. The burning reaction spreads along the interface of liquid explosives and air is surface combustion, while the burning reaction spreads along the normal directions is section combustion. Starting of liquid explosive combustion has two ways: spontaneous ignition and forced ignition. Spontaneous ignition is produced through the self-acceleration of chemical reactions of liquids. Forced ignition is reached by external heat source at high temperature. Forced ignition is common in the application of liquid explosives. To ignite the liquid explosives, fire source should have enough high temperature and enough heat to supply.

Burning speed is an important parameter of combustion. There are two ways to show the burning speed: linear speed of flame front spreading and mass speed of combusted liquids. The linear speed (u) of flame front spreading along the liquid

explosives is the reacted volume within unit time and unit area of flame fronts (Eq. 2.1).

$$u = \frac{V}{S}$$
(2.1)

Here, V represents the burned/combusted volume within unit time; S represents the total surface area of flame fronts.

The mass speed (m) of combustion is defined as the mass amount of explosives consumed per unit time and unit flame front area. The mass speed of combustion is a function of the explosive density and the linear speed (Eq. 2.2).

$$m = \rho u$$
(2.2)

Combustion process has stable and unsteady combustions. The stable combustion of explosives presents that single component explosive has a constant burning/combustion speed under certain conditions (e.g., fixed pressure, temperature, packed density, etc.). Most of liquid explosives can reach stable combustion. The combustion of explosive is not always stable. For mixed liquid explosives, the combustion speed may accelerate or slow down, sometimes accelerate or slow down suddenly. The main reason is the nonuniformity of mixtures.

Acceleration of unsteady combustion leads to faster combustion, finally detonation. Slowing down results in the slower combustion, to burning off. Whether an explosive explodes finally is determined by its combustion speed.

2.2.1.2 Combustion of Volatile Liquid Explosives

Liquid explosives have different volatilities, which varied the combustion processes. The important characteristic is the variation of reaction phase in the combustion reactions. Generally, because alkyl nitrates and some of alkene nitrates are highly volatile, their combustion reactions proceed in gas state. In contrast, the combustion reactions of nitroglycerine, azide nitrate ether, and aqueous hydrazine proceed in both gas and solid phases. The reactions of mercury fulminate and urea perchlorate mainly proceed in solid state.

To simplify the flame propagation, the assumption is based on flame propagation with a fixed speed toward the liquid in only one dimension. Butyl nitrate is filled in a pipe. The ignition device is used to induce the combustion of liquid explosives from one end. At first, only the explosive (which is very close to the ignition device) starts burning. The propagation of flames is shown in Fig. 2.1.

The propagation of flames proceeds the reaction zone forward till the end of the pipe. The flame fronts isolate the reacted and nonreacted zones. Every moment of flame propagation reaction is in process of the thin layer close to flame fronts. The preheating layer isolates the nonreact zone and flame fronts. The speeds of flame propagation are determined by the chemical properties of liquid explosives.
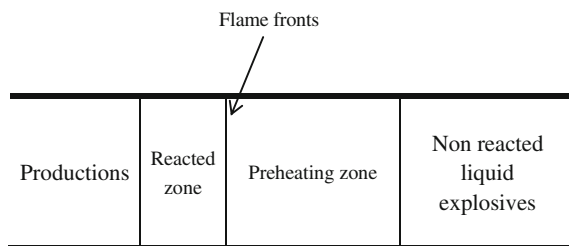
Fig. 2.1 Schemes of flame spreading of volatile liquid explosives

In ignition or combustion, the energy transferred to the surface of explosive is to activate reactions and evaporate the molecules. If the evaporation is faster than reactions, the combustion is conducted under gas phase after liquids become gases.

In the combustion, the surface layer receives heat Q and its surface temperature raises to T. The reaction proceeds under $MAe^{-E/RT}$ speed (M is the mass of preheating zone) for one molecule mechanism, while the evaporation undergoes $M'\upsilon e^{h\upsilon/RT}$ (M' is the mass of evaporative materials/molecules. υ is the vibration frequency, and $h\upsilon$ is heat of evaporation per mole).

Now let's compare all the parameters in the equation by starting with M and M'. When the vapor pressure of liquid explosives is higher than the outside pressure, all liquid explosives evaporate. When the vapor pressure of liquid explosives is lower than the outside pressure at temperature T, the evaporation only occurs on the liquid surface, and not the whole heating layer will evaporate. Under this condition, $M' < M$.

During the combustion of explosives, the heat is only transferred onto the surface. Because of the surface evaporation, the energy cannot reach the deep inside of explosives. Under this condition, M' is approximately equal to M. In the first order reaction, A is similar to υ, the vibration frequency of molecules per minute, which is about 10^{13}–10^{14}.

To further explain the reaction in the liquids, $e^{-E/RT}$ is compared with $e^{-h\upsilon/RT}$. $e^{-E/RT}$ represents the possibility of obtaining activation energy E for each molecule. $e^{-h\upsilon/RT}$ is the possibility of receiving evaporation energy $h\upsilon$ of one molecule.

Alkyl nitrates and part of alkene nitrates are volatile materials when the temperature is close to the breaking point. Their evaporation energy $h\upsilon$ is much smaller than activation energy E.

For most volatile liquids, their evaporation energy is less than 41,800–50,200 J/mol, while their activation energy is more than 12,500–15,600 J/mol. At 200 °C, diethyleneglycol dinitrate has activation energy $E = 146,440$ J/mol, while evaporation energy $h\upsilon = 41,840$ J/mol.

$$e^{-E/RT} = e^{-146440/1.99 \times 473.2} = e^{-155.51} \tag{2.3}$$

$$e^{-h\upsilon/RT} = e^{-41840/1.99 \times 473.2} = e^{-44.43} \tag{2.4}$$

At 200 °C, for each diethyleneglycol dinitrate molecule, the possibility of obtaining evaporation energy is 1,012 times of activation energy. The evaporation $M'v e^{-hv/RT}$ is much faster than the reaction $MA e^{-E/RT}$, even when M is larger than M'. For some explosives, A is larger than v. For nitroglycerine, $A = 1,020$ and E is also a large number ($E = 179,912$ J/mol). The speeds of evaporation and activation still follow the above conditions. It is concluded that the transferred heat evaporates the liquid molecules. The evaporation is much faster than reaction in the liquids. Evaporation processes absorb both the transferred energy and the released energy from reactions. The schematics of evaporation–combustion are shown in Fig. 2.2.

The temperature at the intersurface of the gas-condensed phase (N–N) is the boiling point, at which the vapor pressure of liquid explosives equals the environment pressure. The temperature of the condensed phase decreases with the increase of the distance to the intersurface, and it gradually reaches the starting temperature T_0. Under this condition, there is a heating layer between gas and condensed phases. When no evaporation occurs, the heating layer becomes thicker with time prolong. In fact, because evaporation continues, the surface of condensed phase shifts and the shift of stable combustion is much faster than the heat conduction heating condensed phase. As a result, the thickness of heating layer does not change. According to some nonsystematic data, the heating layer of condensed phase is several millimeters at most when the amount of explosive is not large and it combusts. Because of the continuous evaporation of liquids, the preheating depth ($T_k - T_0$ step) does not change. The vapor formed by evaporation of liquids does not combust immediately; it needs time to be heated and for the reaction to progress. The combustion of vapor does not occur on the surface of the liquid, but at a certain distance from the liquid. Combustion proceeds in the preheating zone. The highest temperature of products is

$$T_1 = T_0 + \frac{Q}{C} \tag{2.5}$$

Here, T_0 is the original temperature; Q is the energy released from the combustion; and C is the heat capacity of products.

Later, the products are cooled down, and the temperature drops.
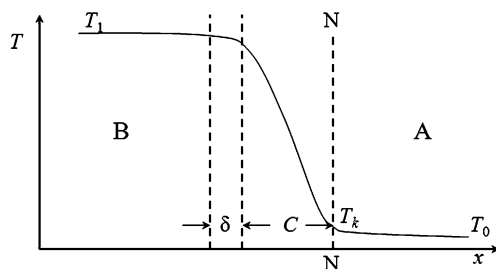
Fig. 2.2 Schematics of evaporation–combustion of liquid explosives A condensed phase; B production of combustion; T_0, T_k, T_1–temperature distribution curve

In the deduction of the explosive combustion, study of liquid and solid explosives separately is not a must. When heat is transferred to the solids, they start to liquefy. And the liquids follow the above combustion rules. Figure 2.2 indicates that the combustion of condensed explosives is similar to that of flammable gases under steady condition. The only difference is that for gas combustion all mixtures are gases while the gases are obtained by evaporation of liquids.

From the above analysis of volatile explosives, it is concluded that the mass speed of combustion equals the evaporation speed of liquids (Eq. 2.6).

$$\rho u = \rho_1 u_n \tag{2.6}$$

Here, u is the linear speed of evaporation; ρ is the density of explosives; u_n is the normal speed of evaporation–combustion; ρ_1 is the density of evaporation.

According to the equation of evaporation–combustion, the mass combustion speed of evaporation is Eq. 2.7.

$$\rho u = \sqrt{\frac{2\lambda}{q}\left(\frac{RT_1}{E}\right)^{n+1}(T_1 - T_0)^{-n}(n+1)!W(T_1)} \tag{2.7}$$

Here, T_1 is the temperature of combustion; $W(T_1)$ is the reaction speed at T_1; q is the heat of combustion; λ is the thermal conductivity of evaporations; n is the reaction order.

If the combustion is the first-order reaction, the mass combustion speed of volatile explosives is written in Eq. 2.8.

$$\rho u = 2\frac{RT^2}{E}\sqrt{\frac{\lambda}{q(T_1 - T_0)}\rho_2 A e^{-E/RT}} \tag{2.8}$$

Here, ρ_2 is the evaporation density at T_1; A is the preexponential factor.
The second equation of mass combustion speed is Eq. 2.9.

$$\rho u = \sqrt{\frac{2\lambda}{q}\left(\frac{RT_1^2}{E}\right)^{n+1}(T_1 - T_0)^{-n}(n+1)!DP^n e^{-E/RT}} \tag{2.9}$$

Here, $DP^n e^{-E/RT}$ is the reaction speed of several orders; n is the reaction order; D is the scale factor.

Equation 2.9 can be rewritten in Eq. 2.10.

$$\rho u = \sqrt{\frac{2\lambda}{q}\left(\frac{RT_1}{E}\right)^{n+1}(T_1 - T_0)^{-n}(n+1)!De^{-E/RT}}\sqrt{P^n} \tag{2.10}$$

Because the value of the above square root has nothing to do with pressure, use B to replace it.

$$\rho u = B\sqrt{P^n} = BP^{n/2} \tag{2.11}$$

The linear speed of combustion is a function of pressure (Eq. 2.12).

$$u = \frac{B}{\rho}\sqrt{P^n} = bP^{n/2} \tag{2.12}$$

When the reaction is first order, the linear combustion speed of explosives is written in Eq. 2.13.

$$u = BP^{0.5} \tag{2.13}$$

When the reaction is second order, the linear combustion speed of explosives is written in Eq. 2.14.

$$u = BP \tag{2.14}$$

If the above index is 0.5–1, the assumed theory is correct.

To verify the correctness of above theory, experimental data of diethyleneglycol dinitrate are compared with theory ones. The combustion reaction of diethyleneglycol dinitrate in nitrogen (1 atm) is below.

$$C_2H_4(ONO_2) = 2NO + 1.7CO + 1.7H_2O + 0.3CO_2 + 0.3H_2$$
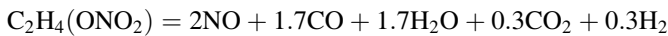
The calculated combustion heat of diethyleneglycol dinitrate is 1921.05 J/mol, and the average heat capacity of products is 1.423 J/mol. In the combustion of diethyleneglycol dinitrate, the temperature increases $\Delta T = T_1 - T_0 = 1{,}350$ K. The detonation temperature is $T_1 = T_0 + \Delta T = 300 + 1350 = 1{,}650$ K.

At combustion temperature, the thermal conductivity of reaction products is $\lambda = 8.37 \times 10^{-4}$ J/cm s °C. The combustion reaction is a decomposition process, which is the first-order reaction. According to the chemical kinetics, the reaction speed is Eq. 2.15.

$$W(T_1) = \frac{M}{N}Ze^{-E/RT_1} \tag{2.15}$$

Here, M is the molecule weight of diethyleneglycol dinitrate; Z is the number of collisions; and N is Avogadro constant.

Combine Eqs. 2.15 and 2.7 at $T_1 - T_0 = \frac{Q}{C_p}$, the resulting equation is in 2.16.

$$\rho u = \sqrt{\frac{4\lambda R_2 T_1^4 \bar{C}_p}{q^2 E^2} \frac{M}{N} Z e^{-E/RT}} \tag{2.16}$$

The collision number $Z = \sqrt{2}\pi d^2 u m^2$. Here, d is the diameter of diethylene-glycol dinitrate molecules; u is the moleculer speed; m is the number of diethyleneglycol dinitrate molecules in cm^3. According to kinetic moleculer theory,

$$Z = \sqrt{6}\pi d \sqrt{\frac{RT_1}{M} \frac{P^2 N^2}{R^2 T_1^2}} \tag{2.17}$$

It is difficult to determine the diameter of diethyleneglycol dinitrate from experiments. Zeng et al. [3] analyzed the thermal decomposition mechanism of nitrate ether and suggested the diameter $(d = 5.10 \times 10^{-8}\text{ cm})$ of one ether, whose molecular weight is very close to diethyleneglycol dinitrate. The collision number is,

$$Z = 1.19 \times 10^{28}$$

Use the collision number in Eq. 2.16. Then, the calculated mass combustion speed is

$$\rho\mu = \sqrt{\frac{4 \times 2 \times 10^{-4} \times 2^2 (1650)^4 \times 0.35}{(1921.05)^2 \times E^2} \times \frac{152}{6.10^{25}} \times 1.19 \times 10^{28} \times e^{-E/2 \times 1050}}$$
$$= \sqrt{\frac{1.12 \times 10^{11}}{E^2} e^{-E/2 \times 1050}}\ \text{g}/\text{cm}^2\ \text{s}$$

The experiment data is 0.045 g/cm^2 s. The activation energy of diethyleneglycol dinitrate is 146,440 J. These data match the calculated ones.

2.2.1.3   Combustion of Nonvolatile Liquid Explosives

When the nonvolatile liquid explosives are heated, they do not evaporate, but decompose before the temperature reaches the boiling point. The reaction in the liquid takes a very important part such as in nitro compounds, nitra-amine explosives, nitrocellulose gunpowders, nitroglycerine gunpowders, etc.

The combustion/reactions of the nonvolatile liquid explosives have three different stages.

The first stage is the exothermic reactions of the condensed phase. The reactions proceed on the surface or close to the surface. Because the reactions are in progress in the condensed phase, pressure does not impact a lot for the react rates, but temperature does. This reaction space is the condensed zone.

The second stage is the reactions of products from the first stage, and the reaction space is the gas phase intermediate reaction zone. The released heat from second stage is transferred to the condensed phase, and accelerate the reactions in the condensed phase.

The third stage occurs in the place, which is certain distance from the surface of condensed phase. The products from the second stage react violently. The reactions release a lot of heat, flames are generated, and final combustion products are engendered. Passing through intermediate reaction zone, the released heat is transferred to the condensed phase.

In the second stage, the temperature is relatively low, and the color of the intermediate reaction zone is dark blue. It is also named as flameless reaction zone.

In stable/steady combustion, the combustion speed of liquid explosives has a relationship of Eq. 2.18 with pressure.

$$u = a + bP^v \tag{2.18}$$

Here, u is the linear speed of combustion reactions; a is a constant which is determined by the reactions in condensed phase and the thermal conductivity; b is a coefficient which is determined by reactions in gas phase; v is an index which is determined by the reaction order of dominant reactions in gas phase.

Overall, for nonvolatile liquid explosives, proportion of reactions in condensed phase is the dominant at low pressure; the reactions of flame zone is the main stage at high pressure; while both reactions in condensed phase and flame zone works comprehensively.

2.2.1.4   Combustion of Fast-Burning Liquid Explosives

The combustion/burning speeds/rates of explosives are related to their evaporability. When the explosives are difficult to vaporize, the reactions in condensed phase take a large proportion. H_2O_2-azidoethane is a traditional/classic explosive which is difficult to vaporize. In the combustion of H_2O_2-azidoethane, the reactions in condensed phase are faster. They released a lot of gas products and heat burst the surface of condense phase violently. Then the gas products and some reactants go into gas phase directly and the reactions continue. The reactions terminate in the zone which is a little far from the intersurfaces. Under certain pressure and temperature, this preheating zone is fixed. The surface bursting of the condensed phase occurring with the vaporization together increases intersurface area and accelerates
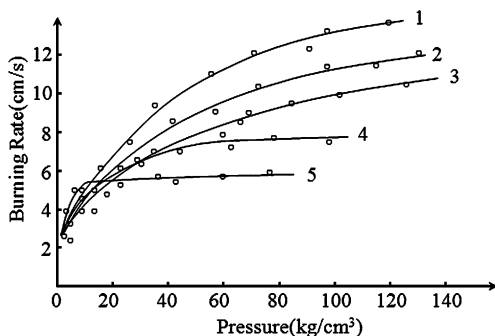
Fig. 2.3 The relation plots of combustion speed of H_2O_2-azidoethane mixture and the pressure. *1* H_2O_2-azidoethane; *2* N_2O_4-unsym-dimethylhydrazine; *3* Mercury fulminate; *4* Nitroglycerine; *5* hexogen

the reaction. The combustion of this explosive is much faster than the above two kinds of explosives. The burning rate is a function of pressure.

$$u = a + bP^v$$

The index v is about 0.5. Figure 2.3 indicates the relation between combustion speed of H_2O_2-azidoethane mixture and the pressure.

The burning rate is less affected by pressure if the pressure is 20–40 atm. Probably, the reason is that the main stage of burning reacts in the condensed phase and the burning rate is controlled by the reaction in the condensed phase. This kind of explosive usually have large burning rates and high melting points.

2.2.1.5 Burning Stability of Liquid Explosives

The vortex of the liquids brings a disturbance for the flame front and results the deformation of flame front. So the burning stability of liquid explosives is broken. The deformation and disturbance increase gradually, and makes the burning rate lower, finally leads to the detonation. Stable burning reaches only when the mass burning rate is within certain ranges.

The gravity, surface tension, and viscosity of the liquids help to hinder the deformation of flame fronts. After calculating the stability impaction of gravity and surface tension, the normal burning limit rate is guaranteed if the below condition is met.

$$u_m = \left(4\alpha_k g \rho_1 \delta_1\right)^{1/4} \tag{2.19}$$

Here, u_m is the mass burning rate with unit g/cm^2 s; α_k is the surface tension of a liquid and its saturated vapor; ρ_1 is the density (g/cm^3) of gas productions; δ_1 is the density of a liquid explosive.

According to α_k, ρ_1, and δ_l values from experiments, the calculated mass burning rates u_m of methyl nitrite, diethyleneglycol dinitrate, and nitroglycerine in one standard atmosphere press are 0.25, 0.26, and 0.25 g/cm^2 s, separately. It is concluded that the right side of Eq. 2.19 is approximated as a constant. If the pressure is 1 atm, it is 0.25 g/cm^2 s. When the burning rate is over 0.25 g/cm^2 s, detonation of liquid explosives is possible.

If the impact of liquid viscosity is considered, the normal burning limit rate is Eq. 2.20.

$$u_m = \left(3\sqrt{3}g\mu\rho_2^{3/2}\delta_l^{1/2}\right)^{1/3} \tag{2.20}$$

Here, u_m is the mass burning rate (g/cm^2 s) with impact of liquid viscosity; μ is the viscosity of a liquid (poise); ρ_2 is the density (g/cm^3) of gas productions; δ_1 is the density of a liquid explosive.

If the detailed burning study of nitrate ether is planned, the impact of liquid viscosity should be in consideration. The viscosity of nitroglycerine is 0.36 Poise. When $\rho_2 = 1.72 \times 10^{-4}\,\text{g}/\text{cm}^3$ and $\delta_1 = 1.6\,\text{g}/\text{cm}^3$, the calculated limit rate is 0.17 g/cm^2 s. The experiment rate is 0.28 g/cm^2 s. The viscosity of nitroglycerine could not guarantee the stable burning. If the above values of gas production and liquid explosive are applied, stable burning is guaranteed only when the viscosity of nitroglycerine is larger than 1 poise. Plastic process of nitroglycerine enlarges the viscosity, so plastic nitroglycerine has stable burning. Experiments proved that the burning of mixtures of nitroglycerine and colloxylin (99:1) is unsteady before colloxylin becomes colloidal. After colloxylin becomes colloidal, the viscosity of mixtures of nitroglycerine and colloxylin (99:1) increases to 3.5 Poise. According to the viscosity, the burning limit rate is 0.37 g/cm^2 s. So the colloidal has a stable burning rate of 0.24 g/cm^2 s.

Pressure boot greatly impacts the viscosity of stable burning guarantee. At 1 atm, the required viscosity is $\sim$1 Poise. The required viscosity increases dramatically when pressure is boosted. For example, the required viscosity at 100 kg/cm^2 is 1,000 times of that at 1 atm.

2.2.1.6 Burning/Combustion to Detonation of Liquid Explosives

Burning/combustion and detonation are two different concepts, but they interconnect with each other. Breaking the stable burning/combustion of explosives may lead to detonation.

When the products of liquid explosive burning reaction do not diffuse well, the reaction surface increases and the burning rate also accelerates. Once the critical value

is reached, the stability of combustion is broken, and the combustion experiences an abrupt transform to detonation. For flammable gas mixture, the shock wave is produced in the nonreacted liquids close to flame front, while the shock wave is generated in the gas products of incomplete reactions. The shock wave plays dual roles here. It increases the pressure of the liquid explosives, which is close to the burning fronts, uniforms the liquid surfaces, reduces the gaps of intersurfaces, and lowers the burning rate. The shock wave also leads to the thermal explosions of intermediates or liquid explosives of local area. The pressure jumps from thermal explosions, impacts back to unreacted liquid explosives, and leads to detonation.

The change of burning of liquid explosives to detonation experiences four stages —steady self-sustaining combustion, convection combustion, deflagration, and steady detonation. Heat transfer and initiated mechanisms are different in these four stages. Heat transfer of steady self-sustaining combustion is achieved by heat conduction. In convection combustion, the gas products inside spare surfaces ignite the inside surfaces of the gaps of liquid explosive molecules which is immigrated from the liquid bulk. It helps to increase the surface area/unit volume/mass, and the mass burning rate is about hundreds times than that of steady self-sustaining combustion. The stability of combustion is broken, and heat transfer comes true through forced convection. Heat transfer of deflagration is initiated by weak shock waves. Stable detonation is induced by strong shock waves. The total reactions accelerate, and the relative active stages have something with the physical and chemical properties of liquid explosives and the experiment conditions.

It is believed that after the stable combustion is broken, the explosion rates of explosives straighten up until stable detonation occurs. But the writer does not agree with it. In the writer's opinion, there is a deflagration stage between unsteady burning and normal detonation. It is also the new discovery from the explosion characters/features of liquid explosives.

The deflagration is stable under certain conditions. For example, when the charge diameters of the liquid explosives (e.g., H_2O_2–$(CH_3)_2NNH_2$ or N_2O_4–$CH_2(NO_2)CH(NO_2)CH_3$) are large (1,500–2,000 mm), the burning may not be stable. The deflagration stage is void and the reactions change from burning to detonation directly.

According to the experiments, when the pressure inside the containers (it is charged explosives) is lower than certain critical value P' ($P < P'$), the deflagration is stable. If $P > P'$, the deflagration changes to detonation. The exchange of deflagration to detonation is achieved in a jump range.

For the bicomposition liquid explosives or severely volatile explosives, there is no obvious deflagration stage in the change process from combustion to detonation. Convection combustion develops into detonation directly. The key feature of this change is that the detonation occurs in the fronts of convection combustion. In volatile liquids, the convection combustion develops rapidly, and forms shock waves in the front of flame fronts. The pressure of liquid surfaces accelerates the heat transfer into the inside of liquids, and leads to the heat explosion in local zone, then to the detonation of other space. If liquid explosives are charged in closed containers, it takes a time period from ignition to detonation of explosives.
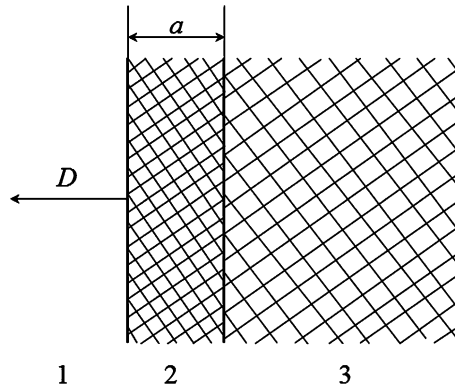
Fig. 2.4 Schematics of combustion and detonation. *1* Liquid explosives; *2* exchange zone of chemical reactions; *3* change front width of chemical reactions; *D* spread speed of fronts in liquid explosives

The passing distance of burning within the time period from ignition to detonation of explosives is detonation front. Under different conditions, the detonation front and degree of difficulty from burning to detonation are various.

In the combustion, detonation materials on the chemical exchange fronts shift along the media. These processing chemical exchange fronts are detonation fronts. The explosive materials react to products within the front ranges. In general, detonation is a phenomenium of fast self-spreading of detonation wave along the explosives. The spreading speed is less affected by environment. The pressure near the explosion point rises dramatically. Whether explosion is in the closed container or not, the products of explosion impact the around media drastically, then break and deform the staff around. The schematics of detonation is shown in Fig. 2.4.

The mechanisms of combustion and detonation are different. In burning, the chemical exchange fronts spread slower than the sound in liquid explosives. But in the detonation, the chemical exchange fronts shift faster than the sound in liquid explosives. Burning is spread through heat conduction, diffusion, and radiation inside the explosives. But detonation is through shock waves. Detonation waves are the shock waves following the fast chemical reactions.

These two forms of explosion of liquid explosives can interchange with each other. In certain case, combustion may transform into unstable detonation and further evolute into stable detonation.

2.2.2 Detonation of Liquid Explosives

Detonation is a process in which chemical changes occur inside explosives or flammable mixtures, whose process has some similarity with combustion. The feature of detonation is that chemical reactions do not occur within the materials at

the same time, but it spreads layer by layer. Under combustion, the chemical exchange fronts shift along the media. The fronts of chemical exchange are detonation fronts. On the fronts, the explosives experience the change from reactants to products. Detonation waves are shock waves with high-speed chemical reactions. In other words, detonation is transported through shock waves.

From detonation physics, the charging and application of liquid explosives are not as wide as condensed explosives because liquid explosives are not compressible. Liquid explosives have an elusive outstanding feature, which is that the reactions of detonation absorb energy first, later release heat. The combination of exothermicity and endothermicity complicates the chemical reactions, and results in the parameter distribution characteristics of macrokinetics different from detonation characteristics of general high-energy explosives.

To study the detonation of liquid explosives and its spreading/transportation, nitromethane, nitroglycerine, diethyleneglycol dinitrate, and methyl nitrite are designed as the objectives of liquid explosives to study the chemical dynamics and the complex unsteady process of shock waves' combustion. These phenomena determine the structure of detonation wave fronts and spreading limit of detonation waves. They help to clear the flow dynamics of wave fronts, and refer suggestions for the formula of liquid explosives, study and application of equipment features. They help to improve and perfect the detonation theory.

To simplify the study, five explosives are designed. Same amount of tetranitromethane, nitroglycerine, diethyleneglycol dinitrate, methyl nitrite, and AstroliteG (hydrazine nitrate 59 %, hydrazine perchlorate 24 %, hydrazine 10 %, and methylamine 7 %) are initiated at exactly same conditions. At the same time, the same inert solvents are used to dilute the above five explosives to conduct the contrast experiments. It mainly explains the energy release of wave fronts at different time. First-hand information is obtained by this way. The equipment setup is shown in Fig. 2.5.

Fig. 2.5 Luminous equipment setup of detonation wave fronts from liquid explosives. *1* Initiation toner; *2* booster; *3* plane wave length; *4* organic glass; *5* metal pipe with liquid explosives; *6* illuminated mirror
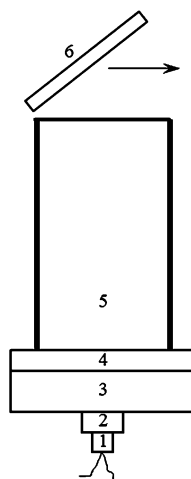
There is steady detonation and unsteady detonation. The steady detonation has constant propagation velocity/rate; while the unsteady detonation has changing propagation velocity/rate. Generally, all detonation is steady detonation, and unsteady detonation is explosion.

When the toner initiates the detonation, in its first stage, detonation rate varies and increases gradually. This stage is unsteady detonation. Detonation experiences unsteady acceleration period and reaches the maximum steady velocity/rate/speed, and this maximum velocity is maintained until all explosives react completely.

Until now, there is little report for the study of chemical reaction zone in the detonation wave fronts of liquid explosive explosion. For a long time, the detonation mechanism of liquid explosives is considered to follow the one-dimensional model of Zeldovich, the same detonation mechanism as that of gas explosive. Although this assumption is accepted, and gets some approvement by the calculation of condensed media impact heating, the calculation and approvement are just one-sided and superficial. The detonation of liquid explosives is different from that of condensed explosives. Detonation growth process of liquid explosives is a process of weak detonation to strong detonation, from unsteady combustion/burning to steady combustion/burning, finally to detonation. Only the development of techniques and renewal of equipment help prove and clear below issues: the chemical reactions and dynamics of complex organic molecules under high pressure, the change of state function in energy releasing processes, the rule analysis of condensed medium expansion, distribution, and calculation of elastic energy and heat from chemical energy, work contribution of explosion methods and produced pressure platforms, numerical simulation of liquid explosive detonation, etc. Only after the differences from condensed explosives are settled down, the pressure profile of chemical reaction zone in the explosion of liquid explosives can be explained or calculated.

In the past, it is believed that the detonation of an explosive only has over-compressed detonation, and normal detonation, or DTT detonation from self-sustaining spread combustion/burning to detonation. Although there are detonation phenomena, which are not normally explained, only CJ detonation and its features gained the attention. Other kind of detonation is seldom being referred. If proper ignition method is used, most detonation can be transited into under-compressed detonation. "Under compressed detonation" is corresponding to the "over compressed detonation state". Earlier it was also named "weak detonation" [4, 5].

Because shock waves from liquid explosives have a stronger influence than that of condensed explosives with the same mass and especially in closed or semiclosed space, we started to investigate the characteristics of self-sustaining detonation of liquid explosives, as well as the underlying detonation mechanisms.

2.2.2.1 Detonation Mechanisms of Liquid Explosives

In the overpressure detonation, Rayleigh line represents the line of momentum and mass conservations; Hugoniot curve represents the curves of energy conservation.

The crosspoints of these two lines are S and W. But in normal detonation, Rayleigh line is tangential to Hugoniot curve (the detonation adiabatic curve). And the contact point is P. Figure 2.6 gives the relative positions of Rayleigh line and Hugoniot curve.

The contact point P corresponds to normal detonation or CJ detonation. The high crosspoint S correlates super pressure detonation. The low crosspoint W corresponds to under-compressed detonation.

N and N′, which are the crosspoints of two Rayleigh lines and shock/impact adiabatic curve, correlate with the shock/impact compression condition of initiations.

Point W, which is different from S, is in the weak branch under the contact point P of the detonation adiabatic curve. Point P is also weak detonation point.

Zel'dovich founded classic detonation theory [6]. In the book "Shock Waves of Condensed Media" [7], Dremin proved that in general under-pressure detonation is not reachable using thermal dynamics and gas kinetics.

The impossibility of under-pressure detonation is discussed. Figure 2.7 shows the relative positions of detonation adiabatic curve H with balance conditions and detonation adiabatic curve k_i (k_i is the intermediates with certain amount ratio). The released energy is more if the subscript i of k_i is larger. The adiabatic curve of k_0 equals the impact adiabatic curve of the original explosives.

Fig. 2.6 The relative positions of Rayleigh line and Hugoniot curve
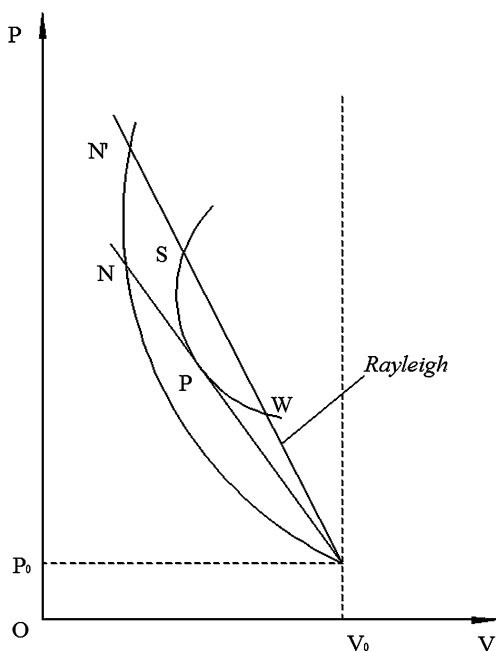
Fig. 2.7 The relative positions of balanced detonation adiabatic curve and the detonation adiabatic curves of all intermediates for the exothermic chemical reactions
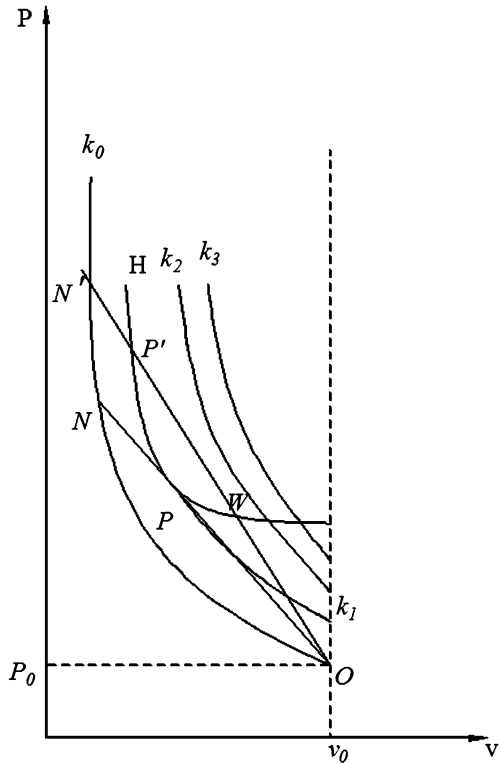
According to the equation of momentum conservation, the state point, which depicts the thermodynamics of media, must shift follow one Rayleigh line until it crosses with the detonation adiabatic curve under balance.

Under the conditions, if the state points move up from O, which is the original state, it is reachable for all balance points of the weak branch (the branch under CJ point P) of detonation adiabatic curve. According to the specific reaction mechanisms, normal detonation comes true. The only mechanism is that momentum compression of explosives initiates the chemical reactions. All kinds of transportation and the transfer of radiation are negligible within the normal range of detonation shock wave fronts. The front interfaces of reaction zone are shock wave fronts, which jumps state O to Point N or N'.

Following the proceeding of detonation reactions, the pressure drops down, and the state point starts from point N or N', and moves toward the contact point P or P' along the Rayleigh line. So within the detonation wave front range, there is a chemical peak pressure increase zone of chemical peaks. The pressure distribution inside the chemical peaks depends on chemical kinetics of chemical reaction zone.

If the state point moves down from point P or P', the state point is an isentropic curve, which conflicts with the second law of thermodynamics (principle of entropy increase for any spontaneous process). If the state point moves up, it compresses the

production. But the shock wave fronts transport in ultrasound rate, all points of P and above P follow Eq. 2.21.

$$C \geq D - u \qquad (2.21)$$

So compression of products is impossible.

In summary, under the study conditions, the state W, which represents all points on the weak branch of balance detonation adiabatic curve is not achievable. So under-pressure or weak detonation points do not exist. Equation 2.21 is a prerequisite for the stable transportation of detonation wave fronts.

On the other hand, ultra compression fronts are not compatible with sparse waves. Stable self-sustaining states need to meet the second prerequisite—Eq. 2.22.

$$C \leq D - u \qquad (2.22)$$

Therefore, only when

$$C = D - u \qquad (2.23)$$

These two prerequisites should not conflict with each other. That is the famous CJ selection rule.

In the same book, Dremin studied another condition. The reaction from k_0 to k_1 is exothermic, while the reaction from k_1 to the balance composition is endothermic. Now the smallest detonation rate is the ratio of Rayleigh line ON, which represents the denotation rate. Rayleigh line is the tangential one of the intermediate k_1 under detonation and in adiabats. The notation of exothermic energy becomes negative when it is passing this line. The detonation wave fronts spread faster than normal detonation. In other words, CJ rule (Eq. 2.23) is not applicable.

In Fig. 2.8, when the state point shifts from point N or N′ along Rayleigh line to point P or P′, the pressure drops, and a chemical peak shows up again. The state point cannot shift down from point P′ because the intermediate/mean detonation adiabatic curve of composition k_1 is above all other detonation adiabatic line/curve. So the state point can only shift along Rayleigh line from P′ to balance point S′.

If the state point starts from point P, the shift along Rayleigh line has two directions: up to point S with pressure increase, and down to point W (it corresponds with the under-pressure detonation) with pressure drop. Under suitable environmental conditions, under-pressure detonation is also possible when the pressure continuously decreases in the detonation wave range.

The detonation of liquid explosives is different from that of general condensed explosives. In common, for same mass/weight of explosives, liquid explosives do more work than condensed explosives. The under-pressure detonation of self-sustaining spreading is studied below.

More than one time, Dremin [7] referred two-stage detonation theory. The pressure inside detonation waves is determined by two-stage detonation. If the reactions inside detonation waves start slowly, and accelerate gradually, which is

Fig. 2.8 The relative positions of balanced detonation adiabatic line H, moment adiabatic line k_0, and detonation adiabatic line k_1 with maximum exothermic energy
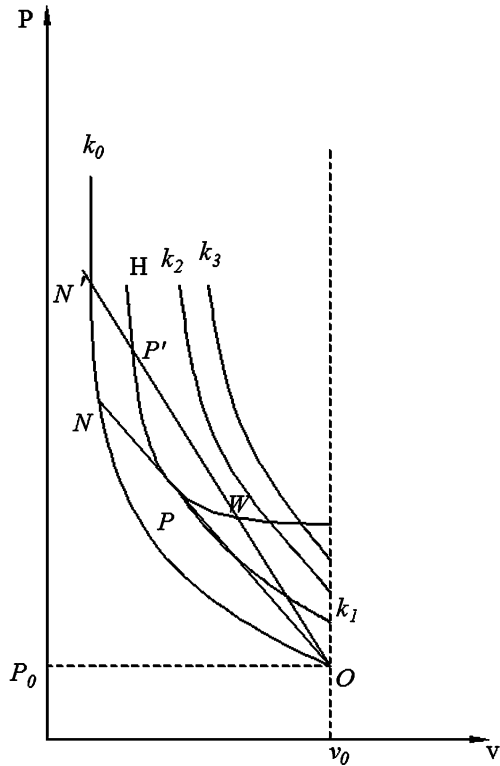
like the early stage of hot spot initiation of detonation to homogeneous detonation. The pressure distribution of two-stage detonation is the dashed curve in Fig. 2.9. If all reactions from early to final stages are faster reaction, the pressure distribution is the solid curve of Fig. 2.9.

Bdzil and Davis [8] first put forward two-stage theory, which has attracted the attention of detonation. The first fast stage releases most of exothermic detonation energy. In the second relatively slow stage, the energy released is only the remnants (e.g., 4 %). According to the above theory, if the assumption is based on the reaction rates and the calculated CJ pressure of Comp B explosives PH = 26.4 GPa, and 96 % of chemical energy released in the first stage, the theory data match the experiment ones.

This study will discuss the two-stage detonation theory. The first stage is the rapid/fast reaction stage, which releases almost all energy; while the reactions of the second stage are slow, and there are possible endothermic reactions. The stable/steady under-pressure detonations would be proved.

After the detonation of liquid explosives, the detonation rate is determined by the inclination/dip angle of Rayleigh line, which is tangential to the detonation adiabatic curve with the most heat released. The detonation pressure is determined by

Fig. 2.9 The pressure
distributions of two-stage
detonation. The pressure
distributions of normal
detonation wave for *solid line*
(all reactions are faster
reaction from early to final
stages) and *dashed line* (the
origin reactions start slowly,
and accelerate graduate). PD
is the unsteady sparse waves
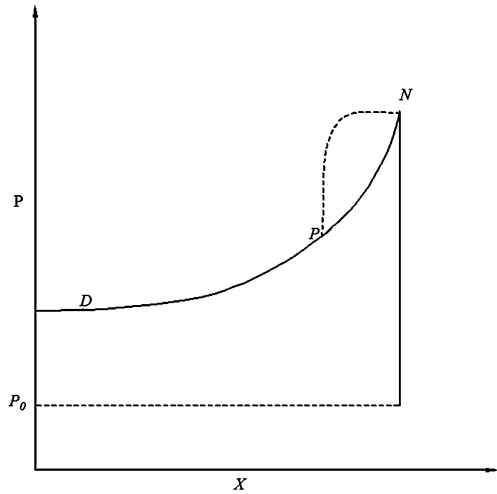
the crosspoint (W) of Rayleigh line and the adiabatic curve of detonation final
products. Figure 2.10 displays the adiabatic curve of detonation final products.

In Fig. 2.10, the reactions in the first stage of detonation are fast/rapid and
exothermic, while the reactions in the second stages are slow and endothermic. In
the steady/stable under-pressure detonations, the inside structures of detonation
waves have five parts.

Fig. 2.10 *p-V* plots of the
under-pressure detonation
W of liquid explosives
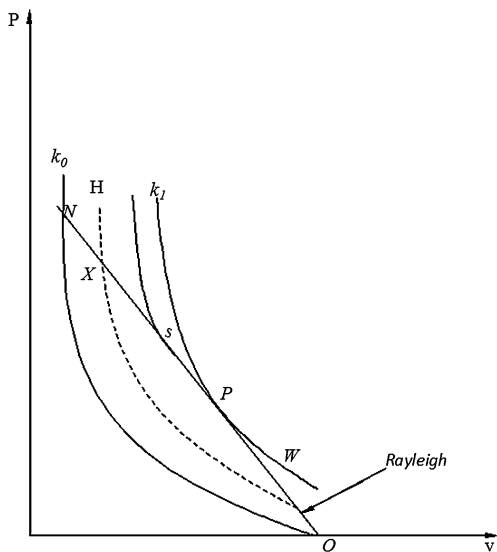
Fig. 2.11 Schematics of five parts, which compose the structure of under-pressure detonation of liquid explosives
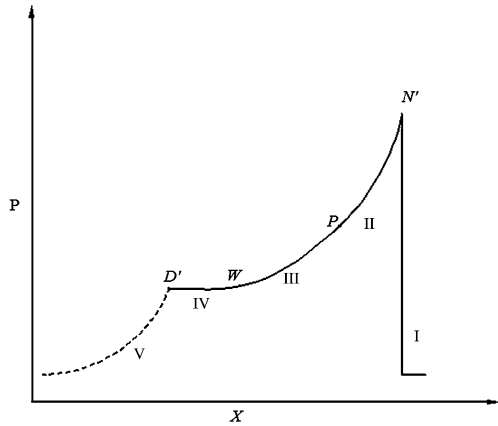
(1) The jump compression of shock waves reaches almost all the exchanges of detonation and energy releasing.
(2) The endothermic reactions rapidly drop down the pressure inside detonation wave area from N to P.
(3) After endothermic reactions, the flat transition interval of P-W' forward to under-pressure detonation W.
(4) The transportation rate is the constant self-preserving/simulating expansion area W-D', which is in direct proportion to $D' - (CW + uW)$.
(5) The area below D' is the sparse area of sputtered explosion productions.

All exchanges in detonation are shown in Fig. 2.11.

The pressure flat-forms deserve the attention, which are the key features of the constant self-preserving/simulating expansion area in the structures of under-pressure detonation. There is no pressure flat-form if detonation structures are different.

Above, the special detonation of liquid explosives is discussed. In the detonation wave range of under-pressure detonation, there is constant flow area—the flat-form of pressure. After the feature is proved, there will be potential applications in explosion industry.

2.2.2.2 Eigenvalue Detonation of Liquid Explosives

The classic detonation theory has proved that the stable/steady detonation waves of explosives propagate with CJ rate and there are sonic flows in the boundaries of detonation reactions. If the detonation waves propagate faster than CJ rate, there are subsonic flows in the boundaries of reactions. The classic detonation theory predicted that there were sustaining stable/steady detonation waves and possible special unsustaining detonation waves. The spread rates of ultrasonic waves in the boundaries of reactions are eigenvalue detonation rates.

Why eigenvalue detonation is referred here? According to Chapman and Jouguet, the founders of the classic detonation theory, the theory is completely based on the kinetic theory of gases. This is not absolutely right. The detonation theory does not have close relation with kinetic theory of gases, but also chemical kinetics. Besides the three conservation equations in the kinetic theory of gases, the equation of chemical kinetics is also being considered. In the equation, the rate of chemical reactions is important. In the kinetic theory of gases, mechanical quantities are functions of flow gradients. But in classic chemical kinetics, reaction rates, which are different from mechanical quantities, are not the functions of flow gradients, but functions of local thermal dynamic states. Mechanical quantities are different from chemical reaction rates.

How to solve the problem of combining the chemical reaction equations and the three equations of gas kinetic theory? It's extremely difficult because of the complexity of chemical reaction inside detonation area. There must be a simplified approach, which stipulates that chemical compositions react stoichiometrically according to some way, and the proceeding variable (λ_i) of stoichiometric reactions represents the complex changes of chemical compositions. This makes a chemical problem into a physical one. The simplest stoichiometric reaction is Eq. 2.24.

$$A \rightarrow B \tag{2.24}$$

In the above equation, A is an explosive, B is the product of detonation, and λ is the decomposition degree of the explosive (the ratio of decomposed explosive mass to the original explosive mass). The proceeding variable λ reports the chemical changes.

The state function of detonation reaction is Eq. 2.24.

$$E = E(p, \rho, \lambda) \tag{2.25}$$

While the chemical reaction rate of detonation is Eq. 2.26.

$$r = \lambda = \frac{d\lambda}{dt} = r(p,\ \rho,\ \lambda) \tag{2.26}$$

Here, r is the chemical reaction rate; p is the pressure of detonation waves; ρ is the media density of detonation waves.

Please notice that the reaction rate is assumed to only have relationships with local state, not with flow gradients.

Von Neumann [9] studied the suspended detonation of aluminum in the oxygen gas. Al_2O_3 is not the only product because Al_2O_3 decomposes under high temperature and high pressure. So the chemical formulae have Molar reduction, and a lot of heat is given off. In irreversible reaction, Von Neumann set up the reaction in Eq. 2.27.

$$A \rightarrow (1 + \delta)B \tag{2.27}$$

The reaction is Moore fraction reduction. One molecule A reacts to $(1 + \delta)$ molecule B ($\delta < 0$). According to the mass conservation, if the molecular weight of A is MA, the molecular weight of B is $\text{MB} = \frac{\text{MA}}{1+\delta}$. The state equation changes to Eq. 2.28.

$$pV = (1 + \lambda\delta)\, \tilde{R}_T \tag{2.28}$$

Here, $\tilde{R} = R/M_A$, and $\tilde{R}$ is the gas constant of material A.
The state internal energy function is Eq. 2.29.

$$e = m_A^0 \tilde{h}_{0A} + \left[\frac{\widetilde{C_p}}{1 + \lambda\delta\tilde{R}} - 1 \right] pV - \lambda q \tag{2.29}$$

Here, $\widetilde{C_p}$ is the heat capacity under constant pressure; $\tilde{h}_{0A}$ is the enthalpy of composition Molar fraction; q is the heat fraction vector frozen point.
Hugoniot curve is Eq. 2.30.

$$\left[\frac{\widetilde{C_p}}{1 + \lambda\delta\tilde{R}} - 1 \right] pV - \left(\frac{\widetilde{C_p}}{\tilde{R}} - 1 \right) p_0 V_0 = \frac{(p + p_0)}{2} (V_0 - V) + \lambda q \tag{2.30}$$

So, the envelope of *Hugoniot* curve is Eq. 2.31.

$$q = -\frac{pV\delta\widetilde{C_p}}{(1 + \lambda\delta)^2 \tilde{R}} \tag{2.31}$$

Because the reaction is irreversible, $\gamma \geq 0$, and σ is not always larger than 0. When $\sigma = 0$, the curves of $\sum = \sigma r = 0$ are in Fig. 2.12 (Σ include all areas except Rayleigh line).

From Fig. 2.12, the curve of $\Sigma = 0$ and the frozen *Hugoniot* curve enclose into one line/curve. Because the line of $\Sigma = 0$ is the enclosed line of *Hugoniot* curve, the crosspoint of the sound track line and the curve of $\Sigma = 0$ is the tangential point (CJ) of *Rayleigh* line and the curve of $\Sigma = 0$. The corresponding detonation rate of *Rayleigh* line is $\tilde{D}$. When $D > \tilde{D}$, the mass point starts from the original state, passes shock waves, and jumps the point N of *Hugoniot* curve ($\lambda = 0$). For point N, $\eta > 0$, $\Sigma > 0$, so the mass point only moves along the Rayleigh line from the left to right, until the point Σ of Rayleigh line and $\Sigma = 0$ curve. Because $\Sigma = 0$, all parameters have extrema. When $\Sigma < 0$, the reaction shifts along *Rayleigh* line from the right to left, and finally reaches the final stage S1 of *Hugoniot* curve. S1 is a strong detonation point. The pressure of reacting zone/area reduces from N1 to point Σ, then increases to S1. There is a minimum pressure. The capacity V increases from N to point Σ, then reduces to S1. There is a maximum value of
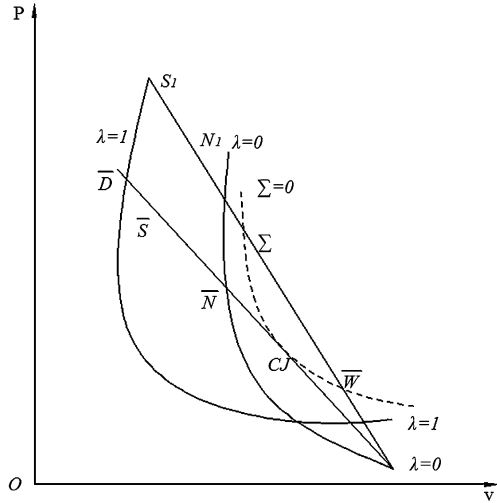
capacity. When $D = \widetilde{D}$, the mass point passes shock waves, and jumps to Point $\tilde{N}$, shifts along *Rayleigh* line to the right until CJ point. In CJ point, $\Sigma = 0$ and $\eta = 0$. (Here, σ is the constant of thermal conductivity; η is the coefficient of sound speed; $\sigma = (\partial P/\partial \lambda)_{E,v/\rho c^2}$, $\sum \sigma \gamma$, $\eta = 1 - (u/c)^2$; c is sound speed; u is mass velocity) [4]. Then the mass point can return to strong detonation point $\widetilde{S}$ along Rayleigh line, or move to the right until the point $\widetilde{W}$ of under-pressure detonation, and then the under-pressure detonation occurs. When $D < \widetilde{D}$, the mass point starts from $\lambda = 0$ of *Hugoniot* curve along *Rayleigh* line. There is no crosspoint of *Rayleigh* line and $\Sigma = 0$ line. When *Rayleigh* line crosses the sound track line, $\eta = 0$, so $\frac{\mathrm{d}p}{\mathrm{d}t} = -\infty$. There is no time-independent solution.

In the explosion of liquid explosives, the two prerequisites of classic under-pressure detonation are the final Hugoniot curve, (not the up boundary covered by frozen Hugoniot curve), and that Rayleigh line passes point $\Sigma = 0$ ($\eta = 0$), and reaches point W finally.

Figure 2.13 gives the simultaneous solution of gas dynamic equation and reaction rate equation (in plane *p-λ*).

In Fig. 2.13, the contact point of envelope line is at $\lambda = 1/2$. There are special situations from Fig. 2.6 through Fig. 2.13 (Fig. 2.11).

(1) There is a special detonation rate $\widetilde{D}$, which is the D value when Rayleigh line is tangential with the envelope curve. When $D > \widetilde{D}$, the subsonic speed of *Hugoniot* curves separates with supersonic speed (Fig. 2.13) because part of *Rayleigh* line is above the envelope curve. So the detonation only occurs on the top part of *Hugoniot* curve. Following the proceeding of reactions, state point starts from shock wave point N, moves down along *Rayleigh* line until it meets envelope curve, and this point is the minimum p. Then state point of *p-V*

Fig. 2.13 Pathological
detonation of reactions in the
p-V plane
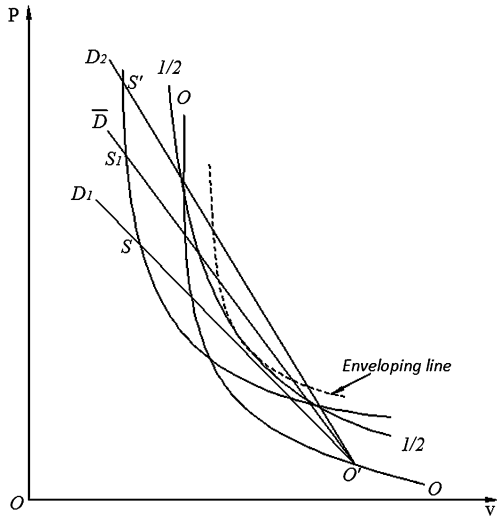
plane moves up along *Rayleigh* line, until it meets the *Hugoniot* curve ($\lambda = 1$).
The shock wave of the whole flowing area is subsonic. The sparse waves from
the rear degrade the flowing.

(2) When $D = \widetilde{D}$, the state point starts from shock wave point N to *Rayleigh* line.
The state point line is tangential to the envelope curve. The state point reaches
strong compression point S or weak detonation point W of the *Hugoniot* curve
($\lambda = 1$). The contact point P of *Rayleigh* line and the envelope line is between S
and W. Von Neumann named point P as the pathological point.

(3) For an irregular reaction, there is a $\widetilde{D}$ in the reaction of the molecular amount
reduction. The value of $\widetilde{D}$ is related with the property of explosives (state
function) and reaction rate. The under-pressure detonation occurs when $\widetilde{D}$ is
with certain value.

(4) When $D < \widetilde{D}$, Rayleigh line cannot cross or contact with *Hugoniot* curve. So
there is no envelope line, and no time-independent solution.

Von Neumann explained the key features of pathological detonation with Molar
reduction using one reaction in Fig. 2.14. When $D > \widetilde{D}$, there are two vertical
segmentations. The segmentation, which starts from point N and ends point S, is at
the top. Subsonic fluctuation is at the end point S. When $D < \widetilde{D}$, there are two
horizontal segmentations. The reaction starts from point N, and only reaches partial
reaction point T. When $D = \widetilde{D}$, there is saddle-backed configuration at point P.

Figure 2.14 shows that the detonation with propagation velocity $D = \widetilde{D}$ starts
from the crosspoint N of the *Hugoniot* curve and shock adiabatic curve. Only after
passing point P is under pressure detonation point (or weak detonation point) is
reached. Von Neumann named the detonation velocity as eigenvalue detonation

Fig. 2.14 The reacted pathological detonation in p-λ plane
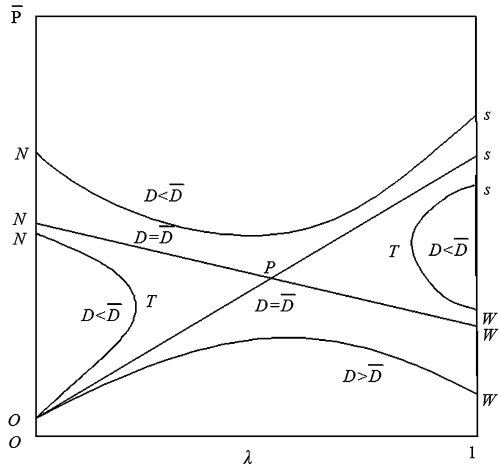
velocity. The pathological detonation discussed above is one example of eigenvalue detonation [10–13].

Although the pathological detonation stated by Von Neumann is very interesting in theory, its application value in condensed explosives is not clear yet. The time of detonation reaction and positive pressure action of liquid explosives is far longer than that of the condensed explosives. This explained why the detonation theory of condensed explosives is not supported by the detonation theory of liquid explosives [14–16].

This book will discuss the detonation of liquid explosives—the first exothermic reaction, and the second exothermic reaction and endothermic detonation, which is one example of eigenvalue detonation. This case has application value because most of solid explosives are composed by one kind of explosives and a mixture, which deactivates adhesives. In the detonation, the deactivation of adhesives is endothermic. The eigenvalue detonation of this kind of explosives is achievable. Figure 2.15 explains the key features of the eigenvalue detonation.

In the second stage after detonation initiation, there are two irreversible reactions. The first is exothermic, and the second is endothermic. In the partial reaction *Hugoniot* curve of p-V plane, *Rayleigh* line represents momentum and mass conservation rules. $\widetilde{D}$ is the eigenvalue detonation velocity/speed/rate. Only when $D = \widetilde{D}$, under-pressure detonation point below point P is achievable.

2.2.2.3 Under-Pressure Detonation Wave of Liquid Explosives in Pistons

The piston is introduced to discuss the detonation of liquid explosives [17]. Compared to the key features of condensed explosives, the piston issues/cases of liquid explosives are a little more complex. Based on different piston rates μ_p have
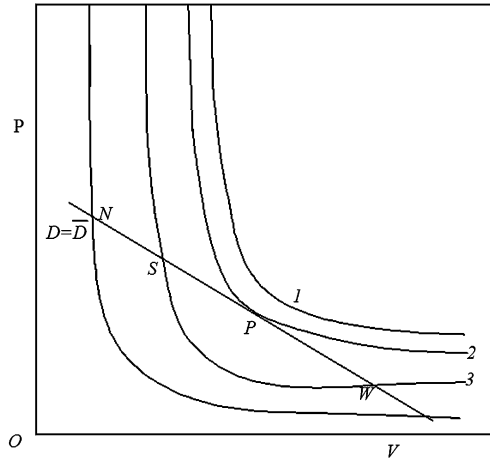
Fig. 2.15 Eigenvalue detonation curve of liquid explosives
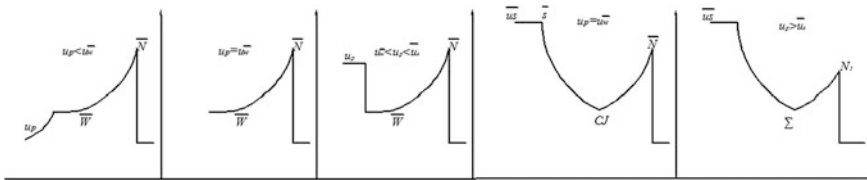
Fig. 2.16 The pressure distribution plots/curves of under-pressure detonation

different mass speed, the pressure distribution curves/plots are displayed in Fig. 2.16 [4, 5, 7].

When $\mu_p > \mu_{\widetilde{S}}$, detonation waves have a minimum value in the area of strong detonation reaction area ($\Sigma = 0$), and the reaction area ends at point S1. The media is homogeneous range, and the mass velocity of uniform area is the same with point S1 (μ_{S_1}). When $u_p = u_S$, the detonation is CJ one, and the reaction area ends at point $\widetilde{S}$. After detonation, there is a homogeneous range with mass velocity $u_{\widetilde{S}}$. When $u_{\widetilde{W}} < u_p < u_{\widetilde{S}}$, the detonation is under-pressure detonation, and the reaction area ends at point $\widetilde{W}$. Because $u_p > u_{\widetilde{W}}$, there are shock waves (compressing waves) to accelerate the mass to velocity u_p. Compared to the waves, detonation has supersonic velocity, so the homogeneous range is broaden continuously. If the piston velocity reduces further, there are velocity reduce mass points of sparse waves, which uniform the boundary velocities. After the waves of under-pressure detonation, the wave head point $\widetilde{W}$ of sparse waves further broadens the homogeneous range.

After the above discussion, we already have enough understanding and theoretical basis for under-pressure detonation. There are two prerequisites for under-pressure detonation.

(1) The final state *Hugoniot* curve is not the top boundary of covered area by frozen Hugoniot curve groups. Under-pressure detonation never occurs if the first prerequisite is not met.
(2) Under-pressure detonation only occurs when Rayleigh line passes $\Sigma = 0$, at the same time $\eta = 0$.

The work passes of liquid explosives are different from that of condensed explosives. The under-pressure detonation makes detonation overpressure value larger than that of condensed explosives. So the detonation of the hydrazine-urea nitrate liquid explosive is more powerful than HMX. These are the detonation features and advantages of some liquid explosives.

2.3 Explosion Work Ability of Liquid Explosives

The high temperature and pressure products of liquid explosives violently lash against and compress the media around to make them moving, deformation, broken, and blown apart. This is the direct impact of detonation products. When the target is far from the explosion point, the damage of products is not very sharp. When explosion is in the air or water, the expansion of explosion products compresses the surrounding media, and produces shock waves. The transportation of the shock waves in the media can damage the staff/materials far away from explosion. The impact of explosion for the surrounding media has both close and far ranges.

Explosion blasting includes all mechanical impacts of explosion for the surrounding materials. The blasting of explosives are related to the packed mass, properties of explosives, the geometric figuration, and the surrounding media property (within a distance).

Study of the explosion blasting helps to evaluate the explosion characteristics and proper application of explosives, make the effectiveness of explosives complete, and supply necessary theoretical basis for packing design [18–20].

2.3.1 Work Capacity of Liquid Explosives

The shock waves of explosion in free space, the soil compression and throwing of explosion on the ground, the high-energy bubbles produced by the explosion under the water, the deformation from the engineering blasting underground or in the mines, and broken pieces produced in packing armed explosives have different damage ability and killing effects. The work of liquid explosives has various forms.

But for certain purpose, only one or several kinds of explosion are effective. The total work capacity of liquid explosives is expressed in Eq. 2.32.

$$A = A_1 + A_2 + A_3 \dots + A_n \tag{2.32}$$

Here, A_1, A_2, A_3,...A_n is the work of each explosive effect. A_T is the sum of all work.

The sum of all explosion effect of liquid explosives for the surrounding media is the work of explosives, or the work capacity of explosives. The capacity is also the power of explosives. It can be calculated from theory or obtained from experiments.

2.3.1.1   Ways to Express the Work Capacity of Liquid Explosives

If the work of liquid explosives to the surrounding is done through the adiabatic expansion of high-temperature and high-pressure gas products, according to the first law of thermodynamics, the decrease in the internal energy of a system is equal to the total released heat and work done to the surroundings.

$$-\mathrm{d}u = \mathrm{d}Q + \mathrm{d}A \tag{2.33}$$

Here, $-\mathrm{d}u$ is the decrease in the internal energy of explosive system; $\mathrm{d}Q$ is the heat released to the surroundings from the explosive system; $\mathrm{d}A$ is the work done to the surroundings.

According to the adiabatic assumption of expansion, $\mathrm{d}Q = 0$. So Eq. 2.33 is changed to

$$\mathrm{d}A = -\mathrm{d}u = -\bar{C}_v \mathrm{d}T$$

After integration of A, Eq. 2.34 is obtained.

$$A = \int_{T_1}^{T_2} -\bar{C}v \mathrm{d}T = \int_{T_2}^{T_2} \bar{C}_v \mathrm{d}T = \bar{C}_v(T_1 - T_2) \tag{2.34}$$

Here, T_1 is the explosion temperature; T_2 is the final temperature after cooling down (15 °C is usually used as the standard temperature); $\bar{C}_v$ is the average constant volume heat capacity of explosive products between T_1 and T_2.

The explosion heat has below relationship.

$$Qv = \bar{C}v(T_1 - T_2) \tag{2.35}$$

Here, E is the mechanical equivalent of heat; Q_v is the explosion heat of an explosive; $A = EQ_v$ is the potential energy of an explosive, which is the total work

of product adiabatic expansion to cool down to the original temperature of an explosive, also the theoretical data of the work capacity of an explosive.

The work done by unlimited adiabatic expansion of explosive products until to absolute zero is the real potential energy of an explosive. But the absolute zero is nonreachable in real proceedings, and the explosion heat at absolute zero is very close to that at 15 °C. So the explosion heat at 15 °C takes the potential energy of an explosive.

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1}$$

or

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

The work done by the adiabatic expansion of detonation products to 1 atm pressure is expressed in Eq. 2.36.

$$A = \bar{C}_v(T_1 - T_2) = \bar{C}_v T_1\left(1 - \frac{T_2}{T_1}\right) = \overline{C_v}T_1\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}\right]$$
$$= \bar{C}_v T_1\left[1 - \left(\frac{V_2}{V_1}\right)^{\frac{k-1}{k}}\right] \tag{2.36}$$

If $\bar{C}_v T_1$ is replaced by explosion heat Q_v, which approximately equals $\bar{C}_v T_1$, the Eq. 2.36 becomes 2.37.

$$A \approx Q_v\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}\right] = Q_v\left[1 - \left(\frac{V_1}{V_2}\right)^{k-1}\right] = \eta Q_v \tag{2.37}$$

Here, η is the work efficiency; P_1 and P_2 are the pressures of initial and final states separately; and V_1 and V_2 are the specific volumes of initial and final state separately.

Equation 2.37 shows that the real work of detonation products is less than the potential energy of an explosive. The value of the work is related to the potential energy of an explosive, the expansion ratio $\frac{V_1}{V_2}$ of detonation products, and isentropic index k.

When the explosion products expand unlimitedly (V_2 is unlimited), the work done by explosion products equals to the potential of an explosive. If the explosion heat is higher, the work is more. When the energy potential of an explosive and the expansion ratio $\frac{V_1}{V_2}$ are fixed, a larger isentropic index k means the more complete

exchange of the potential energy to work. Because $k = 1 + \frac{nR}{\bar{C}_v}$, if $\bar{C}_v$ is smaller, k is larger. So the work A is larger.

In the evaluation of work capability of a liquid explosive, the amount of condensed products in detonation should be taken into consideration. If there are condensed products in detonation, the gas products reduce relatively, and the specific volume is small. In the expansion process, the gas products transform the internal energy into work, and its temperature drops down. The process of the internal energy from condensed products to work is that the energy of condensed products is transferred to gases, and then transformed into work. The expansion of gases is a fast process, in which it is difficult to reach the thermal balance of condensed and gas phases. Part of the energy is still stored in the condensed phase. This energy is finally lost through thermal conduction. So the measured work ability is smaller.

From the above, the explosion heat of an explosive is the conclusive parameter of work capability; while the gas products of detonation are the medium of work. More gas products and larger the specific volume, the efficiency of heat to work is higher. The specific volume of explosives also plays an important role for the work capability.

2.3.1.2   Evaluation of Work Capacity

(1) Measurement of work capacity using a lead cast method

The working capacity of explosives is usually measured/evaluated using lead cast method. This method measures the increased lead-hole volume of the lead cast in the explosion of certain explosives inside the lead hollowness. The configuration and effect are shown in Fig. 2.17.

In Fig. 2.17, the lead cast is made of fine lead. In the center of lead cast, there is a cylindrical hollowness with 25 mm diameter and 125 mm height. In experiments, the measured explosive with 10 ± 0.01 g is put in the cylindrical hollowness (24 mm in diameter) of aluminum foil. After the detonator is installed, the aluminum foil with detonator is put into the cylindrical hollowness of lead cast.
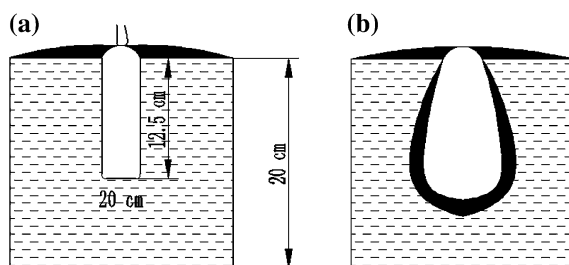
Fig. 2.17   Measurement of explosive work capacity using lead cast method. **a** The configuration of lead cast before test; **b** the effect of lead cylinder after explosion
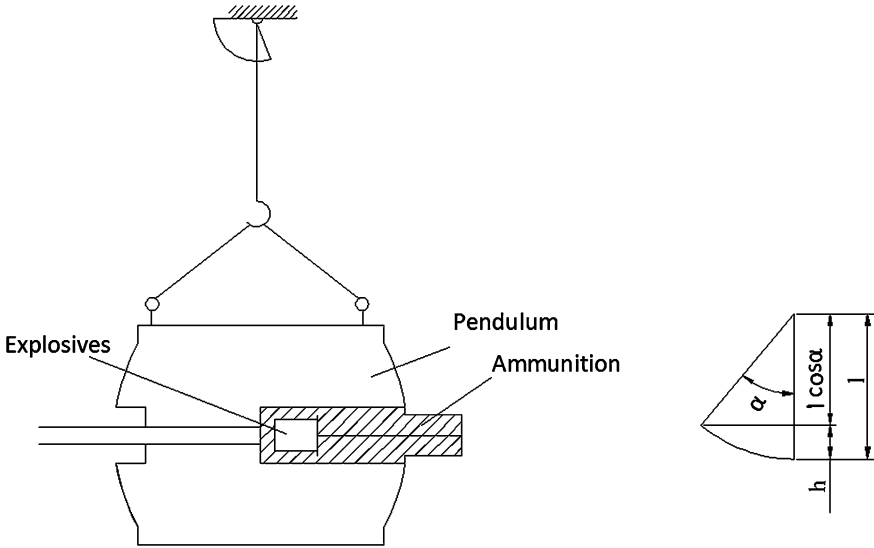
Fig. 2.18 The principle schematics of work capacity by a pendulum [18]

The remaining top space of lead cylindrical hollowness is filled by selected dry arenaceous sand to prevent the flying of explosion products. The increased volume is used to represent the work ability or capacity. Obviously, the more increased hollowness volume, the more powerful work ability/capacity. Because of the temperature effect for lead and the detonator also involves in the enlargement of hollowness, the measured data should be calibrated.

(2) Measurement of work capacity/power using a pendulum

A work capacity/power pendulum method is also named as ballistic mortar test. The measured work value is used to evaluate the relative work capacity. Its principles are in Fig. 2.18.

The explosion of liquid explosives produces high-temperature and high-pressure products. The expansion of these products works for the surrounding. Its work has two parts. One part is used to eject a bullet, and the second is to swing the pendulum to angle α with gravity center lifted up to h. The work ability/capacity of explosives is the sum of the two works.

$$A = A_1 + A_2 \tag{2.38}$$

Here, A is the work of the explosive; A_1 is the swing of the pendulum to angle α; A_2 is the mechanical work of ejecting the solid bullet.

A_1 is the swing of the pendulum to angle α. It equals the work of lifting the gravity center of the pendulum up to h.

$$A_1 = Mgh$$

$$h = l - l\cos\alpha = l\,(1 - \cos\alpha)$$

So,

$$A_1 = Wl(1 - \cos\alpha) \tag{2.39}$$

Here, W is the weight of the pendulum; α is the swing angle; l is the distance of gravity center to the rotary center.

A_2 is the work of the bullet ejection. It equals the kinetic energy of the bullet when it leaves the mortar.

$$A_2 = \frac{1}{2}mv^2 = \frac{1}{2g}qv^2 \tag{2.40}$$

Here, q is the weight of the bullet; m is the mass of the bullet; v is the initial velocity of the bullet.

The pendulum and the bullet have same momentum, but their directions are reverse.

$$Mu = mv$$

In the above equation, M is the mass of the pendulum; u is the velocity of the pendulum when it starts to swing.

While $v = \frac{M}{m}u = \frac{W}{q}u$, Eq. 2.40 is rewritten in Eq. 2.41.

$$A_2 = \frac{1}{2}\frac{q}{g}\left(\frac{W}{q}u\right)^2 = \frac{1}{2}\frac{W^2u^2}{gq} \tag{2.41}$$

If there is no energy loss in the swinging, the original kinetic energy of the pendulum equals its potential energy at the highest point.

$$\frac{1}{2}Mu^2 = Mgh$$

$$u^2 = 2gh = 2gl(1 - \cos\alpha)$$

$$A_2 = \frac{W^2g}{g}l(1 - \cos\alpha) \tag{2.42}$$

So,

$$A = A_1 + A_2 = Wl(1 - \cos\alpha) + \frac{W^2}{q}l(1 - \cos\alpha) = Wl(1 - \cos\alpha)\left(1 + \frac{W}{q}\right)$$

$$(2.43)$$

The pendulum weight W, the bullet weight q, and the distance of gravity center to the rotary center l are fixed. The structure constant of the swing is $c = Wl\left(1 + \frac{W}{q}\right)$.

$$A = c(1 - \cos\alpha) \qquad\qquad (2.44)$$

Because the structure constant c is known, the work capability/ability is directly calculated from the swing angle. In general, each country takes TNT as a standard. The ratio of the work ability/capacity of an explosive to that of TNT is its TNT equivalent. The TNT equivalent of one explosive equals A (an explosive)/A (TNT).

(3) The work capacity/ability evaluation of an explosive by blasting cone method

Throwing blasting cone is an intuitive and convincing method to evaluate the work capability/ability of explosives. The specific volume of blasted cone is related with the properties and mass of explosives, the properties of being blasted materials, and the relative positions of media. All above factors are in consideration in the work capability evaluation of explosives using throwing blasting cone. The standard explosive and being test explosive with same mass are conducted in the exact same conditions. The work ability/capability of an explosive is roughly evaluated by comparing the volume of blasted cone to that obtained by the standard explosive.

In Fig. 2.19, the blasting cone is measured by the ratio of its radius r to depth w. $n = \frac{r}{w}$, n is index of throwing blasting action. If $n = 1$, the cone is standard throwing cone; if $n > 1$, the cone is power throwing cone.

Fig. 2.19 Throwing blasting cone
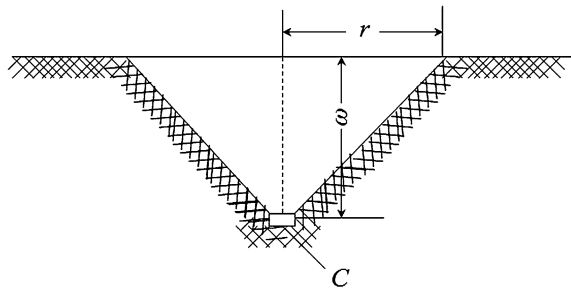
The volume of a standard cone is

$$V = 1/3_\pi\ _r W \propto W^3$$

The relationship of a standard cone volume and the explosive mass ω is in Eq. 2.45.

$$\omega = KV\alpha KW^3 \tag{2.45}$$

The index K represents the required explosives for throwing unit volume of media in the formation of standard blasting cone, or the uniconsumption of explosives. K is related with the properties of the media, and the properties and experiments with explosives.

The packing mass of explosives for power throwing blasting is calculated by below equation.

$$\omega = KW^3 f(n)$$

While,

$$f(n) = 0.4 + 0.6n^3$$

In the evaluation of the explosives by casting cone method, the places of explosion and the packing diameters are exactly the same. The variation of uni-consumption displays the different work capability/ability of explosives. In the same conditions, K_1 is for explosive 1 and K_2 is for explosive 2. The work ability of two explosives is inversely proportional to their values, $A_1/A_2 = K_2/K_1$. This comparison should be conducted when the two values of n are very close to each other. The repeatability of this method is poor. Packing with relatively large amount of explosives is better.

All above three methods have their own disadvantage for measuring the work ability of explosives. There are new experiment methods in study. For example, when the explosion is under water, the new experiments include the broken dome method of spray center initiate velocity or dome method of water cylinder, the measurement of water impact energy, and bubble energy. For explosive cylinders with certain diameter, it's also a method to measure the velocity of radial displacement of cylinder shell after the explosion from one end. The earthquake method measures the highest pressure of shock waves in the water (sand, or earth), which are certain distance away from the explosion center. The experiment data of earthquake method match the calculated one very well. Because the experiment earthquake energy is linearly proportional to the mass of packed explosives, it's suitable for measuring the work ability of explosives.

2.3.1.3 Evaluation of Work Ability of Explosives by Other Methods [21, 22]

(1) The special product of explosives

The special product of explosives is the product of the explosion heat Q_v and specific volume V_0. It has two important factors to determine the work ability of explosives, and has practical significances.

Los Alamos National Laboratory confirmed the functional relation of work capacity and mortar energy using the bullet–mortar. The function is in Eq. 2.46.

$$A_m = \frac{0.31}{850} Q_v V_0 \qquad (2.46)$$

Here, A_m is the mortar energy; Q_v is the explosion heat; V_0 is the amount of gas products.

Equation 2.46 clearly shows that the bullet–mortar energy is linearly proportional with the product of Q_v and V_0.

The explosion heat Q_v and specific volume V_0 are obtained by both experiments and calculations. In the process of obtaining Q_v and V_0, the exact explosion chemical reactions should be fixed first because there are theoretical and empirical formations. The special product of Q_v and V_0 to evaluate the work ability of explosives matches the experiment results. For negative oxygen balance explosives, there are several different explosion reactions for one explosive. So several different product values of Q_v and V_0 would be obtained. The measurement values of explosion heat of negative oxygen balance explosives are different following the change in measuring conditions. How to choose explosion reaction equation is very important in the evaluation of explosive work ability using $Q_v V_0$ product. The released heat from secondary reactions in explosion participates blasting work, and it is also related with the work ability of explosives. Many experiments show that the product of maximum explosion heat Q_{max} and its corresponding V_m is better to express the work capability of explosives. It is that taking $H_2O + CO_2$ type explosion products sets up chemical reaction equation to calculate the maximum explosion heat Q_{max} and the corresponding specific volume V_m.

(2) Power index of work capability/ability of explosives

Power index is based on the study of relationship between explosive molecular structures and the work power. Power index method refers that the work power of an explosive is the sum of all composition functions. It puts forward power index π. The calculation of work capability/ability of an explosive using power index method is in Eq. 2.47.

$$A \,\%(\text{TNT equivalent}) = (\pi + 140)\,\% \qquad (2.47)$$

Here, π is the power index; n is the number of atoms in an explosive molecule; f is the number of characteristic groups; x is the eigenvalue of one characteristic group.

2.3.2 Improving the Work Ability of Explosives

From the theoretical expression of explosion work and extensive research, increasing the explosion heat helps to improve the working ability/capacity of an explosive. The study and application results of liquid explosives indicate that the gas products of liquid explosives are much more than condensed explosives, and when the specific volume is fixed, the work capacity of liquid explosives increases following the explosion heat. When the explosion heat increases up 100 J/gm, the wok capacity raises up 5–7 %. The generalized empirical formula is below

$$A\%(\text{TNT equivalent}) = 51 + 0.05 Q_v$$

Addition of hydrazine, urea perchlorate, hydrazine nitrate, or hydrogen peroxide (H_2O_2) into the formula of liquid explosives significantly increases the explosion heat. Besides above chemicals, adding the powders of aluminum, magnesium, or beryllium also raises the explosion heat of explosives. Increasing the explosion heat improves the work capacity of explosives.

Increasing the specific volumes also helps to improve the work capacity of explosives. For example, addition of hydrogen peroxide (H_2O_2) in the nitro liquid explosives, and the effect of dual oxygen (peroxide) raise the specific volumes of explosives by big percentages. This makes the work capacity improve and reachable.

The work capacity of explosives is related with oxygen balance. Improving oxygen balance of explosive is one way to increase the work capacity. This is especially important for the preparation of mixed liquid explosives. The explosives with zero oxygen balance have complete explosion reactions with maximum exothermic heat. Their work capacity is relatively high. For monomer liquid explosives, if the oxygen balance is negative, the work capacity reaches the summit with oxygen balance at −10 to −30 %. For liquid explosives with nitrate ester, nitro compounds, and nitric acid, or urea perchlorate compositions, especially when the organic fuels can undergo secondary reactions, the aluminum flakes can react with the detonation products such as CO_2 and H_2O, in some case, react with N_2 to form AlN. The oxygen balance is smaller when there is flake aluminum in liquid explosives.

Figure 2.20 displays that the relative work capacity of other explosives to TNT. The work capacity of TNT is set 100 here.

Figure 2.20 shows that the explosives with zero oxygen balance have maximum work capacity, while negative or positive oxygen explosives have lower work capacity.
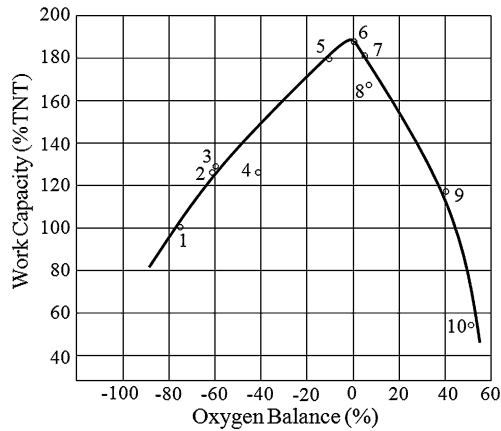
Fig. 2.20 The oxygen balance and work capacity of an liquid explosive. *1* TNT; *2* ethyl nitrate; *3* 2,2-dinitropropane; *4* special Kuehl; *5* taean; *6* diethyleneglycol dinitrate; *7* NG; *8* hexanitro-mannite; *9* Hexanitroethane; *10* tetranitromethane

2.3.3 Brisance of Liquid Explosives [18, 19, 21, 22]

The work capacity of a liquid explosive determines its damage ability. The brisance of a liquid explosive shows its local damaging effects. Local damaging effects are also the direct effects or brisant effects. It refers the violent effect of detonation products to the surrounding media or contact staff and causes the intense damage of direct contact objects. The brisance of explosives is widely applied in rock blasting, explosion working, explosive welding, throwing objects by explosion, steel cutting of explosion, bridge destruction, broken pieces of projectile explosion, antitank, etc.

The direct effect of explosion only occurs within the close enough range. Only within close enough range, detonation products have enough energy density and high enough pressure to damage the contact objectives. The detonation theory refers that the initial stage of product expansion from condensed explosives follows state equation.

$$P\rho - \gamma = \text{Constant} \ (\gamma \approx 3)$$

Here, P and ρ are the pressure and density of detonation products.

For explosives with general brisance, when the expansion of detonation products increases to 1.5 times of the original radius, the pressure drops to $\sim 2,000\,\text{kg/cm}^2$, which is less effect for metal, i.e., high-intensity objects. Although the energy density of liquid explosives is higher than explosives with general brisance, their shock waves attenuate faster. The direct effect of detonation products is distinctly displayed only when the explosives contact targets or the targets are within very close range to objectives.

(1) Brisance

The ability of direct effect or brisant effect from explosive explosion is the brisance of explosives, which is another parameter to measure the blast action of explosives.

The direct effect of explosive explosion is determined by the pressure of detonation products and action time, also the pressure and momentum to the target. Actions of pressure and momentum are different under various conditions. So the pressure or momentum of detonation products is used to describe brisance.

(1) The pressure (P_2) of products in the ending of detonation reactions

The breaking surrounding media in the detonation of explosives is a result of strong impact of high-temperature and high-pressure detonation products to the media. The higher pressure of detonation products, the breaking ability to the surrounding media is more powerful. So, the brisance of condensed explosives is expressed in Eq. 2.48.

$$P_2 = 1/4\rho_0 D^2 \tag{2.48}$$

The above equation shows that the faster detonation velocity and greater density, the higher brisance. Liquid explosives are noncompressible; the density cannot be changed. Their densities and detonation velocities are constants.

For mixed or monomer liquid explosives, $D \approx A\rho_0$ when the packing density is 1.0–1.7 g/cm^3. A is the detonation velocity when the density is 1.0 g/cm^3. Equation 2.28 is changed to $P_2 = 1/4A^2\rho_0^3$.

The above equation fully describes that the brisance is linearly proportional to the cubic of explosive density. Increasing the density of an explosive, raises its brisance dramatically.

(2) The specific impulse affecting the target

When the affecting time of detonation products to one target is longer than its natural period of oscillation, the damage ability for the targeted object is only determined by the pressure of detonation products. When the affecting time is shorter than its natural period of oscillation, the damage is determined not only by the pressure of detonation products, but also the effecting time. The brisance of an explosive is explained by the momentum, which is related to pressure and time.

The momentum aimed on one target is the product of affecting force and affecting time (Eq. 2.49).

$$I = \int SP\mathrm{d}\tau \tag{2.49}$$

Here, I is the momentum aimed on the target; P is the pressure on the target; S is the area; τ is the affecting time.

The momentum within unit area is the specific impulse. If the affecting area of the target S does not vary in time, Eq. 2.49 is changed to 2.50.

$$i = \frac{I}{S} = \int P \mathrm{d}\tau \qquad (2.50)$$

Once pressure is known, specific pulse is calculated.

Figure 2.21 assumes that the detonation is in one dimension; the explosive is closely contacted with the target; and the target is an absolute rigid body.

Figure 2.21 shows the pressure affecting on the target According to one-dimensional isentropic gas dynamics, the function of pressure affecting on the target from the detonation products is Eq. 2.51.

$$P = \frac{64}{27} P_2 \left(\frac{h}{\mathrm{d}\tau} \right)^3 \qquad (2.51)$$

Here, h is the length of the packed explosive.

When the detonation ends, $\tau = h/D$ and the pressure is in Eq. 2.52.

$$P = 64/27 P_2 \qquad (2.52)$$

The pressure on the target is 64/27 times of detonation pressure. The pressure on the target comes from the pressure of products, and the pressure, which is produced by moving/transportation of products with velocity u_2. The target blocks the moving or transportation, and the shock waves are reflected, which gives the target large mobile pressure.

When $\tau = 4h/D, P = 1/27 P_2$, it shows that when the time is four times of explosive detonation, the pressure on the target is only 1/27 of detonation ending. The pressure decay of detonation is very fast, and the decay curve is in Fig. 2.21.

If the pressure expression (Eq. 2.51) is substituted into the integration (Eq. 2.49), the below equation is obtained.
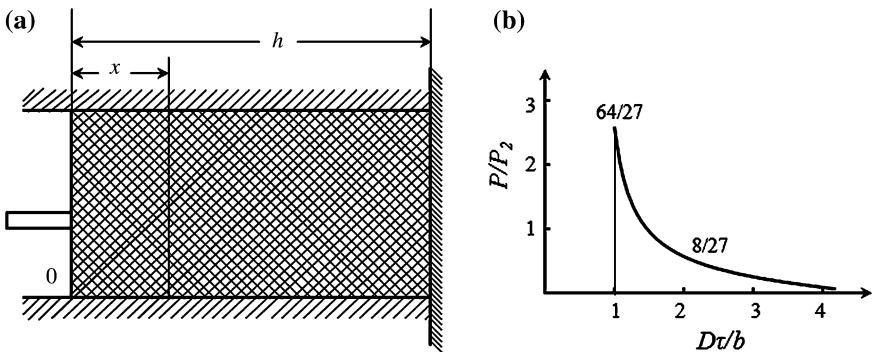
Fig. 2.21 The pressure affecting on the target. **a** Explosive properties. **b** Impulse characteristics

$$I = \int_{\frac{h}{D}}^{\infty} SPd\tau = \int_{\frac{h}{D}}^{\infty} S\frac{64}{27}P_2\left(\frac{h}{D\tau}\right)^3 d\tau = \frac{64}{27}\left(\frac{h}{D}\right)^3 SP_2 \int_{\frac{h}{D}}^{\infty} \frac{d\tau}{\tau^3} = \frac{32}{27}S\frac{h}{D}P_2$$

Substitute $P_2 = 1/4\rho_0 D^2$ into above equation,

$$I = \frac{32}{27}S\frac{h}{D}\frac{1}{4}\rho_0 D^2 = \frac{8}{27}Sh\rho_0 D = \frac{8}{27}mD \tag{2.53}$$

Here, m is the total mass of the explosive, $m = Sh\rho_0$.
The specific impulse on the target is

$$i = 8/27 \times mD/S = 8/27h\rho_0 D \tag{2.54}$$

The above Eq. (2.54) shows that the direct specific impulse from detonation products is linearly proportional to the explosive mass and detonation velocity (Lateral scattering is not considered). As we all know, the detonation products are isotropic scattered, and not all products affect the target. So m is not the total mass of the explosive, but the partial explosive, which directly affects the target (m is also named effect mass)

(2) Effective mass of the packed explosive

(1) Mass of packed/charged explosive for scattering in a given direction

The effective mass (ma) of packed explosive represents the partial explosive, which is equivalent of the explosive in a given direction. There are two different conditions.

① The effective mass (ma) of packed explosives in simultaneous detonation

To effectively solve the detonation problems, the detonation is assumed to be simultaneous. The detonation reactions react at the same time, all explosives become detonation products suddenly, the detonation products occupy the original container of explosives, and all parameters of detonation products are the same everywhere. The detonation process is extremely short. Such as the detonation of explosives inside a container or projectile body, the detonation velocity is much faster than the deformation of container, so detonation is considered to be simultaneous. Calculation of the effective mass (ma) of packed explosives simplifies the detonation process, without the places of detonation and directions of transportation in consideration.

After the simultaneous detonation of cylinder packed explosives, the expansion waves diffuse into the inside of the detonation products, and the detonation products scatter in all directions. The scattering of detonation products in all directions is schematized in Fig. 2.22.

In Fig. 2.22, h is the height of packed explosives; r is the radius; ae, be, ef, cf, and df are wave fronts of expansion waves to all directions. The cone cdf is the effect packing of cylinder end. The effect packed explosive mass of the cone with height r, base area πr^2, and volume $1/3\pi r^3$ is given Eq. 2.55.

Fig. 2.22 The scattering of detonation products after simultaneous detonation
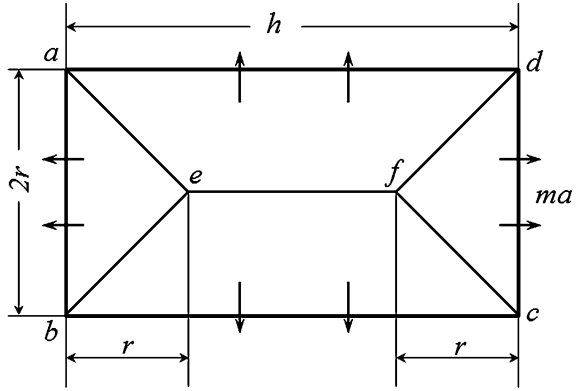
$$ma = 1/3\pi r^3 \rho_0 \qquad (2.55)$$

Here, ρ_0 is the mass density of explosives.

When $h \gg 2r$, Eq. 2.55 is exactly correct. When $h = 2r, e$ and f are the same point, now the side scattering is the least.

② The effective mass (ma) of packed explosives when detonation products scatter to two ends

If the two sides of packed explosives are strong rigid shells, the detonation products only fly toward two ends rather than sides (Fig. 2.23).

When the detonation starts from the left end, the detonation products flying to the detonation end is Eq. 2.56.

$$ma = 5/9m \qquad (2.56)$$

The detonation products flying to the right end is Eq. 2.57.

$$ma = 4/9m \qquad (2.57)$$

ma is the effect mass of explosives.
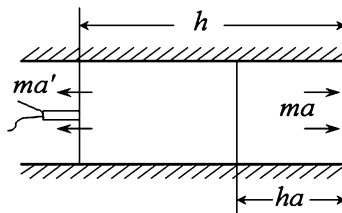
Fig. 2.23 End flying/scattering of detonation products [18]
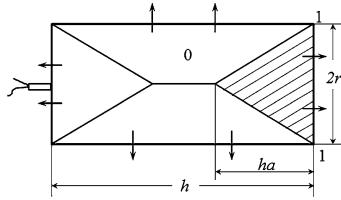
Fig. 2.24 The effective mass of packed explosives with side scattering/flying [18]

If the packed height of explosives is h, the effect height flying to the right end $ha = 4h/9$.

(2) The effective mass of packed explosives with side scattering/flying

The most common conditions are that the detonation starts from one end, the products fly/scatter in any direction (Fig. 2.24).

In Fig. 2.24, cylinder 101 is the effective mass of packed explosives with flying to the bottom. Its height is ha and radius is r.

Determination of ha is based on the assumption that the time of expansion waves transportation to the packed center equals that of detonation waves passing ha. So $\tau = r/c = ha/D$.

The velocity of side expansion waves is approximate $c \approx D/2$. And $r/(D/2) = ha/D$, so $ha = 2r$. The height of effect packed explosives equals its diameter. The volume of effective packed explosives is $1/3(2r\pi r^2) = 2/3\pi r^3$.

The mass of effective packed explosives is Eq. 2.58.

$$Ma = 2/3\pi r^3 \rho_0 \tag{2.58}$$

Substitute $S = \pi r^2$ and 2.58 into Eq. 2.54, then

$$i = \frac{8}{27}\frac{mD}{S} = \frac{8}{27}\frac{2}{3}\frac{\pi r^3}{\pi r^2}\rho_0 D = \frac{16}{81}r\rho_0 D \tag{2.59}$$

When the packing of explosives is long enough and detonation starts from one end, the specific impulse of the bottom is $i = \frac{16}{81}r\rho_0 D$.

(3) The effective height of packed explosives

When the height of packed explosives is not long enough, the effective packed explosives flying to the base are not guaranteed to be cone. When the effect height $h = 3r$, according to the theory of two ends flying/scattering, the packed height to the bottom is $4/9h = 4/9(3r) = 4/3r$. This height is shorter than effect height $2r$, which is the theoretical value (Fig. 2.25).

Figure 2.25 describes that the measurement of brisance without enough packing height does not need to take the packed mass into consideration. But the effective packed height should meet $4/9h = 2r$.
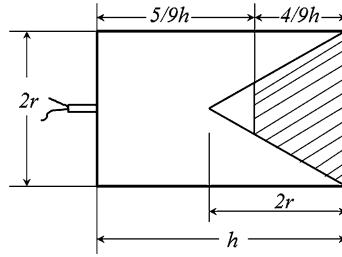
Fig. 2.25 The effective packed explosives when the height is not enough [18]

So,

$$h = 9/2r = 2.25d \tag{2.60}$$

The effective height is 2.25 times of diameter.

When the packed height is longer than the effective height, the effective packing mass for base does not increase. The effective mass is the volume of a cone with base diameter. If the packed height is shorter than the effective height, the effective packed explosive mass is a truncated cone. The relative packed masses ma under these two conditions are Eqs. 2.61 and 2.62, separately.

$$h \geq 4.5r, \ ma = \frac{2}{3}\pi r^3 \rho_0 \tag{2.61}$$

$$h < 4.5r, \ ma = \left(\frac{4}{9}h - \frac{8}{81}\frac{h^2}{r} + \frac{16}{2187}\frac{h^3}{r^2}\right)\rho_0 \tag{2.62}$$

(3) Measurement of brisance

The measuring methods for the brisance of liquid explosives are similar to that of condensed explosives. The measuring difficulty is larger because of the noncompressibility of liquids. The writer/author measured the brisance of liquid explosives using the setup of Fig. 2.26, and summarized a set of methods for evaluating the brisance of liquid explosives.

In Fig. 2.26, the plastic shell is hard polyethylene with 1.0 mm thick. The thickness of the bottom, which is in contact with a lead cylinder, is 0.015 mm. The dissipative energy of breaking the plastic shell is negligible.

Fig. 2.26 Setup for brisance measurement of liquid explosives

2.4 Explosion Impact of Liquid Explosives

2.4.1 Explosion Impact of Liquid Explosives in Free Space

2.4.1.1 Detonation of Liquid Explosives in Free Space

When the explosion of liquid explosives occurs in free space, the detonation reactions release large amount of energy in the form of pressure, and the gas products expand rapidly to the surrounding. This results in the pressure of gas products and temperature increase of local areas, which impacts the surrounding media by high temperature and high pressure in the explosion direction, presses the air and forms air shock waves. Following the further expansion of detonation products, the air shock waves increase in their layer thickness. The pressure distributions of detonation products and air shock waves are shown in Fig. 2.27.

Fig. 2.27 Pressure distributions of detonation products at initial expansion stage
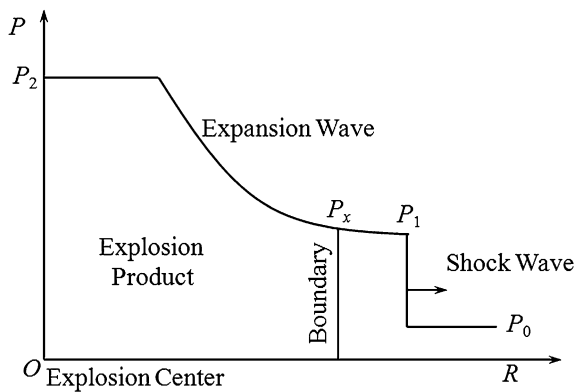
Here, P_0 is the air pressure without disturbance; P_1 is the pressure of air shock wave fronts; P_x is the interface pressure of detonation products and air.

The pressure of detonation products drops rapidly in the expansion process. When $P \geq P_k \approx 2{,}000 \, \text{kg/cm}^2$, the detonation products of general explosives in their initial expansion follow the rule of $P = A\rho^3$. The pressure changes following the cubic density. The density of detonation products reduces rapidly following the radius increase. If the packing geometry of explosives is spherical, $\rho \propto r^{-3}$, hence,

$$P \propto r^{-9}$$

When the radius of detonation products increases up 1 time, the pressure drops to $\frac{1}{2^9} \approx \frac{1}{500}$.

The limiting volume of detonation products is the volume of products when their pressure drops to the pressure of surrounding media. The volume of detonation products may be roughly estimated using the below method. When the pressure of detonation products $P < P_k$, the expansion process follows the rule of $P = A\rho^k$ (here, $k = 1.2\text{--}1.4$).

The volume of detonation products is V_L at pressure P_0.

$$P_0 V_L^k = P_k V_k^k = C \ (C \text{ is a constant})$$

$$\frac{V_L}{V_0} = \frac{V_k}{V_0} \frac{V_L}{V_k} = \left(\frac{\overline{P_2}}{P_k}\right)^{1/3} \left(\frac{P_k}{P_0}\right)^{1/3} \tag{2.63}$$

Here, P_2 is the initial average pressure of detonation production.

If $P_2 = 100{,}000 \, \text{kg/cm}^2, P_0 = 1 \, \text{kg/cm}^2, P_k = 2{,}000 \, \text{kg/cm}^2$, when $k = 7/5 \frac{V_L}{V_0} = 50^{1/3} \times 2000^{5/7} = 800$;

when $k = 5/4$, $\frac{V_L}{V_0} = 50^{1/3} \times 2000^{4/5} = 1600$.

For most of explosives, the volumes of detonation products which expand to pressure P_0 is about 800–1,600 times of their original volumes. If the limit volume of detonation products is known, the limit impact distance can be calculated. The geometry of explosives is assumed to be a sphere, so

$$\frac{V_L}{V_0} = \left(\frac{r_L}{r_0}\right)^3 \quad \text{or} \quad r_L = r_0 \left(\frac{V_L}{V_0}\right)^{1/3} \tag{2.64}$$

Here, V_L is the limit volume of detonation products; V_0 is the volume of explosive sphere; r_L is the limit radius of detonation products; r_0 is the radius of explosive sphere.

Most of experiments show that the volume of detonation products from liquid explosives is about 20–60 % larger than that of condensed explosives. Under standard condition, the expansion ratio is 920–1,600. For a spherical 1 kg liquid explosive with density 1.58 g/cm^3, the r_L is calculated below.

When $V_L = 920$ L/kg, $r_L = \sqrt{\frac{920}{1.58}} \times r_0 = 3.81 r_0$

When $V_L = 1,000$ L/kg, $r_L = 11.7 r_0$

For sphere explosives, the direct effect/impact range of detonation products is about $10-12 r_0$ For cylinder explosives, the direct effect/impact range is about 30 times of the radius. The detonation products decay very fast in unlimited space, the effect range for the target is very close.

Because of the inertia, the expansion of detonation products does not stop at pressure P_0 until it reaches the maximum value of expansion (about $135-145 V_L$). Now the average pressure of detonation products is lower than undisturbed air pressure P_0. The surrounding air in return compresses the detonation products and increases their pressure. By the same reason of inertia, the maximum pressure of products is a little higher than P_0. The second and multiple expansion-being compression pulsations occur. The pulsation and whirlpool in the intersurfaces blur the intersurface, and finally the detonation products and air mix together.

When the detonation products stop expanding and contract back, the air shock waves separate with the detonation products and propagate independently. For the detonation of liquid explosives, the separation occurs at about the place, which is $10-15 r_0$. Now the pressure of air shock wave fronts is $10-20$ kg/cm^2 and the propagation velocity is $1,000-1,400$ m/s. The mass velocity after fronts is $800-1,400$ m/s. Figure 2.28 gives the pressure distribution of shock waves.

In Fig. 2.28, the center is the position of liquid explosives. The middle is the detonation products with median pressure. The most outside is the air shock wave front, whose pressure is the highest. The pressure of the compression area after the wave front decays faster. It is sparse area when the pressure is less than 1 atm.

The geometries of packed/charged explosives also impact the air shock waves differently. If the measurements of packed/charged explosives are very similar in all directions, the packed/charged geometry impact direction differently in the area, which is contactable with or very close with explosives. For a little far away places,

Fig. 2.28 Pressure distributions of pulse waves in the detonation of liquid explosives
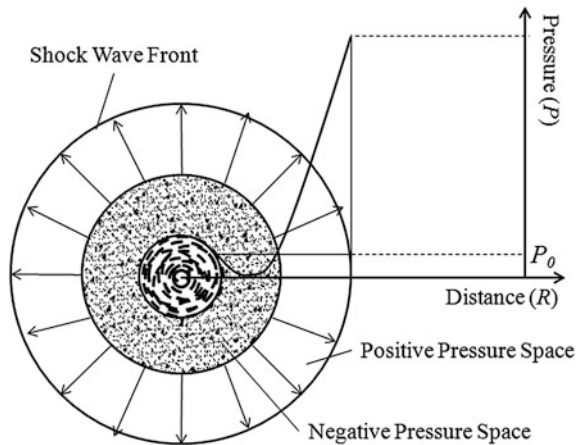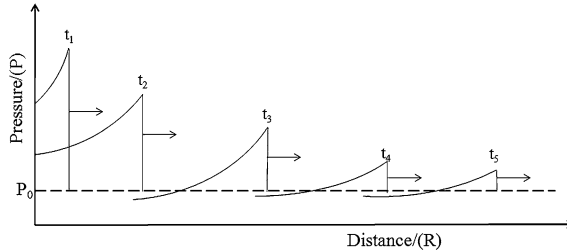
Fig. 2.29 Transportation of pulse waves in the explosion of liquid explosives

the average impact is equivalent to that of spherical charge/packing explosives. If the charge or packing is obviously larger in one dimension than other dimensions, the impact within two times of two small dimensions is equivalent to the cylindrical charge/pack. When it is far away, such several times of the longest charge/packing dimension, the impact is equivalent to that of spherical charge/packing. This is because the air shock waves are gradually homogenized in all directions.

The high-temperature and high-pressure detonation products of liquid explosives expand rapidly. This expansion is regarded as the piston motion in a pipe, which compresses the surrounding media air and increases its pressure. After the air detonation waves separate from the detonation products, the detonation waves transport in the air following what in Fig. 2.29.

In Fig. 2.29, $t_1, t_2, \ldots$ are the reaching time of shock waves. Figure 2.29 indicates that the positive pressure area is broadening following the transportation of air shock waves. Because the shock wave front transports at supersonic velocity D, while the shock wave end does at sound velocity c_0, and $D > c_0$, the positive area broadens, following the transportation of air shock waves. In Fig. 2.29, the pressure of wave front and transportation velocity D drop faster. There are several reasons for the rapid dropping of pressure and transportation velocity. First, the shock waves expand spheroidally, their surface area of shock wave fronts is continuously growing, but the energy passing the unit area shock wave fronts decrease. Second, the average energy of the air shock wave fronts declines. Beside that, when the shock wave passed the air, the temperature of the air increases, so part of shock wave energy is used to heat the air. Based on above reasons, in the transportation process of air shock waves, the pressure of wave fronts declines faster, and decays into sound wave finally.

2.4.1.2 Parameter Calculation of Shock Waves Produced by Detonation of Liquid Explosives in Free Space [23, 24]

The detonation products just impact within short ranges, air shock waves create the main damage of explosion of liquid explosive in free space. The damage and killing effect of air shock waves are more violent in the closer ranger with smaller impact

area; the effect is weak if far away from the explosion center, but the effective area is larger. For an explosion in the air, if the super pressure of shock waves is 0.2 kg/cm^2 with total area 100, the area with super pressure >20 kg/cm^2 is only 1.3 %; while the area with super pressure 2–20 kg/cm^2 is about 6.7 %. For more than 92 % area, its super pressure is 0.2–2 kg/cm^2. Nonetheless, we cannot underestimate the damage ability of shock waves. When shock waves impact the building in large area, the super pressure 0.2–2 kg/cm^2 of wave fronts has enough killing capacity for human and damage for glasses of buildings and buildings with wood–brick structure. In general, the shock waves from liquid explosives are stronger than that of condensed explosives, so liquid explosives are more damageable. The parameter change law study of shock waves in the explosion is a must to study the damage capacity of explosives.

(1) Explosion similarity law of air shock waves

The shock wave impacts from same explosives with different masses follow the geometry similarity law in the space before the shock waves meet the boundaries or obstacles. For an explosive with packed radius r1, the super pressure of shock wave front at R1 is ΔP; and if the second explosive with r2, the super pressure of shock wave front at R2 is ΔP. These two explosives are similar in geometries of packing. The geometric similarity rate is of practical importance for the design of engineering. The experiments can be studied with small amount of explosives and measure all parameters in free field. The conditions of explosion with large amount explosives can be calculated/predicted based on the experiments. It helps to reduce the experiment numbers and lower the cost of experiments.

In all the shock wave parameters, if the super pressure of shock wave front is known, all other parameters can be calculated according to the relationship of shock waves. Once the dimension relationship is fixed, the relationship of shock wave parameters and explosive packing is reachable.

For the explosion of liquid explosives in air, the fundamental physical quantities, which influenced the pressure of shock wave fronts, are detonation heat Q_v, packed density ρ_0 of an explosive, packed radius r, distance to explosive's center R, air pressure P_a, and its origin density ρ_a. After ignoring the viscosity and thermal conduction of air, the super pressure of air shock wave is a function of all parameters (Eq. 2.65).

$$\Delta P = f(Q_v,\ \rho_0,\ r,\ R,\ P_a,\ \rho_a) \tag{2.65}$$

If the distance to an explosive's center R is taken as unit to measure the distance, air pressure (P_a = 1.0332 kg/cm^2) to measure the pressure, and air density (ρ_a = 1.25 × 10^{-3} g/cm^3) to measure the density, the distance to an explosive's center, air origin density, and origin pressure are all 1.

$$\overline{R} = 1\overline{p_a} = 1\overline{\rho_a} = 1 \tag{2.66}$$

The super pressure of air shock waves, packed radius, packed density, and detonation heat of explosives are displayed below, separately.

$$\Delta\overline{p} = \frac{\Delta P}{p_a}$$

$$\overline{\rho}_0 = \frac{\rho_0}{\rho_a}$$

$$\overline{r} = \frac{r}{R}$$

$$\overline{Q}_v = \frac{Q_v}{p_a/\rho_a} \tag{2.67}$$

All these are ratio without any unit. Now it's time to infer and prove the detonation heat.

$$\overline{Q}_v = \frac{Q_v}{R^\alpha p_\alpha^\beta \rho_\alpha^\gamma} \tag{2.68}$$

The denominator in Eq. 2.68 is the product of unit physical quantities R, P_a, and ρ_a after potential operations to get the values of α, β, and γ. If the dimension of length is L, mass is M, time is T, the dimensions of Q_v, R, P_a, and ρ_a are as in below equations separately.

$$[Q_v] = L^2 T^{-2};$$

$$[R] = L;$$

$$[p_a] = ML^{-1}T^{-2};$$

$$[\rho_a] = ML^{-3} \tag{2.69}$$

Equation 2.68 becomes 2.70.

$$L^2 T^{-2} = L^\alpha (ML^{-1}T^{-2})^\beta (ML^{-3})^\gamma = L^{\alpha-\beta-3\gamma} M^{\beta+\gamma} T^{-2\beta} \tag{2.70}$$

Compare the powers of L, M, and T, so

$$L : 2 = \alpha - \beta - 3\gamma$$

$$M : 0 = \beta + \gamma$$

$$T : -2 = -2\beta \tag{2.71}$$

The solution for above simultaneous equations is Eq. 2.72.

$$\alpha = 0;$$

$$\beta = 1;$$

$$\gamma = -1 \tag{2.72}$$

The relations of all physical quantities are certain, which do not change after their units vary. So the function of $\Delta \bar{P}$, $\bar{Q}_V$, $\bar{\rho}_0$, $\bar{r}$, $\bar{R}$, $\bar{p}_a$, and $\bar{\rho}_a$ is similar to the function of ΔP, Q_V, ρ_0, r, R, p_a, and ρ_a.

$$\Delta P = f(\bar{Q}_V, \bar{\rho}_0, \bar{r}, \bar{R}, \bar{p}_a, \bar{\rho}_a) \tag{2.73}$$

Substitute 2.66 and 2.67 into 2.73,

$$\frac{\Delta P}{p_a} = f(\frac{\bar{Q}_v}{p_a/\rho_a}, \frac{\rho_0}{\rho_a}, \frac{r}{R}, 1, 1, 1) \tag{2.74}$$

In Eq. 2.74, the three constants 1 do not have any special meaning, so the dimensionless Eq. 2.75 is obtained.

$$\frac{\Delta P}{p_a} = f\left(\frac{\bar{Q}_v}{p_a/\rho_a}, \frac{\rho_0}{\rho_a}, \frac{r}{R}\right) \tag{2.75}$$

The function f is still not clear yet. Its determination needs the support of more experiments. But Eq. 2.75 is much simpler than 2.65. By using dimensionless parameters, the three augments are reduced, and it decreases the experiment work. If the experiments are conducted under the same conditions using same explosive with same packing density, $\frac{\bar{Q}_v}{p_a/\rho_a}$ and $\frac{\rho_0}{\rho_a}$ are constants. Equation 2.75 is simplified as Eq. 2.76.

$$\frac{\Delta P}{p_a} = f\left(\frac{r}{R}\right) \tag{2.76}$$

After multiple experiment, only if

$$\frac{r_1}{R_1} = \frac{r_2}{R_2} = \frac{r_3}{R_3} = \cdots = \text{Constants} \tag{2.77}$$

All measured super pressure are the same, this is the explosion geometric similarity law of air shock waves.

The above geometric similarity law is not applied for the explosive with different packing densities. If the super pressure of shock waves from explosive W_1 is ΔP at R_1, and the super pressure of shock waves from explosive W_2 is ΔP at R_2, Eq. 2.78 is established.

$$\frac{R_1}{R_2} = \sqrt[3]{\frac{W_1}{W_2}} \tag{2.78}$$

ΔP is a function of $\frac{\sqrt[3]{W}}{R}$, so

$$\Delta P = f\left(\frac{\sqrt[3]{W}}{R}\right) \tag{2.79}$$

The above geometric similarity law is applied for the same explosives with different packing density, but it is not applied for explosives with different detonation heat. For explosives with different detonation heat, even with same packing mass, the explosion effects are different at the same distance. Because of their explosion heat is similar, $\frac{\sqrt[3]{E}}{R}$ is used as a parameter. Here, E is the energy of explosion, which is transferred into the shock waves.

$$\Delta P = f\left(\frac{\sqrt[3]{E}}{R}\right) \tag{2.80}$$

Energy similarity law is applied not only in different kinds of explosives, but also in different kinds of explosions. In general, the function $f\left(\frac{\sqrt[3]{E}}{R}\right)$ is extended to a polynomial 2.81.

$$\Delta P = A\frac{\sqrt[3]{E}}{R} + B\left(\frac{\sqrt[3]{E}}{R}\right)^2 + C\left(\frac{\sqrt[3]{E}}{R}\right)^3 \tag{2.81}$$

The constants A, B, and C are obtained from experiments. $E = WQ_V$, for TNT, $Q_V = 4180$ J/g, substitute this into 2.81, Eq. 2.82 as below.

$$\Delta P = A_1\frac{\sqrt[3]{E}}{R} + B_1\left(\frac{\sqrt[3]{E}}{R}\right)^2 + C_1\left(\frac{\sqrt[3]{E}}{R}\right)^3 \tag{2.82}$$

Parameter $\frac{\sqrt[3]{E}}{R}$ is also one of the parameters of energy similarity. For all explosives, all their mass can be changed into TNT equivalents.

$$W_E = W\frac{Q_V}{Q_{V\text{INT}}} \tag{2.83}$$

Here, W is the mass of an explosive; Q_V is the detonation heat of an explosive; Q_{VTNT} is the detonation heat of TNT (4,180 J/g); W_E is the TNT equivalent of an explosive.

(2) Super pressure calculation of shock waves from explosions of liquid explosives

When spherically packed TNT explodes in free space, the super pressure calculation of shock waves follows the below equations.

$$\Delta P = 0.84 \frac{\sqrt[3]{E}}{R} + 2.7 \left(\frac{\sqrt[3]{E}}{R} \right)^2 + 7 \left(\frac{\sqrt[3]{E}}{R} \right)^3$$

or

$$\Delta P = \frac{0.84}{\bar{R}} + \frac{2.7}{\bar{R}^2} + \frac{7}{\bar{R}^3} \tag{2.84}$$

$$1 \leq \bar{R} \leq 10{-}15$$

$\bar{R} = \frac{R}{\sqrt[3]{W}}$ is the contrast distance.

If the explosive is on the ground, the energy transferred into the ground is negligible. All energy is approximately transferred into the hemispherical space. For an open space, the reflection waves are also negligible. For the explosion on the ground, $W_E = 2W$. Substitute this into 2.84, Eq. 2.85 is obtained.

$$\Delta P_E = \frac{1.06}{\bar{R}} + \frac{4.3}{\bar{R}^2} + \frac{14}{\bar{R}^3} \tag{2.85}$$

Here, ΔP_E is the super pressure of shock waves when explosion occurs on the ground.

If the unit of R is meter, and W is kg, all calculated results are basic data for theoretical shock waves. The relationship of shock wave super pressure and distance is in Table 2.2. For all explosives, their explosion heats are TNT equivalents. The application range of Eq. 2.85 is between 1 and 10–15. When $\bar{R} < 1$, the errors are larger.

The packed geometry of explosives impacts the super pressure of shock waves in some degree. Probably because in explosion, the transportation forms of detonation products are impacted by the geometries of explosives. The impaction of packed geometries is in Table 2.3.

(3) Calculation of action time and specific impulse in the positive pressure area

The action time t_+ in the positive pressure area of liquid explosive explosion is another parameter of air shock waves, which paly an important role for the damage of targets. Like the determination of super pressure ΔP, t_+ is an empirical formula using similar principle and experiments.

Table 2.2 ΔP and $\bar{R}$ in the air pulse waves [18]

$\bar{R} = \frac{R}{\sqrt[3]{W}}$	ΔP_E (kg/cm^2)	ΔP_A (kg/cm^2)	$\bar{R} = \frac{R}{\sqrt[3]{W}}$	ΔP_E (kg/cm^2)	ΔP_A (kg/cm^2)
15	0.094	0.07	3.0	1.35	0.85
12	0.126	–	2.75	1.63	–
10	0.163	0.118	2.50	2.00	1.21
9	0.19	–	2.0	3.35	1.99
8	0.227	0.161	1.8	4.21	2.50
7	0.281	–	1.6	5.75	3.29
6	0.36	0.247	1.4	7.94	4.52
5	0.469	0.332	1.3	9.73	5.43
4.5	0.602	–	1.2	12.00	6.60
4.0	0.743	0.488	1.10	15.00	8.20
3.5	0.981	–	1.0	19.4	10.54

Table 2.3 Figurations and ΔP [18]

Explosive	Configuration geometry	Packed mass (kg)	ΔP (kg/cm^2)	
			$\bar{R} = 1$	$\bar{R} = 10$
TNT	Rectangular	0.23	29.9	0.094
TNT	Cylinder	1.81	18.5	0.114
TNT/PETN (50/50)	Cylinder	3.6	20.7	0.112
TNT/PETN (50/50)	Sphere	1.71	11.9	0.124

Note T/P = TNT/PETN from the above table, it is clear that the places near explosives are influenced by the geometries of explosives; the far away place is less influenced by it

The calculation uses TNT sphere as a reference, and the extension calculating of explosion in the air. When TNT explodes,

$$t_+ = 1.5 \times 10^{-3} \sqrt{R} \sqrt[6]{W} \qquad (2.86)$$

If the explosion is on the ground, $W_E = 2\,W$.

$$t_+ = 1.7 \times 10^{-3} \sqrt{R} \sqrt[6]{W} \qquad (2.87)$$

Here, the unit of action time t_+ is millisecond (ms); the mass W is gram (g); the distance R is meter (m).

The conclusions from the several hundred measurements suggest that the reaction time of positive pressure shock waves from condensed explosives is generally 2–10 ms; from the liquid explosives is 15–49 ms, for certain special liquid explosives, the action time reaches 80 ms. In certain degree, the detonation velocity/rate is lower than condensed explosives, but the impact capacity of liquid explosives are higher than condensed ones.

The specific impulse (i) is directly determined by the super pressure ΔP of air shock wave fronts and the reaction time (t). Because the calculation is much complex, it is obtained using empirical formulations of experiments.

$$i = A\frac{W^{2/3}}{R} = A\frac{W^{1/3}}{\bar{R}} \qquad (R > 12r) \tag{2.88}$$

$$i = B\frac{W^{2/3}}{R^2} = B\frac{W^{1/3}}{R^2} \qquad (R \le 12r) \tag{2.89}$$

Here, r is the radius of an explosive; the unit of specific impulse i is kgs/m^2. For the explosion of TNT in unlimited space, $A = 40$, and $B = 25$. For all other explosives, A and B need calibration.

$$i = A\frac{W^{2/3}}{R}\sqrt{\frac{Q_{vi}}{Q_{v\text{TNT}}}} \tag{2.90}$$

Here, W is the mass of an explosive; R is the distance to explosion center; Q_{Vi} is the detonation heat of explosive i; and $Q_{v\text{TNT}}$ is the detonation heat of TNT.

2.4.1.3   The Damage of Air Shock Wave for the Target in the Explosion of Liquid Explosives in Free Space

The shock waves, which are produced from explosion of liquid explosives in free space, damage and fracture the surrounding targets (for example, building, equipment, and human) in certain degrees. But the damage and fracture of various targets from the shock waves of explosives are a very complex process. It is related with not only the impact of shock waves, but also the shape, rigidity, flexibility of the targets. The loads and damage of buildings from shock waves are determined by below factors.

(1) the super pressure ΔP of shock wave fronts
(2) the action time of shock wave and the pressure change
(3) the positions of buildings (the relative relation of buildings and shock wave fronts, e.g., the fronts of shock wave are parallel or perpendicular with the buildings)
(4) the sizes and figurations of buildings
(5) the vibration periods of the buildings

The work capacity of explosives determines damage of explosion. They are different following the change of explosive, packed mass, the surrounding media. And the damage is also different if the distance to the explosion center varies.

The work capacity and the related damage increase following the potential capacity and specific volume become larger. When the explosive properties and packed mass are given, the effect action distance is related with the geometry and detonation methods.

According to isentropic law of detonation production expansion, the theoretical work capacity of an explosive is below.

$$dA = -dE = -C_v dT$$

Because

$$C_v = \frac{nR}{k-1}$$

So

$$A = \frac{nRT_D}{k-1}\left(1 - \frac{T_1}{T_D}\right) \tag{2.91}$$

If A is the work of per kilo gram explosive, and $Pv^k = c$ (constant), $Tv^{k-1} =$ constant and $T^k p^{1-k} =$ constant, the final equation of work is eq. 2.92a

$$A = \frac{F}{k-1}\left(1 - \frac{T_1}{T_D}\right) = \frac{F}{k-1}\left[1 - \left(\frac{v_D}{v_1}\right)^{k-1}\right] = \frac{F}{k-1}\left[1 - \left(\frac{P_1}{P_D}\right)^{\frac{k-1}{k}}\right] \tag{2.92a}$$

Here, $T_D \cdot v_D$ and P_D are the temperature, specific volume and pressure independently of explosion. T_1, v_1, and P_1 are the temperature, specific volume and pressure independently in expansion process.

$F = nRT_D$ is the power of an explosive. n is the mole number of gas products from 1 kg explosive.

$R = P_0 V_0/273$, P_0 is the air pressure, V_0 is the standard volume of 1 mol gas. If the unit of P_0 is atm, V_0 is liter, the unit of F is (L atm)/kg.

When the expansion of explosion products is unlimited, $P_1 = P_0$, $T_1 = T_0$, $V_1 = V_0$.

$$A = A_{max} = IQ_w \tag{2.92b}$$

Here, I is the heat work equivalent; $A_{max} = IQ_w$ is the potential energy of an explosive.

Equation 2.92b assumes that all explosion products are gases. If the explosion products are not only gases, they have gases, solids, and liquids, $A_{max} < IQ_w$. In the

calculation of theoretical $A_{\max}$, the heat transfer of gas–solid and gas–liquid should be taken into consideration.

For the explosion in free space, the separation of shock waves from detonation fronts sometimes occurs before the heat transfer of gas-condensed states. The energy transferred to shock waves is only part of the explosion heat/energy. When explosion occurs in the air, not all chemical reactions are complete because of the scattering of reactants, and the explosion heat/energy is not used completely and efficiently in work. Increasing the diameter of the packed explosive benefits the above reactions. When the radius r_0 of the packed explosive and the particles radius r are fixed, 70 % of chemical energy is transferred into shock waves.

Though the detonation pressure is not as high as brisant explosives, the reaction time of detonation is longer. Followed by the explosion products impacting the surrounding media and the formation of shock waves, the action time of positive pressure is much longer than the condensed explosives. This is the key feature of explosion from liquid explosives. Figure 2.30 is the explosion of 3,000 g liquid explosive.

(1) The damage of air shock waves for buildings

The damage ability and degree of air shock waves for buildings are related with the building's vibration periods, and the action time t_+ of positive pressure of air shock waves. Most experiments show that when $t_+/T \leq 0.25$, the impulse of air

Fig. 2.30 Explosion of 3 kg liquid explosives

Fig. 2.31 Deconstruction/damage of *n*-butyl nitrate for brick structure buildings, **a** before explosion, **b** in explosion, **c** after explosion

shock waves plays the most important role for the damage of buildings. The writer designed an experiment of nitro *n*-butyl nitrate for buildings' damage.

Figure 2.31 indicates that the damage of *n*-butyl nitrate to brick structure building is very clear/obvious. When $t_+/T \geq 10$, the damage of air shock waves to building is determined by the super pressure of shock waves.

The positive pressure action time t_+ in the explosion of liquid explosive is very long. The boundary conditions of buildings to explosion center is a topic which is worth the study. According to energy conservation law:

$$R = \sqrt{\frac{BW}{\sigma h}} \cdot \sqrt[4]{\frac{3E}{\rho}} \tag{2.93}$$

Here, R is the distance of one building to explosion center; E is the elastic modulus of building materials; σ is the stress of building materials; ρ is the density of building materials; B is a coefficient; and W is the mass of an explosive.

If the stress σ in Eq. 2.93 is replaced by allowance stress $[\sigma]$, the resulted R is the nearest distance with building not being damaged, or safe distance. If the stress is replaced by limit strength σB, the resulted R is the destruction range. Table 2.4 lists the limited strengths of common construction materials.

Table 2.4 σ_B, E, and volume–weight values γ of construction materials

Materials	E (kg/m^2)	σ_B (kg/m^2)	Volume–weight γ (kg/m^3)
Wood	10^9	3×10^6	600
Concrete	2×10^9	5×10^6	2,600
Steel	2×10^{10}	2×10^6	7,800

Table 2.5 k values of several objectives

Objectives	k	Damage degree
Plane	1	Complete damage of airplanes
Locomotive	4–6	
Ship	0.44	Damage of buildings on a ship
Nonarmored ship	0.375	Damage of ships ($W < 400$ kg)
Assembly glass	7–9	Broken into pieces
Wood siding wall	0.7	Damage ($W > 250$ kg)
Anil wall	0.4	Breaches ($R = k\sqrt{\frac{W}{h}}$, h is the thickness of wall with unit m, $W > 250$ kg)
Anil wall	0.6	Cracks
Nonfirm wood–stone buildings	2.0	Damage
Concrete all	0.25	Severe damage

Table 2.6 Anti-air-shock wave ability of buildings

Pressure of air shock waves ΔP (MPa)	Damage of buildings
<0.002	Little damage of buildings, few cracks on the window glass, seldom window shaking out
0.002–0.012	Little mild damage, part or large part of window glass broken
0.012–0.030	Mild damage, all glass broken, part doors and windows broken, cracks (<0.5 mm) and tilt of brick walls, building top shaking out
0.030–0.050	Medium damage, cracks (0.5–5 mm) and tilt (10–100) of brick walls, cracks of concrete walls, building top shaking out, most part damage
0.050–0.076	Severe damage, windows and doors destroyed, cracks (>50 mm) and high tilt of brick walls, partial falling down, severe cracks of concrete walls, falling down of brick buildings
>0.076	Falling down of brick walls and concrete buildings

After all constants are merged, Eq. 2.93 is simplified as 2.94.

$$R = k\sqrt{W} \tag{2.94}$$

The coefficient k is related with targeted staff. Some are found in Table 2.5

According to the experiments and experience from scientists of all over the world, the anti-air-shock wave ability of buildings is concluded in Table 2.6.

(2) Damage of air shock waves for human

Liquid explosives have very strong shock waves, especially the resonant waves produced in the group explosion. The writer used 200 kg XJ-1 explosive, and separated them into 66 bottles/cans with 3,000 g each. These 66 bottles are placed on 900 mm × 900 mm square ground with two layers. The explosion effect is in Fig. 2.32.

The super pressure data of group explosion are listed in Table 2.7.

The data in Table 2.7 indicate that the explosion super pressure of XJ-1 liquid explosive reaches 1.063 MPa at 20 m away from explosion center. It is imaginable

Fig. 2.32 Explosion of XJ-1 explosive (200 kg)

Table 2.7 The super pressures of shock waves from 200 kg XJ-1 explosives

Distance (m)	20	25	30	35	40	45	50
Pressure (MPa)	1.063	0.916	0.515	0.392	0.0892	0.0423	0.0187
Distance (m)	55		60	65	70	75	80
Super pressure (MPa)	0.0102		0.0137	0.0106	0.0096	0.0091	0.0062

that the super pressure of shock waves is very high in the explosion of liquid explosive.

The writer tried a lot of experiments of shock waves. The animals in experiments were a breed, which is close to human. All experiment conditions and results are below.

XJ-1 liquid explosive of 80 kg was used in the explosion. The animals were put into places, which were different away from explosion center with different super pressures. The damage of animals is listed in Table 2.8. The classic shock wave curve of 30 m away from explosion center is schematic in Fig. 2.33.

Table 2.8 shows that when the super pressure is 0.152–0.164 MPa, there is not any injury for 6 animals; while when the super pressure is 0.166–0.20 MPa, there is only one animal which is mild injured, and it dies of myocardial necrosis. So 1.66 MPa is the bottom super pressure value which can cause injury for animals. Following the peak value increase of super pressure, the injuries are heavier, and the incidence is higher. When the super pressure is lower than 0.2 MPa, the incidence rate is only 8 % (only one injured among the 12 animals), and the degree is mild. When the super pressure is 0.2–0.45 MPa, the incidence rate increases notably and reaches 71 % (10/14). When the super pressure is larger than 0.529 MPa, all animals are injured with 100 % incidence. And there are also medium and severe injuries.

If there are some protective facilities in experiment, the shock waves first break the protective facilities, then impact crafts. This prolongs the time of pressure increase, and the pressure increase of shock wave curve need longer time. The anti-impact ability of animals improves notably. Severe injuries or death occurs at 0.60 MPa.

The special experiments with shortening pressure increase time and prolonging the impact time of positive pressure are designed. All results are in Table 2.9.

The data of Table 2.9 indicates that decreasing the booster time with similar super pressure peaks obviously increased the shock injury degrees of animals. So for the places/position without protection, the shock waves significantly increase the shock injury for staff. The injury degrees of shock waves for staff are listed in Table 2.10.

Table 2.8 Injury statistics of animals from the different super pressure of air shock waves

Group number	Parameters of shock waves			(1)	(2)	Injury																Injury degree			
	ΔP (kg/cm²)	t_f (ms)	t_+ (ms)			(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)
1	1.52–1.64	200–237	1,040–1,100	6	0																				6
1	1.66–2.00	202–218	1,040–1,140	6	1						1													1	5
1	2.25–4.09	162–218	1,040–1,380	10	7			5			2			3	1									7	3
1	4.09–4.79	138–169	1,380–1,800	4	3			2			1			1	2		1		1	1			1	3	1
1	5.29–5.87	137–140	1,324–1,900	6	6			1	1	2	3			3	4		1	1			1	2	1	3	
1	6.00–6.38	142–154	1,960–2,320	3	3			1	1	1	1	1		1	3				3	3		1		1	
Total				35	20			9	2	3	8	1		8	10		2	1	4	4	1	3	2	15	15

Note (1) Number of animals in experiment; (2) number of being injured; (3) myocardial blooding; (4) myocardial necrosis; (5) mild; (6) medium; (7) severe; (8) severe; (9) medium; (10) severe; (11) empsyxis; (12) severe; (13) blooding of other organs; (14) bladder; (15) stomach; (16) epinephros; (17) spleen; (18) brain; (19) severe; (20) medium; (21) mild; (22) no

Fig. 2.33 Classic shock wave curve of 30 m away from explosion center

2.4.2 Explosion of Liquid Explosives on the Ground

The application of liquid explosives refers the explosion in rocks and earth. The stratum (including rocks and soil) is a kind of nonuniform media. There are large gaps between rocks and rocks, rocks and the soil, soil and soil. Even in the same rocks, there are big differences in the textures, structures, or mechanical properties. Study of explosion in the rocks is more complex compared to that in the air or under water. To study the impact of liquid explosives in the mining, explosions in infinite rocks and infinite half rocks are discussed here.

2.4.2.1 Explosion Characteristics Inside Rocks and Soil

Physical phenomena of explosion in infinite rocks. Figure 2.34 represents the explosion cross section of spherical or cylindrical explosives. After ignition, detonation waves spread at the same speeds. The transportation velocities depend on the species of explosives. The transportation of liquid explosive waves is faster than that of stress waves in the rocks. The deformation of rocks and soil is much slower. So in the explosion, the surrounding media is approximately impacted directly from explosion products. And the impacts from detonation positions and detonation waveforms are negligible. So the explosion in the rocks is a classical spherical detonation. The explosion induces the fast deformation process. There is no heat exchange between the surrounding media and detonation productive gases. This explosion is an adiabatic process.

   After detonation, the pressure of explosion product gases reaches several ten kilo atmospheres. Under the impact of high-temperature and high-pressure explosion product gases, the surrounding rocks are severely compressed. Their structures are damaged, and particles are crushed, even are liquefied suddenly. The whole rocks move radially, and exclusion zone or empty zone are formed. Outside the zone, deformation slip surfaces are induced. Inside the zone, structure damage and crush

Table 2.9 Injuries of animals by shortening pressure increase time (t_I) and prolonging the impact time (t_+) of positive pressure

Group number	Parameters of shock waves			(1)	(2)	Injury						Injury								Injury degree			
	ΔP (kg/cm²)	t_I (ms)	t_+ (ms)			(3)			(4)			(11)	(12)	(13)						(19)	(20)	(21)	(22)
						(5)	(6)	(7)	(8)	(9)	(10)			(14)	(15)	(16)	(17)	(18)				
III	6.43–6.56	51	1,160–1,180	4	4			2		2		2	4			2	1	3	2	2		
II	6.07–6.15	177–188	3,700–5,060	3ᵃ	3		2	1	1	2		2	3	2		2		1	1	2		
I	6.0–6.38	142–154	1,960–2,320	3ᵃ	3	1	1	1	1	1	1	1	3						1	1		

ᵃ Means death in the explosion. One animal is not in the statistics because it was dead in the explosion

Table 2.10 The injury degrees of shockwaves for staff

Super pressure of shockwaves (without booster) (kg/cm^2)	Injury degrees
0.02–0.03	Slight (slight contusion)
0.03–0.05	Medium (hearing injury, medium contusion, mild bleeding of organs, fractures)
0.05–0.10	Severe (severe contusion of organs, may cause death)
>1.0	Extremely severe (may cause death in large extent)

Fig. 2.34 Explosion of liquid explosives inside the rocks and soil. *1* Crush zone; *2* crack zone; *3* permanent and elastic deformation zone; *4* top free soil subsidence because of reflective waves. *a*, *b*, *c* the sequence change of pressure waves in the dry soil; *d*, *e*, *f* the sequence change of pressure waves in the rocks
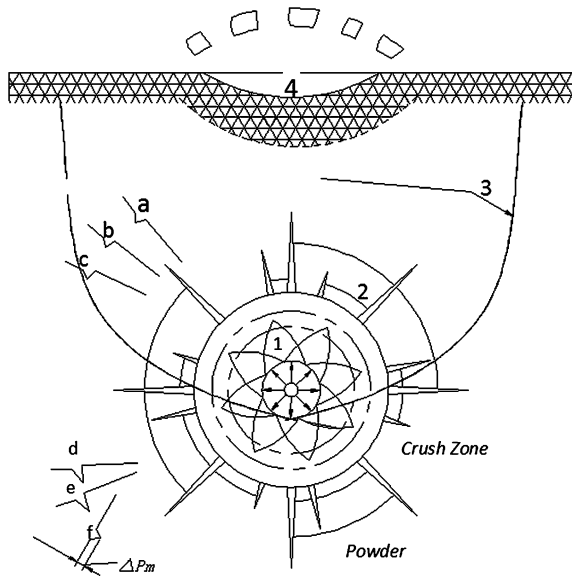
of rocks result in fine cracks with compression. In this zone, the shock waves transport with super sonic velocity.

Following the shock wave fronts travel far away from explosion center, the energy distributes the space, which is linearly proportional to the cubic of distances. So the pressure of shock waves decreases rapidly. At certain distance, the super pressure is lower than the limit strength of rocks, and the deformation changes with crushing and slip surface disappearing, the structure of rocks and soil kept. Under the compression of shock waves, the rocks and soil move out radially. Each cycle unit is under drawing stress. When this drawing stress is larger than the limit tensile strength of rocks and soil, the radial cracks from explosion center to out are produced. This zone is destruction zone, which is much larger than above two zones.

Because of inertia, after the explosion shock waves leave the explosion zone, the earth continues to leave from the explosive places and lasts some time. It induces the negative pressure of explosion zone, and the transportation of sparse waves.

The shock waves are very weak outside of the crack zone. These shock waves could not induce the deconstruction of rocks and soil, but only the vibration of particles. And the amplitude of vibration are smaller if the particles are further from explosion center, finally it decays into sound waves. For brittle soils, explosion zone is surrounded by compressive zone, crack zone, and vibration/oscillation zone. For cohesive soils, the compressive zone is the closest to explosion zone. The sizes of different zones are related with the properties of explosives, the explosive mass, the packing structure, and the soil properties.

2.4.2.2 Explosion of Liquid Explosives in Infinite Half Rocks and Soils

In engineering blasting, explosion occurs under ground with certain depth. The earth surface greatly impacts the explosion effects. Figure 2.35 gives the explosion in the earth of rock–soil free surfaces. In the first stage of explosion, the explosion waves transport to all directions from the explosion center.

When the explosion pressure waves reach the free interface of soils and air, they transport down from the free interface (Fig. 2.35b). Because of expansion waves and the pressure of product gases, the top soils above the explosives lift up (Fig. 2.35c). The tensile waves and shear waves are produced. These second stage producing waves transport radially to all directions have the maximum amplitudes, and induce the waves with maximum oscillations on the earth surface.

The transportation of earthquake waves is faster in rocks than in soils. In blasting engineering, there are loose blasting and throwing blasting.

(1) Loose blasting [21]

In loose blasting, explosives are deeper than throwing blasting. The explosion waves loose the surrounding rocks and soils, but they do not throw rocks and soils. After explosion, the explosion waves transport in all directions. When explosion
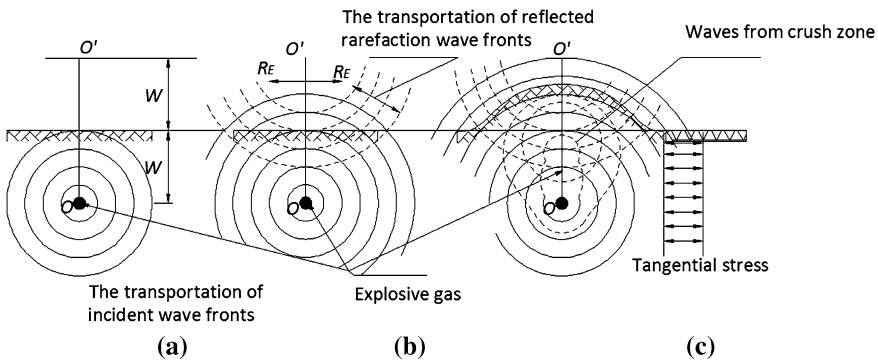
Fig. 2.35 The three stages of explosion in the surface media [21]. **a** the transportation of pressure waves; **b** radiation of pressure waves from free surface and the formation of sparse; **c** uplifting of soils
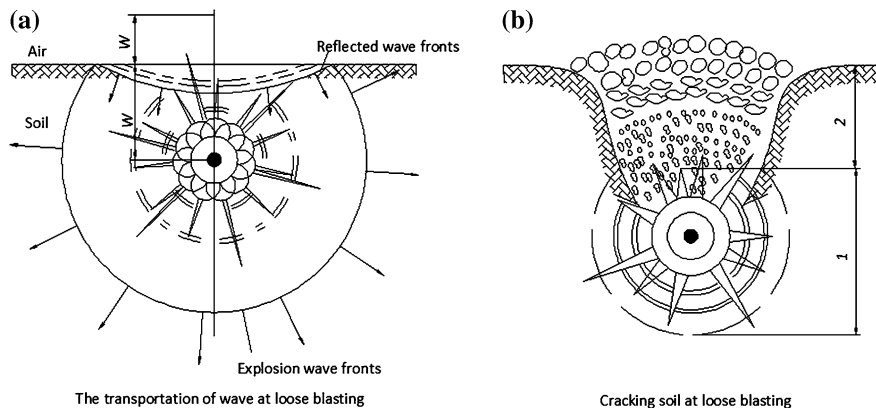
Fig. 2.36 Phenomena of loose blasting [21]. *1* inside cracking zone; *2* out cracking zone

waves pass through, the particles of media move out radially, and stop by the outer layer media. But if there are ground surfaces or other free surfaces, the rocks and soils of the free surfaces are not stopped by the outer layer media, and move out radially. At the same time, the explosion waves become tensile waves from free surfaces with transportation velocity of sound (Fig. 2.36a).

Wherever the radiant waves reaches, the rocks and soils are under drawing extension. If the drawing tension is larger than the limit of ultimate tensile strength, the free surfaces expand inside layer by layer. Reflected extension waves are approximately spherical waves from optical mirror virtual center O′ of explosives.

The damage of loose boosting has two parts.

(1) Part 1 is inside cracking zone (Fig. 2.36b), which is a spherical zone with radial cracks, and with fine medium particles.
(2) Part 2 is out cracking zone, which is produced by the damage of tensile waves from free surfaces. The key feature of this zone is that the cracks expand along the spheres of virtual centers with relatively larger medium particles. The shape of this zone looks like a funnel. So this zone is also named as loose funnel.
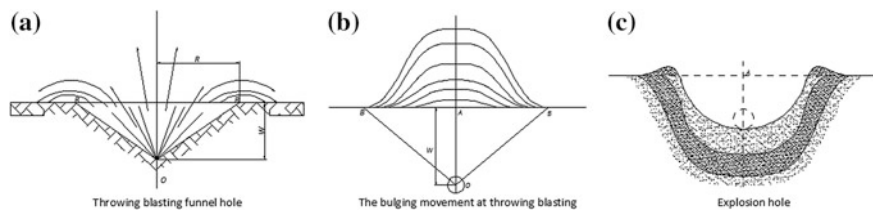
Fig. 2.37 Three different phenomena in the throwing blasting [21]. **a** A throwing blasting cone, **b** the bulging motion in a throwing blasting, **c** an explosion cone

The existence of free surface increases the damage. In engineering explosion, increasing the free surfaces is used to improve the efficiency of explosion.

(2) Throwing blasting [21]

When the packing mass of an explosive is increased and the explosive is closer to the ground, once the energy of explosion is larger than the resistance of the media above the explosive, the crushed rocks and soils are thrown upward in the shape of a speaker. At the same time, a throwing blasting cone is generated, which is from the explosion center to the ground (Fig. 2.37).

In Fig. 2.37, the vertical distance from the explosive center to the free surface is the smallest resistant line, which is represented by W^*. The radius of the blasting cone is R.

Figure 2.37 also indicates that the throwing blasting is a process of rock and soil transportation. After a single explosion or detonation, the position OA, which is the smallest resistant line, protrudes first, and the protrusion extends to the surrounding. The lifted height and extending range increase following that time prolongs. Though the height lifting continues, the range extension stops once it reaches a certain range. This process is the bulging motion stage. The bulging breaking and scattering stage is that the crushed rocks and soils move upward as an entirety, when the lifted height reaches 1–2 times of the smallest resistant line, the top bulging breaks, then the explosion products and rock and soil fragmentations scatter upward together. The rock and soil fragmentations fly in air, and finally fall on the ground under the impact of gravity. Part of fragmentations fall into the cone, and part fall on the ground near the cone. Compared to the protrusion of the ground, this cone is named "rim" (Fig. 2.37c). In the above stages of a single blasting explosion, the bulging motion of rocks and soils has the maximum linear speed in the direction of the smallest resistant line OA. The linear speed is smaller when it is farther away from OA. And the speed of point B (the edge of the cone) is the smallest, zero.

When the rocks and soils are just thrown up, the sparse waves transport into them because of the relatively lower surrounding pressure. At the same time, the sparse waves crush the rocks and soils further. According to the throwing index n, there are several explosion/detonation conditions, which are listed below.

(1) $n > 1$ is the strong blowing blasting. The vertex of crater pit is larger than 90°
     $(n = \frac{R}{W^*})$
(2) $n = 1$ is the standard blowing blasting. The vertex of crater pit is 90°
(3) $0.75 < n < 1$ is the weekend blowing blasting. The vertex of crater pit is smaller than 90°
(4) $n < 0.75$ is the loose blasting. There are no rocks and soils to blow.

2.4.3 Explosion of Liquid Explosives in Semienclosed Space [22, 24–26]

The explosion of liquid explosives releases more gases. The super pressure of explosion on the ground within 0.5–1.0 m is lower than condensed explosives. But the detonation positive pressure impacts longer time than condensed explosive, especially the places, which are far from the explosion center, for example, the zone outside of explosion reactions. The explosions of liquid explosives are more powerful in semienclosed space, especially in semiunderground or under ground.

2.4.3.1 Reflection of Shock Waves from Rigid Barriers

When the air shock waves of explosion from liquid explosive meet the vertical rigid wall (barrier), the velocity of air mass points drops down to zero suddenly, which accumulates the mass point, and the pressure and density increase dramatically until certain degrees. Then the mass points reflect to the opposite direction, the reverse shock waves are produced. Semienclosed space is different from free space. The superposition of reverse waves rises the pressure to an extremely high level.

(1) Explosion from the reflection of shock waves

Figure 2.38 gives the reflection of shock waves when they meet the vertical rigid unlimited walls. If the incident waves are one-dimensional steady ones, the refection waves are also one-dimensional steady waves. The parameters of air are P_0, T_0, ρ_0, $v_0 = 0$ before being bothered and the parameters of incident wave fronts are, P_0, ρ_1, T_1, and v_1. Because the wall is absolutely rigid, the air particles close to the wall are in a stationary state before reflection. When shock waves meet the rigid wall, the air particles near the wall produce the reflection waves with velocity/speed D_2. The direction of reflection waves is the opposite of incident waves. The parameters of reflection wave fronts are P_2, T_2, ρ_2 and $v_1 = 0$ because of the rigidity of the wall.

From the basic functions of shock waves, below equations are obtained.
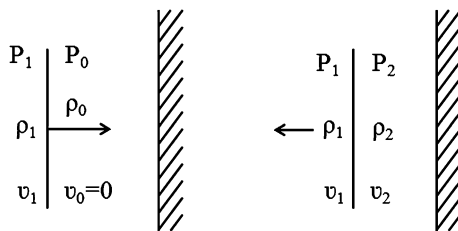
Fig. 2.38 The reflection of shock waves in semienclosed space when liquid explosives explode

$$\vartheta_1 - \vartheta_0 = \sqrt{(P_1 - P_0)\left(\frac{1}{\rho_0} - \frac{1}{\rho_1}\right)}$$

$$\vartheta_2 - \vartheta_1 = -\sqrt{(P_2 - P_1)\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)}$$

Because the direction of reflection waves are opposite from the incident ones, the incident waves are positive, the reflection waves are negative, and $\vartheta_1 = \vartheta_2 = 0$, so

$$(P_1 - P_0)\left(\frac{1}{\rho_0} - \frac{1}{\rho_1}\right) = (P_2 - P_1)\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)$$

or

$$\frac{P_1 - P_0}{\rho_0}\left(1 - \frac{\rho_0}{\rho_1}\right) = (P_2 - P_1)\left(1 - \frac{\rho_1}{\rho_2}\right) \tag{2.95}$$

The adiabatic function of shock waves is below.

$$\frac{\rho_1}{\rho_0} = \frac{\frac{k+1}{k-1} \cdot \frac{P_1}{P_0} + 1}{\frac{k+1}{k-1} + \frac{P_1}{P_0}}, \quad \frac{\rho_2}{\rho_1} = \frac{\frac{k+1}{k-1} \cdot \frac{P_2}{P_1} + 1}{\frac{k+1}{k-1} + \frac{P_2}{P_1}}$$

Substitute the adiabatic function into Eq. 2.95

$$\frac{2(P_1 - P_0)^2}{\rho_1[(k-1)P_1 + (k+1)P_0]}$$

$$= \frac{2(P_2 - P_1)^2}{\rho_1[(k+1)P_2 + (k-1)P_1]}$$

$$= \vartheta_1^2$$

The super pressure of incident waves is $\Delta P_1 = P_1 - P_0$
And the super pressure of reflection waves is $\Delta P_2 = P_2 - P_0$
The above equation is changed to

$$\frac{\Delta P^2}{(k-1)\Delta P_1 + 2kP_0} = \frac{(\Delta P_2 - \Delta P_1)^2}{(k+1)\Delta P_2 + (k+1)P_2 + (k-1)\Delta P_1 + 2kP_0}$$
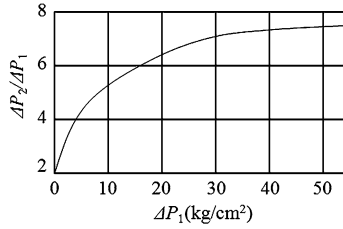
Fig. 2.39 The pressure relationship of reflection waves and incident shock waves [21]

The peak super pressure of reflection waves is Eq. 2.96.

$$\Delta P_2 = 2\Delta P_1 + \frac{(k+1)\Delta P_1^2}{(k-1)\Delta P_1 + 2kP_0} \tag{2.96}$$

For air, $k = 1.4$. Substitute it into 2.96, the super pressure of shock waves is 2.97.

$$\Delta P_2 = 2\Delta P_1 + \frac{6\Delta P_1^2}{\Delta P_1 + 7P_0} \tag{2.97}$$

For strong shock waves,

$$P_1 \gg P_0$$

so

$$\frac{\Delta P_2}{\Delta P_1} \approx 8$$

For weak shock waves, $P_1 - P_0 \leq P_0$ so

$$\Delta P_2/\Delta P_1 \approx 2$$

The above conditions conclude that in semiclosed space, the pressure of reflection wave is 2–8 times of the pressure from incident shock waves. It is listed in Fig. 2.39.

One thing is worth noticing that under strong shock waves, the pressure of reflection waves is 8 times of that from incident, which is not always correct. The strong shock waves are high-temperature and high-pressure, and perfect gas is different from the real air. Döering, Burkhardt, Shear, and Mecane referred that if the dissociation and ionization of gases are in consideration, $\Delta P_2/\Delta P_1$ is much larger than eight, and it reaches twenty or even more.

The transportation velocity of reflection shock waves D_2 is Eq. 2.98.
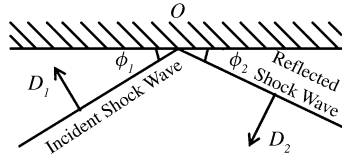
Fig. 2.40 The oblique reflection of shock waves on rigid surfaces/walls [21]

$$D_2 = \sqrt{\frac{2}{\rho_0(k-1)P_1 + (k-1)P_0}} \times [(k-1)P_1 + P_0] \qquad (2.98)$$

The density of reflection shock wave fronts is Eq. 2.99.

$$\frac{\rho_2}{\rho_1} = \frac{kP_1}{(k-1)P_1 + P_0} \qquad (2.99)$$

The above equations apply when $\frac{P_1}{P_0} < 40$. Otherwise, the ionization of air must be considered.

(2) Oblique reflection of air shock waves

The oblique reflection of shock waves occurs when the incident air shock waves have an angle ϕ_1 with the surface of a barrier. The angle ϕ_2 between the reflected waves and the surface of barrier may not be equal to ϕ_1. D_1 and D_2 are the transportation velocities of incident waves and reflected waves. Because of reflection, the velocity component vertical to the surface equals zero (Fig. 2.40).

In Fig. 2.40, point O moves toward the right with rate $\frac{D_1}{\sin \varphi_1}$ on the barrier surface. Moving coordinates with rate $\frac{D_1}{\sin \varphi_1}$ to the left are used for study and recognition of oblique reflection. Thus, the incident shock waves and reflection shock waves are immobile wave fronts; while the still air moves toward the right with rate $q_0 = \frac{D_1}{\sin \varphi_1}$ (Fig. 2.41).

In Fig. 2.41, "O" represents the zone of not being bothered; "I" refers the zone in with incident shock waves passing through and reflected shock waves not reaching;
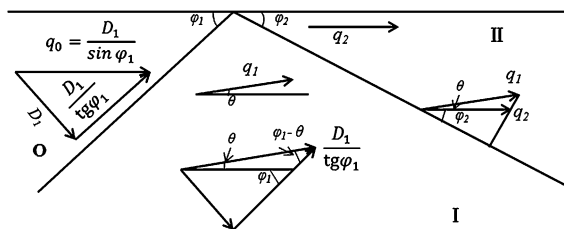
Fig. 2.41 Reflection moving coordinate of shock waves on the rigid surface [21]

"II" means the zone with reflected shock waves passing through. q_1 and q_2 are flow rates of air in "I" and "II" zones separately.

After passing the shock wave fronts, both the velocity/rate and direction of air change. The tangential component parallel to shock wave fronts remains constant, and the normal component becomes smaller. So the direction of flow turns toward the wall/surface. Below equation is obtained from Fig. 2.41.

$$q_0 \cos \varphi_1 = q_1 \cos(\varphi_1 - \theta)$$

In the two sides of incident wave fronts, both energy and momentum are conserved.

$$\rho_0 q_0 \sin \varphi_1 = \rho_1 q_1 \sin(\varphi_1 - \theta)$$

$$P_0 + \rho_0 q_0^2 \sin^2 \varphi_0 = \rho_1 q_1^2 \sin^2(\varphi_1 - \theta) + P_1$$

Likewise, the incident flow in "I" zone is q_1. It inflows "II" zone with an angle of $\varphi_2 + \theta$ from the fronts OR of reflected waves. Because of the impact of velocity component $q_1 \cos(\varphi_2 + \theta)$, the reflected flow q_2 directs outward and it is parallel with the rigid surface. For the two sides of reflected waves, below equations are established.

$$q_2 \cos\varphi_2 = q_1 \cos(\varphi_2 + \theta)$$

$$\rho_2 q_2 \sin\varphi_2 = \rho_1 q_1 \sin(\varphi_1 + \theta)$$

$$\rho_2 q_2^2 \sin^2 \varphi_2 + P_2 = \rho_1 q_1^2 \sin^2(\varphi_2 + \theta) + P_1$$

The impact adiabatic function of incident waves and reflected waves are

$$\frac{\rho_1}{\rho_0} = \frac{(k+1)P_1 + (k-1)P_0}{(k-1)P_1 + (k+1)P_0}$$

and

$$\frac{\rho_2}{\rho_1} = \frac{(k+1)P_2 + (k-1)P_1}{(k-1)P_2 + (k+1)P_1}$$

P_2, ρ_2, φ_2, q_1 and θ are obtainable from above equations. The calculation process is very complex. As a matter of convenience, the oblique reflection is simplified to Eq. 2.100.

$$\Delta P_2 = (1 + \cos\varphi)\Delta P_1 + \frac{6\Delta P_1^2}{\Delta P_1 + 7P_0} \cos^2 \varphi_1 \qquad (2.100)$$
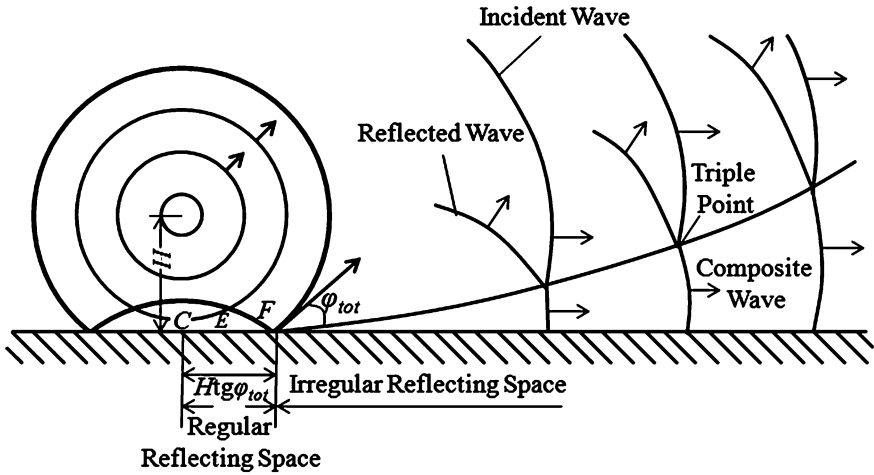
Fig. 2.42 Mach reflection

The properties of reflected waves are listed below.

(1) For a given strength of incident waves, there is critical angle φ_{1c} ,that when $\varphi_1 > \varphi_{1c}$, there is no reflection. For air with specific heat ratio $k = 1.4$, the limit of weak shock waves is $\varphi_{1c} = 90°$; the limit of strong shock waves $\varphi_{1c} = \sin^{-1}\frac{1}{K} = 39.97° \approx 40°$.

(2) For each gas, there is an angle

$$\varphi' = \frac{1}{2}\cos^{-1}\left(\frac{k-1}{2}\right)$$

When $\varphi_1 > \varphi'$, the intensity of reflected waves is larger than that of front reflection. For air, $\varphi' = 39.23°$.

(3) For a given strength of incident waves, there is an incident angle φ_{min}. When $\varphi_1 = \varphi_{min}$, the reflection intensity P_2/P_0 has the minimum value.

(4) Reflection angle φ_2 is a monotonic increasing function of φ_1.

(3) Mach reflection of shock waves [27, 28]

In the regular reflection, when incident angle φ_1 is larger than the critical angle φ_{1c}, the above reflection rule does not work. Ernst Mach indicated that the merge of incident and reflected shock waves produces the third shock waves—Mach waves. This phenomenon is Mach reflection.

The general explosion in air occurs in a limited height. The shock waves are in spherical shape. After transportation in air, the radius of the sphere becomes larger gradually, and exceeds the height H. Now part shock waves run into the ground. On the projected point of explosion center, the propagation direction of shock wave
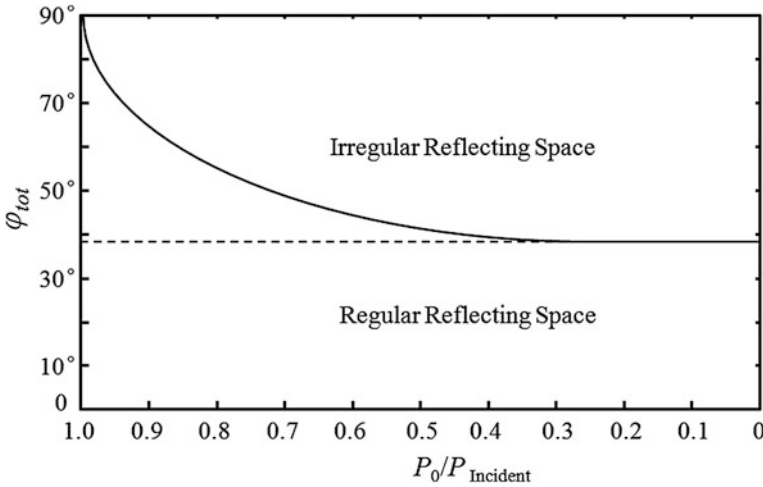
Fig. 2.43 The relationship of reflective critical angle and pressures

fronts is perpendicular with the ground surface (Fig. 2.42). This reflection is the front reflection.

Following the shock wave fronts leave the projected point; the propagation of incident wave fronts has an angle φ_1 with the ground. Now it is the oblique reflection. Following the increase in distance of the shock wave fronts from the projected point, the incident angle φ_1 is larger and larger while the angle between incident shock wave fronts and reflected shock wave fronts. When $\varphi_1 \geq \varphi_{1c}$, the reflected wave fronts catch and attach incident waves to form another single shock waves—composite waves. This composite waves are Mach waves.

Because the attaching of incident waves to reflective waves proceeds gradually along height, the fronts of composite waves have bigger and bigger height following the distance increase to explosion center. In Fig. 2.42, the cross point of wave fronts from the incident, reflective, and composite waves, is triple point.

The whole space above ground is divided into two parts. (1) Regular reflective space, or close space of aerial burst. Its distance to projective point is shorter than $H \cdot tg\varphi_{1c}$. All buildings and targets inside the space experience two shock waves: incident and reflective waves. (2) Irregular reflective space, or far space of aerial burst. Its distance to projective point is longer than $H \cdot tg\varphi_{1c}$. All buildings and targets inside the space and below triple point only experience composite waves.

The propagation of air particles in the vertical direction is stagnated. So the propagation of air particles after fronts of reflective waves (including composite waves) is horizontal. It is zero in the front reflection. But the air particles before fronts of composite waves are still. After composite waves pass them, the air particles obtain propagation, which is horizontal with the ground. In theory, the front of composite waves, or Mach rod, is perpendicular with the ground.

Fig. 2.44 The classic shapes of waves. **a** Incident wave, **b** reflective wave, **c** wave of regular reflection **d** wave of Mach reflection
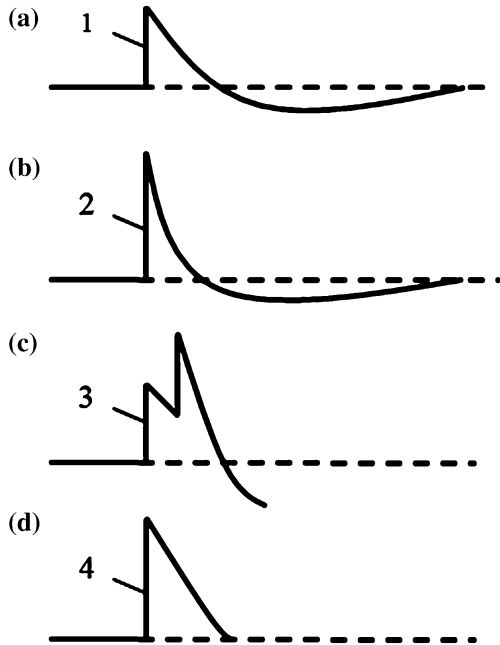
It should be pointed out that the critical angle of Mach reflection is related with the intensity of incident waves. It is shown in Fig. 2.43.

Figure 2.42 gives the reflective conditions of aerial explosion on point C, E, F, etc.

(1) At point C, the incident waves are perpendicular with the ground (Fig. 2.44a). The refection at point C is front reflection. The curve shape of reflection waves is curve 2 of Fig. 2.44b.
(2) At points E and F, the front of incident waves has an angle φ_1 with the ground, and $\varphi_1 < \varphi_{1c}$. The reflection is oblique reflection. Its curve shape is curve 3 of Fig. 2.44c.
(3) When $\varphi_1 > \varphi_{1c}$, Mach reflection produces. Its curve shape is curve 4 of Fig. 2.44d.

The above three conditions are concluded below.

(1) when $\varphi_1 = 0$, front reflection and regular reflection

$$\Delta P_2 = 2\Delta P_1 + \frac{6\Delta P_1^2}{\Delta P_1 + 7P_0}$$

(2) when $0 < \varphi_1 < \varphi_{1c}$, oblique reflection and regular reflection

Fig. 2.45 Explosion of liquid explosives in semiclosed space

$$\Delta P_2 = (1 + \cos \varphi)\Delta P_1 + \frac{6\Delta P_1^2}{\Delta P_1 + 7P_0} \cos^2 \varphi_1$$

(3) when $\varphi_{1c} < \varphi_1 < 90°$, Mach reflection and irregular reflection

$$\Delta P_m = \Delta P_{fG}(1 + \cos \varphi_1)$$

Here, ΔP_m is the super pressure of Mach reflection; and ΔP_{fG} is the super pressure of ground explosion.

2.4.3.2 The Damage of Semiclosed Targets from Air Shock Waves

The shock waves of liquid explosive explosion propagate inside the semiclosed space, release energy produce pressure for the semiclosed space. The shock waves destroy and injure the surrounding targets at different degrees. The damage and destruction of targets under explosion shock waves are a very complex process. The disturbance/perturbation of shock waves induces high pressure, which destroys the vulnerable spots in the semiclosed space, e.g., windows, air chimneys, crafts, etc. The destructiveness is related not only with shock waves, but also with the shapes, intensity, and resilience of targets. The explosion of liquid explosives in semiclosed space is shown in Fig. 2.45.

In Fig. 2.45, 1,800 kg liquid explosives are exploding in 120 m^3 semiclosed room constructed by concrete-steel. The super pressure of shock waves from the explosion reaches 1.83 MPa. The high pressure lashes and devastates the targets inside the building. At the same time, being affected by the reflection, the high-pressure shock waves disturb the targets inside the building. The tremendous pressure difference between in and out of the building destroys windows, doors, etc. and other vulnerable parts. Figure 2.45 indicates that the destruction of windows and doors from liquid explosives is thorough. The damage of soft targets inside the building is hardly avoidable.

2.4.4 Explosion Effect of Liquid Explosives Under Water

2.4.4.1 Physical Phenomena of Explosion Under Water

When the loaded explosives explode under/in the unlimited water, the pressure of high-temperature and high-pressure products is much higher than hydrostatic pressure of water. So when liquid explosives explode under/in water, both shock waves and bubble pulse phenomena are produced. In physical properties, air and water have both similarity and difference. The explosion of liquid explosives in water has not only similar physical phenomena with that in air, but also different ones. The main difference is in three aspects: (1) For the explosion with same amount of explosives, the pressure of shock waves in water is much bigger than that of air shock waves, (2) The impact time of shock waves in water is much shorter than that of air shock waves, and (3) The propagation rate of air shock wave fronts is faster than that of front sound; while the propagation rate of shock waves in water is approximately front sound rate. The main reason for the difference is that water is noncompressible. Experiments indicate that volume change of water is 1/320 from 7.5 to 10.0 MPa. The density change of water is $\Delta \rho / \rho \approx 0.05$ at 100 MPa. But under extremely high pressure, water is compressible. So water shock waves are produced under the high pressure of explosion products. The density of water is much larger than air. The hydrostatic pressure is different if the explosion is in different depth. The expansion of products in water is much slower than in air. The sound rate in seawater with 18 °C is about 1,494 m/s, higher than that in air. The sound rate in water changes if the gas amount in the water is different. When the air occupancy is 0.1–1 %, the sound rate in water drops to 900 m/s. While when the air occupies 6 %, the sound rate in water decreased to 500 m/s. From here we see that the explosion of liquid explosives under/in water is much complex than in air.
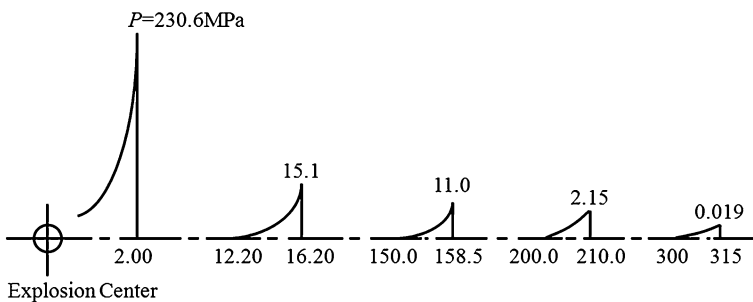
Fig. 2.46 Propagation of shock waves in water

2.4.4.2 The Explosion Shock Waves of Liquid Explosives Under Water

When the packed explosives explode in unlimited, uniform, and static water, the rapid expansion of explosion products first induces the formation of shock waves, which is followed by the generation of sparse waves by explosion products on the intersurface of products and water. The sparse waves propagate to the center of products, which is the reverse of shock waves. The pressure of original shock waves in water is much larger than that in air. For example, when the pressure of original shock waves in air is 80–130 MPa, the pressure of original shock waves in water is larger than 10,000 MPa. In the propagation of shock waves in water, both pressure of wave fronts and velocity/rate drops down faster. And the waves are broadened continuously. For the shock waves from explosion of spherical liquid explosives, their pressure decreases rapidly within 1–1.5 γ_0. The pressure is only 1/100 of the original one. Figure 2.46 gives the measured shock wave pressure changes within different distances from the explosion of 100 kg hydrazine nitrate liquid explosives.

Figure 2.46 shows that the pressure drops faster when it is close to the explosion center; while the pressure drop slows down once it is far from the explosion center. In addition, in the explosion of liquid explosives under/in water, the positive impact time of shock waves is longer following the distance increasing, but it is much shorter than that of air shock waves. The impact time in water is only about 1/100 of that in air because the speed difference between fronts and tails is smaller in water. For example, when the pressure of water shock waves is $P = 500$ MPa, the velocity/rate of water shock waves is 2,040 m/s (when the pressure of water shock waves is 5 MPa (1/100 of water), the velocity of air shock waves is 2,230 m/s). When the pressure drops down to 25 MPa, the propagation velocity of water shock waves is close to sound rate (about 1,450–1,500 m). Now the fronts and waves have similar propagation rate.

The above-discussed shock waves are in unlimited water medium. The real water medium has free surface (intersurface of water–air) and water bottom. After the explosion of liquid explosives, the shock waves in water reach the free surface or water bottom, and then reflection is generated.

(1) Existence of free surface

When the water shock waves reach the free surface, there is a dark gray hydrosphere expanding rapidly on water surface. Its migration velocity is very large. This hydrosphere disappears several milliseconds later. The reflection of shock waves occurs on the free surface. According to the condition that the pressure is close to zero after the incident and reflective waves converge together, the reflective waves are sparse waves. (Because the acoustic impedance of water is much larger than that of air, according to the propagation theory of stress waves in different media, the reflective waves are sparse waves) Under the effect of sparse waves, the water particles/drops are splashed further up, and a special splashed water mizutsuka is generated. Later, the water bubbles of gas products arrive on the water surface, and a splashed water column is formed. The gas bubbles reach the water surface before they start contracting. Because the gas bubbles float slowly,

Fig. 2.47 Explosion of liquid explosives in/under water

they scatter radially. So the water column projects out of water radially. The gas bubbles have maximum compression when they reach the surface. And the floatation velocity of gas bubbles is much faster. Now all water above gas bubbles are projected upward, and a high and narrow fountain column is generated. The height and projection velocity of fountain columns are determined by the depth of explosives. The explosion phenomena of liquid explosives are in Fig. 2.47.

Because of the reflection of sparse waves from free surface, the damage of explosion in water is obviously improved compared to that on ground. This property can be used to improve the utilization rate of explosives. But if the explosion occurs in deep enough water, the bubbles are dispersed or dissolved before they reach the free surface. Now there is no fountain. For general explosives, the depth is calculated by below equation.

$$h \geq 9.0\sqrt[3]{W}$$

Here, h is the depth of explosives in water; and W is the mass of explosives

(2) Existence of water bottom

Like the explosion on the ground, explosion in water increases the pressure of water shock waves. For rigid water bottom, it equals two times of explosion power. In fact, the water bottom is not absolutely rigid, and it absorbs part of energy. Experiments indicate that in the water bottom with sandy soils, shock wave pressure increases up 16 % and impulse goes up 35 %.

In summary, the explosion of explosives in/under water generates water shock waves, bubble impulse, and pressure waves. All of these can cause serious damage for the targets.

2.5 Toxic Gas Production of Liquid Explosives in Explosion

2.5.1 Toxicity of Liquid Explosives

In the past more than 100 years, the application of explosives reached the extreme, in both amount and variety. Before the potential impact of explosives for environment was understood, the explosives and raw materials had already been discarded everywhere, and it caused the serious pollution of water and earth. The pollution makes people's health in potential remedies. And the direct discharge of explosion products endangered the environment and human health in some degree. Liquid explosives have a problem to poisonousness and pollution. The hazards of liquid explosives include two parts: the damage of explosion products and danger of explosive remnants to the environment and human. The two parts have their own hazardous substances and damage mechanisms separately. The detonation of liquid explosives generates complex explosion products, which endanger the environment and human. The complexity of liquid explosives in detonation makes the damage unpredictable and difficult to assess. The damages for environment and human are potential risks, which have not gained enough attention. If the liquid explosives are discharged into water, their components (such as nitric acid, hydrazine nitrate, nitrate ether, alkyl nitrate, aromatic nitro compounds, etc.) cause the water pollution in high levels. Mutagenicity of human organs is one of the invisible damages of liquid explosives

Take the pollution and damage of aromatic nitro compounds as an example. Impressive amount of poisonous aromatic nitro compounds are discharged into the environment each year, which destroys the ecological balance of nature and threatens human life directly or indirectly. According to reports, the danger of aromatic nitro compounds from military bases or disused plants of explosive production has impacted a large crowd and initiated the study boom of bioremediation. In general, nitro aromatic hydrocarbons coexist and impact with each other, which brings joint toxicity. The synergistic effect of joint toxicity increases the damage ability. All extra study concludes that nitro group plays an important role for being toxic and the in vivo reduction of nitro group is the main poisonous reaction. But further study continues now to make sure the toxicity from single electron reduction of nitro group, reaction of free radicals or other toxic reactions.

2.5.2 Toxicity from Explosions of Liquid Explosives

Liquid explosives are compounds, which have different oxygen, nitrogen, and carbon atom ratios. The detonation products have complex chemical ingredients, inorganic materials and organic products. Sample collection and data analysis of explosion products are different from that of air. The specific composition analysis

Table 2.11   Hazard concentration of toxic gases in air (mg L^{-1})

Toxic gas	Mild poisoning after several hours	Severe poisoning after 1 h	Lethal after 0.5–1 h	Dying after several minutes
CO	0.1–0.2	1.5–1.6	1.6–2.3	5
NO_x	0.07–0.2	0.2–0.4	0.4–1.0	1.5
H_2S	0.01–0.2	0.25–0.4	0.5–1.0	12
SO_2	0.025	0.06–0.26	1.0–1.05	

is still a challenge for all scientists. From the mechanisms, the ideal detonation reactions only produce CO_2 and N_2, which are oxidized by oxygen from carbon and reduced from nitrogen oxides. However, the real detonation reactions are not ideal redox reactions. In the initial stage of explosion, the reactions are not complete, and the gas products deviate from expected results. In the detonation products, there are a lot of toxic gases, mainly carbon monoxide and nitrogen oxides (which include N_2O, NO, N_2O_3, NO_2/N_2O_4, and N_2O_5). All of these gases extremely endanger the health of human. For example, breathing in CO reduces the ability of blood transporting oxygen, which leads to severe hypoxia of tissue cells. 0.03 % of CO concentration in air is not safe. 0.15 % CO will causes suffocation poisoning or even death. The toxicity of NO_2 is larger than CO. NO_2 with lower concentration has long-term potential dangers. The toxicity of NO_2 mainly impacts the lungs. After being breathed in, NO_2 reacts with the moisture in the lungs to produce nitric acid and nitrous acid, which severely irritate and corrode the lungs tissues until edema. The toxicity of NO_2 is 6.5 larger than that of CO. If there is not enough oxygen, or the explosion conditions are not good enough, the products may have C_mH_n, NH_3, and HCN toxic gases, etc.; explosives with sulfur may produce SO_2 and H_2S. The toxicity of explosion products are mainly from the below two components.

(1) Interaction of explosion products and the surrounding media

Some rocks can react with detonation products, and also act as the catalysts of second reactions. For example, coal can reduce the CO and CO_2 of products. Iron oxide ore acts as the catalyst of CO oxidization to CO_2. Sulfide ore reacts with detonation products to produce sulfur oxide and hydrogen sulfide.

In addition, blasting operation, charge/packing density, charge/packing length, and stemming blockage of explosion holes impacted the formation of toxic gases to a certain extent. For industry explosives in blasting, ratio of mixtures, selection of oxygen balance, processing of explosives, and blasting operation should be taken into consideration. The hazard concentrations of toxic gases are in Table 2.11.

(2) Incompleteness of explosion reaction

In the preliminary stage of explosion, the incomplete reactions are very common. The quenching or freezing impact of balance reaction deviates products from expected results, and produces a lot toxic gases, especially in composite explosives. In liquid explosives, addition of sensitizers with high reaction activities (such as nitroglycerine, hexagon, hydrazine nitrate, hydrazine perchlorate, aromatic explosives, etc.) helps to complete explosive reactions and reduce the production of toxic

Table 2.12 Toxic gas amount of explosion of ammonium nitrate

Ingredient (%)			Oxygen balance (%)	Toxic gas (L/kg)		
TNT	NH_4NO_3	KNO_3		CO	NO_x	CO Equivalent[a]
37.6	62.4	–	−15.3	125	2.7	142.6
22	78	–	−0.7	30.4	5.5	66
17.6	82.4	–	+3.5	20	13.3	106.5
17.6	62.4	20	+7.4	16.6	5.3	51.1

[a] The conversion factor of NO_x to CO is 6.5

gases. Besides, addition of materials with catalytic activity (e.g., alkaline nitrate KNO_3) helps to significantly lower the nitrogen oxide amount of explosion products from ammonium nitrate explosives. Take pentaerythritol trinitrate as an example. Its oxygen balance is −34.49 %, and its detonation reactions are not complete. The reaction equation is below.

$$C_5H_9N_3O_9 \rightarrow CO_2 + CO + H_2O + N_2 + NO$$
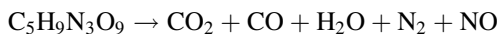
Whether the detonation reactions are complete or not is indirectly estimated from detonation parameters (e.g., detonation rate, brisance, etc.). If the processing time of trihydroxy methyl nitro methane is different, the measured brisance value is also different.

The compositions of liquid explosives are the main factors to produce toxic products. And the oxygen balance of liquid explosives is the determinant of toxic product amount. When the oxygen balance of explosives is zero, the explosion products are almost all H_2O, N_2, and CO_2. When the oxygen balance of explosives is positive, the excess oxygen oxidizes the nitrogen into nitrogen oxides, or converts to free oxygen, which increases the toxic ingredients. The main toxic ingredients are NO and NO_2/N_2O_4, while NO_2/N_2O_4 and N_2O_3 are the oxidization products of NO. When the oxygen balance of explosives is negative, carbon cannot be completely oxidized, which results in the production of CO gas. More the negative oxygen balance, more is the CO gas. Under certain conditions, the oxygen in the surrounding media affects the explosion. More oxygen, oxygen balance is positive. Less oxygen, oxygen balance is negative. To make the explosion reaction complete, it needs zero oxygen balance. This effect is especially obvious for the explosions under water.

Take solid explosives as an example to explain the influence of toxic gases by oxygen balance in explosion. Table 2.12 lists the experimental data of toxic gases released from explosion of ammonium nitrate mixtures.

The reactions of hydrogen and metal with oxygen are faster than the oxidation of carbon. For explosives, with the same amount of oxygen, if the ratio of carbon to hydrogen or carbon to metal is bigger, more CO is produced.

There are other factors for the production of toxic/poisonous composition/compounds. Imperfect explosion condition, noncomplete detonation, or blasting of explosive leads to production of large amount of NO_2. The posttreatment of

explosive also influences the production of toxic gas. Less CO and NO is produced if the compositions are mixed completely.

2.5.3 Countermeasures to Reduce the Toxicity of Liquid Explosive

Based on above factors of poisonous/toxic staff production, there are several methods to reduce the toxicity of liquid explosive. First is to control the emission of liquid explosive into earth and water to reduce the direct pollution and damage, while to reduce the production of large amount of poisonous gases, the oxygen balance, posttreatment and demolishing of liquid explosive are in full consideration. Such as, increasing and making sure enough ignition energy makes explosive to reach a stable detonation and react completely. High-power explosives with proper sensitivity are used as initiators, which is very important for explosives with lower sensitivity. Reasonable explosive charging geometries, waterproofing work of blasting supply, making sure the quality of charging and staff, and voiding half-explosion and deflagration all help to reduce the toxicity of explosion to the environment. Explosion produces an environment with high temperature and high pressure. Under these conditions, the mist (water in the air) reacts with CO to generate CO_2 and H_2, which effectively lowers the concentration of CO in blasting fame. Some nitrogen oxides are freely soluble in water, which reduces the emission of NO_x. In the application of explosives (e.g., rock mining), auto water spray helps to precipitate dust, and at the same time decreases the emission of poisonous gases, and lower down the toxicity of blasting fume.

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Chapter 3
Formulation Design of Liquid Explosives

The explosion power capacity of explosives is related to the properties of explosive materials, it is also closely related to its composition, which means that the explosion strength of explosives is related to its oxygen balance. Therefore, oxygen balance principle should be considered first during the formulation design of liquid explosive mixture from oxidant and flammable agents. Based on the thermochemistry of explosives, only when the oxygen balance is zero or close to zero, the explosive system can release its maximum energy with the best explosion. Single compound liquid explosive mainly has the oxygen balance characteristics of the single compound; however, in liquid explosive mixture, all explosive components should be mixed homogeneously in order to achieve a good consistency. Uniformity of liquid explosive composition and stability of the system are also important factors to be considered during the formulation design.

In a pure solution-type liquid explosive, the miscibility of formulation components is the key factor; stability of the slurry-type and paste-type liquid explosive system with suspended solid particles is the bottleneck of study.

The physical–chemical stability and safe in the designed liquid explosive is related to their practicability, which should be designed according to the general explosive design rules; however, most of liquid explosives are mixed at the construction site or are used within a short time after the preparation, therefore, reasonable indicators of liquid explosives should be listed corresponding to their specific usage.

3.1 Effect of Oxygen Balance on the Explosive Properties and Design Calculation of the Formulation

3.1.1 Design of Oxygen Balance

3.1.1.1 Calculation of Oxygen Balance

Explosion strength of explosives is related to its oxygen balance, most of the explosives are composed of C, H, O, and N, and some explosives also contain other

miscellaneous elements and metal powder [1, 2]. Regardless of the composition, the oxygen balance can be calculated based on the four elements of C, H, O, and N. The universal formula of explosives can be written as $C_aH_bO_cN_d$, wherein C and H are flammable agents, and O is an oxidizer. During the explosion, the explosive molecules are broken, new stable products are formed through the redox and reforming reactions with a large amount of heat released. These products are mainly CO_2, H_2O, CO, N_2, O_2, H_2, C, NO, NO_2, CH_4, C_2N_2, NH_3, and HCN. Types and quantity of explosion products are not only affected by pressure and temperature during the explosion, but also related to the amount of its flammable agents and oxidants. Generally, oxygen balance and oxygen coefficient are used to express the relative content of oxygen and flammable elements.

The oxygen balance of explosives is the excess or insufficient oxygen compared to that completely oxidizes carbon and hydrogen in the explosive to CO_2 and H_2O. If the explosive contains other combustible elements, such as aluminum, the calculation should be done based on that aluminum is completely oxidized to Al_2O_3. The oxygen balance (%) of explosive $C_aH_bO_cN_d$ can be calculated as the following:

$$\text{Oxygen balance} = \frac{\left[c - \left(2a + \frac{b}{2}\right)\right] \times 16}{M} \times 100 \qquad (3.1)$$

where,
16   atomic weight of oxygen;
M molecular weight of explosive.

According to the explosive formulation, oxygen contents of different explosives will be different, and there are three kinds of oxygen balance as the following:

With $c - \left(2a + \frac{b}{2}\right) > 0$, there is excess oxygen after oxygen in the explosive to oxidize all combustible elements completely, which is called as positive oxygen balance. And this explosive is called oxygen-positive explosive.

With $c - \left(2a + \frac{b}{2}\right) = 0$, the oxygen in explosive is just enough to oxidize all combustible elements completely, which is called as zero oxygen balance. This explosive is called oxygen-zero explosive.

With $c - \left(2a + \frac{b}{2}\right) < 0$, the oxygen in explosive is not enough to oxidize all combustible elements completely, which is called negative oxygen balance. This explosive is called oxygen-negative explosive.

For example, in nitroglycerin ($C_3H_5O_9N_3$), its oxygen balance is:

$$\text{Oxygen balance} = \frac{\left[9 - \left(2 \times 3 + \frac{5}{2}\right)\right] \times 16}{227} \times 100 = +3.5\%$$

and it can also be expressed as +0.035 g/g explosive.

In PETN with formula of $C_5H_8O_{12}N_4$, its oxygen balance is the following:

$$\text{Oxygen balance} = \frac{12 - \left(2 \times 5 + \frac{8}{2}\right) \times 16}{316} \times 100 = -10.1\%$$

In mixed explosive, its oxygen balance can be the total of oxygen balance of each component multiplied its corresponding weight percentage.

For example, in the rock explosive containing NH_4NO_3 (85 %) with oxygen balance of +0.2 g/g, TNT (11 %) with oxygen balance of −0.74 g/g and wood powder (4 %) with oxygen balance of −1.38 g/g, the oxygen balance is the following:

$$\text{Oxygen balance} = \frac{+0.2 \times 85 + (-0.74) \times 11 + (-1.38) \times 4}{100} = 0.0334\,\text{g/g}$$

Oxygen balance values of some liquid explosives and their related substances are shown in Table 3.1.

3.1.1.2 Oxygen Coefficient of Explosive

Oxygen coefficient of explosive is the saturated degree of explosive molecule with oxygen. For example, oxygen coefficient of $C_aH_bO_cN_d$ explosive can be calculated according to the following equation:

Table 3.1 Oxygen balance values of some liquid explosives and their related substances [1]

Name	Formula or the mixture	Oxygen balance (g/g of explosive)
Nitroglycerine	$C_3H_5(ONO_2)_3$	+0.035
Ethylene glycol dinitrate	$C_2H_4(ONO_2)_2$	0
Nitromethane	CH_3ONO_2	+0.49
Tetranitromethane	$C(ONO_2)_4$	−0.393
Dinitropropane	$C_3H_6N_2O_4$	−0.597
2,2-dinitropropanol	$C_3H_6N_2O_5$	−0.426
Nitric acid/toluene explosive mixture	Nitric acid/toluene = 86:14	+0.108
Hydrazine nitrate liquid	Hydrazine nitrate/hydrated hydrazine/ methylmethane = 70:20:10	+0.221
Aluminum powder	Al	−0.89
Wood powder	$C_{39}H_{70}O_{28}$	−1.38
Paraffin	$C_{18}H_{38}$	−3.46
Asphalt	$C_{30}H_{18}O$	−2.76
Light diesel	$C_{16}H_{32}$	−3.42
Charcoal	C	−2.667
Paper	$C_{39}H_{70}O_{28}$	−1.3
Coal	C (80 %)	−2.559
ANFO	NH_4NO_3:diesel:wood powder = 92:4:4	−0.0016

$$A = \frac{c}{\left(2a + \frac{b}{2}\right)} \times 100\,\% \qquad\qquad (3.2)$$

or

$$A = \frac{2c}{(4a + b)} \times 100\,\%$$

Thus, oxygen coefficient is the percentage of oxygen contained in the explosive over the required oxygen to completely oxidize carbon and hydrogen in the explosive. Same as the oxygen balance, it is also used to measure the relative relationship between oxygen content of the explosive and its flammable element content. Similarly, it is related to detonation products of the explosive.

The following two examples are going to show the calculation of oxygen coefficient.

(1) The oxygen coefficient of nitroglycerine ($C_3H_5O_9N_3$) is:

$$A = \frac{9}{\left(2 \times 3 + \frac{5}{2}\right)} \times 100 = 105.9\,\%$$

(2) The oxygen coefficient of mixed explosive with nitric acid and toluene (nitric acid of 86, 14 % of toluene) is:

$$A_1(HNO_3) = \frac{3}{\frac{1}{2}} \times 100\,\%$$

$$A_2(\text{toluene}) = \frac{1}{\left(2 \times 7 + \frac{7}{2}\right)} \times 100\,\%$$

$$A = A_1 + A_2 = \left(\frac{3}{\frac{1}{2}} + \frac{2}{35}\right) \times 100\,\% = 605.7\,\%$$

3.1.2 Influence of Oxygen Balance on Explosive Properties

The liquid explosive, with zero or near zero oxygen balance, has relatively large detonation strength and detonation intensity [3–5]. In Table 3.2, a set of oxygen balance, detonation strength, and detonation intensity test data of nitric acid–toluene liquid explosive mixture was listed. The experiment results showed that nitric acid–toluene liquid explosive mixture, when the composition was close to zero oxygen balance, had relatively high explosive property; while, had relatively low explosive

Table 3.2 The relationship between oxygen balance and explosive properties of HNO_3–$C_6H_5CH_3$ explosive [1]

Number	$\omega i \times 100$		$O.B \times 100$	$h_{Le}{}^a$	Explosion funnel volume (the relative value)
	HNO_3 (conc. 90 %)	$C_6H_5CH_3$			
1	86	14	5.3	20.34	1.86
2	85	15	1.6	21.32	2.12
3	84	16	−2.2	21.93	2.13
4	83	17	−6.1	20.19	1.35

^{a} The compressed height of lead column

property and might even had detonation difficulty when the oxygen balance was away from zero.

Fedorov et al. [6] had studied explosive properties of tetranitromethane and nitrobenzene explosive mixture with different proportions in detail. The experiment results were listed in Table 3.3.

Because the lead column in Table 3.3 was not be calibrated, some of the test data might be too large, but they still could be compared relatively. When the liquid explosive had 22.5 % of nitrobenzene, explosion velocity and strength were the most powerful; when nitrobenzene was 20–25 % (oxygen balance was 6.68 to −3.9 %), its explosion velocity and strength were located within the high value area.

Table 3.3 Explosion property of $C(NO_2)_4$-nitrobenzene explosive mixture

Content of nitrobenzene × 100	$O.$ $B \times 100$	v_D (m s^{-1})	ρ (g cm^{-3})	Q_e (calculated) (kJ kg^{-1})	$h_c{}^{a,\ b}$ (mm)	V_L (ml)	50 % Explosion energy/ E50 (N m cm^{-2})
0	49.0	6,400	1.64	1,892	3.47	50	/
5	38.4	6,850	1.61	2,708	4.32	400	48
10	27.8	7,100	1.58	3,687	4.5	535	43
15	17.3	7,400	1.555	4,431	5.25	655	43
20	6.7	7,570	1.537	5,024	5.43	830	36.5
22.5	1.4	7,760	1.515	5,275	5.45	874	51.5
25	−3.9	7,670	1.50	5,831	5.6	850	80.6
30	−14.5	7,500	1.48	5,777	5.25	700	80.6
35	−25.1	7,250	1.457	5,251	5.2	525	150
40	−35.6	7,050	1.433	4,619	4.92	540	150
50	−56.8	6,650	1.37	3,386	4.4	480	/
60	−78.0	6,250	1.35	3,127	3.7	462	/
70	−99.1	5,800	1.30	3,235	3.24	317	/
Nitroglycerine		7,450					47.5
TNT		7,200			4.2		111

^{a} The compressed value of copper column
^{b} Size of copper column as φ 7 × 10.5 mm

Fig. 3.1 Lead cast expansion value of hydrazine nitrate–hydrazine mixture [1]

					w(N$_2$H$_4$)×100
80	60	40	20	0	
20	40	60	80	100	w(N$_2$H$_5$NO$_3$)×100
-78.3	-57.5	-31.9	-13.3	+8.4	氧平衡×100
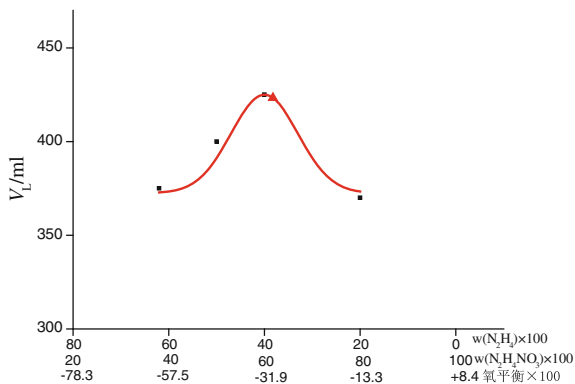
Fig. 3.2 Explosion velocity of hydrazine nitrate–hydrazine mixture [3]

					w(N$_2$H$_4$)×100
50	40	30	20	10	0	w(N$_2$H$_5$NO$_3$)×100
50	60	70	80	90	100	
-45.8	-34.9	-24.2	-13.3	-2.4	+8.4	氧平衡×100
1.21	1.27	1.33	1.40	1.50	1.63	ρ/g.cm^3
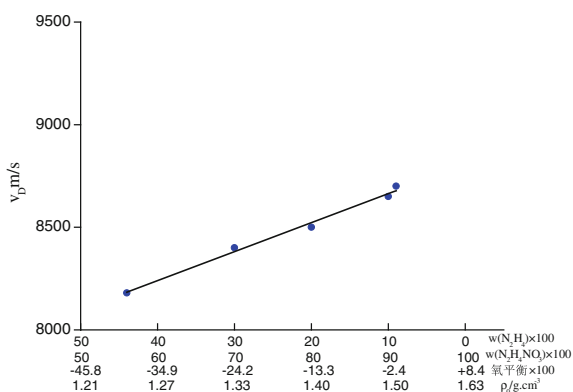
Figures 3.1 and 3.2 shows the relationship of oxygen balance with lead cast expansion value and explosion velocity of the hydrazine nitrate–hydrazine liquid explosive. It could be found that, when the oxygen balance of such explosive mixture was −2.4 % (including 10 % of hydrazine), explosion velocity was the maximum; while, when the oxygen balance was −31.9 % (including 40 % of hydrazine), its power capability was the maximum.

The inconsistent relationship between oxygen balance of hydrazine nitrate–hydrazine liquid explosive and its explosion velocity strength was mainly due to that these explosive systems did not contain carbon-elements, all explosion products were gases and the average molecular weight of products was very small. Explosion velocity of explosive depends mainly on the explosion heat, but explosion strength is proportional to the product of explosion heat and specific volume; although the oxygen balance of the hydrazine nitrate–hydrazine liquid is near to zero with the maximum explosion heat, its specific volume is not the biggest under this condition, which leads this typical characteristics of noncarbon explosives (high hydrogen-content explosives).

3.1.3 Design and Calculation of Liquid Explosive Recipe

According to the impact of oxygen balance of explosive on its explosion strength, the principle of zero oxygen balance should be usually followed during the formulation design of liquid explosive.

During the preparation of 1,000 g of binary liquid explosive, the following equation can be used:

$$\left.\begin{array}{l} m_1 k_1 + m_2 k_2 = 0 \\ m_1 + m_2 = 1,000 \end{array}\right\} \tag{3.3}$$

where,

m_1, m_2 mass of component 1 and 2, individually (g);
k_1, k_2 oxygen balance of component 1 and 2, individually (g/g).

Based on the above equations, qualities of the two components in the 1,000 g of liquid explosive can be obtained as the following: $m_1 = 1,000 k_2/k_2 - k_1$; $m_2 = 1,000 k_1/k_1 - k_2$.

In the multicomponent liquid explosive, in order to simplify the calculation, the product of mass percentage of each component in liquid explosive and the corresponding oxygen balance also can be used to express oxygen balance value of the explosive mixture. If the designed liquid explosive had several components, the mass percentages of $(n - 2)$ nonmain components were decided based on other principles or experience first, then the following equation could be solved:

$$\left.\begin{array}{l} \sum_{i=1}^{n} m_i k_i = 0 \\ \sum_{i=1}^{n} m_i k_i = 100 \end{array}\right\} \tag{3.4}$$

where,

m_i the percentage of the component i,
k_i oxygen balance of the component i.

Mass percentages of the two main components were obtained. Then, several recipes would be obtained according to the method described above, and these recipes should be tested and modified experimentally to optimize. Therefore, the prediction of oxygen balance values of popular components could bring great convenience to the calculation of oxygen balance and formula design of explosive mixture.

3.2 Design of Explosion Property [7]

Explosion property of explosive is related to its explosion heat. In a chemical reaction under certain conditions, the released or absorbed heat is the thermal effect of reaction.

When all elements react to form 1 mol of a substance, the released or adsorbed heat is formation heat of the substance. When 1 mol of the substance was combusted in pure oxygen, the released heat is combustion heat; when 1 mol of explosive was exploded under anaerobic conditions, the released heat is explosion heat, which is different from combustion heat because combustion heat is the heat released from complete oxidation of combustible components in a material. According to Kirchhoff:

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = \sum C_1' - \sum C_2' = \sum \Delta C' \tag{3.5}$$

Thermal effect change with temperature is equal to the thermal capacity difference between the staring material and the final material, which can be expressed as the following:

$$Q_2 = Q_1 + \int_{T_1}^{T_2} \sum \Delta C \, \mathrm{d}T = Q_1 + \sum \Delta C'(T_2 - T_1) \tag{3.6}$$

According to the first law of thermodynamics, the following equation can be obtained:

$$-\Delta E = Q + A = Q + P\Delta V \tag{3.7}$$

where,
E internal energy,
ΔE the change of E,
Q released heat,
A work done by the material,
P Pressure of material,
ΔV volume change of material.

If the reaction is carried out with constant volume, $\Delta V = 0$, the following can be obtained,

$$\begin{aligned} A &= 0 \\ Q_{\mathrm{v}} &= -\Delta E \end{aligned} \tag{3.8}$$

Therefore, energy and state equation of the material can be closely correlated as the following:

$$Q_V = Q_P + nPV \tag{3.9}$$

or

$$Q_V = Q_P + nPV \tag{3.10}$$

where,

n the number of moles of gas products from explosion,

V molar volume of gas.

At 18 °C or 291 K, they are the following,

$$Q_V = Q_P + nPV \tag{3.11}$$

$$Q_V = Q_P + nPV \tag{3.12}$$

The above two equations showed the relationship of explosion gas with constant volume to that with constant pressure. In the design calculation of explosive thermal effects, some further simplifications can be made based on the specific circumstances.

3.2.1 Design Calculation of Properties and Their Factor Relationship of Liquid Explosive

3.2.1.1 Calculation of Explosion Heat

Explosion heat of explosive can be determined experimentally, and can also be calculated with theoretical methods in the design of its formula. During the calculation of explosion heat with theoretical method, chemical composition, explosive reaction equations, and required thermochemical data of the designed explosive must be known first, then the empirical approach Hess law can be used for the calculation.

"Thermal effect of reaction, not related to the reaction pathway, is only related to the initial state and the final state of the system" is the core of Hess Law. In other words, if the same substance turns into the same final product with different pathways, sums of the released or absorbed heat should be equal to each other.

During the design calculations of explosion heat, the following triangle (Fig. 3.3) could be used to explain. As shown in the figure, State 1 corresponds to the state elemental composition of explosive, State 2 corresponds to explosive itself, and
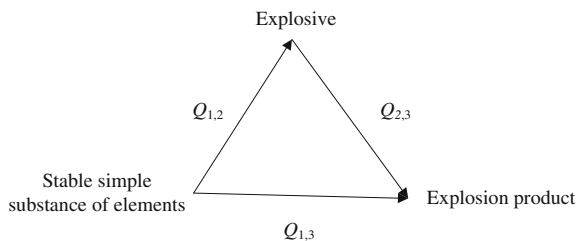
Fig. 3.3 Hess *triangle* diagram of explosion heat of explosives

State 3 is formed product from explosion. It can be imagined that there are two pathways from State 1 to 3. The first is obtain the explosive from all elements with the release or absorption of heat $Q_{1,2}$, then the explosive was exploded to release heat $Q_{2,3}$ (explosion heat); another is to generate explosion product directly from elements with the release of heat $Q_{1,3}$ (formation heat of explosion product).

The sum of reaction heat of the system along the first pathway should be equal to that along the second pathway, which could be expressed as the following:

$$Q_{1,2} + Q_{2,3} = Q_{1,3}$$

Therefore, explosion heat $Q_{2,3}$ is:

$$Q_{2,3} = Q_{1,3} - Q_{1,2} \tag{3.13}$$

where,

$Q_{1,3}$ the sum of formation heat of explosion product,
$Q_{1,2}$ formation heat of explosive.

Therefore, explosion heat of the explosive is equal to the formation heat of explosion products subtracted with that of explosive.

According to Eq. 3.5, explosion ways of explosive, and formation heat values of explosives and explosion products, the explosion heat of explosive can be calculated. Based on the explosion reaction, explosion equations close to the real reactions could be figured out, the formation heat of explosives and explosion products can be found in the relevant manuals, and formation heat values of some substance and explosive were listed in Table 3.4. If the formation heat of explosive is not known, it can be obtained through the combustion heat experiment or the associated calculation methods.

For example, PETN with molecular weight of $M = 316$ and formation heat of 541.28 kJ/mol has the following explosion reaction equation:

$$C(CH_2ONO_2)_4 \rightarrow 4H_2O + 3CO_2 + 2CO + 2N_2 + Q_v$$
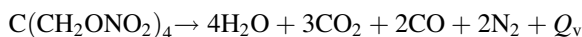
Table 3.4 Heat of formation of some substances and explosives under constant pressure at 18 °C or 291 K

Chemical	Formula weight	Formula	Formation heat ΔH_f (kJ/mol)
Triazidomelamine	204	C_3N_{12}	−91.63
Nitromethane (NM)	61	CH_3NO_2	91.42
Trinitromethane	151	$CH(NO_2)_3$	79.91
Tetranitromethane	196	$C(NO_2)_4$	−35.15
Nitroguanidine	104	$CH_4N_2O_2$	91.46
Guanidine nitrate	122	$CH_6N_4O_3$	381.58
TNT	227	$C_7H_5N_3O_6$	73.22
1,3,5-trinitrobenzene	213	$C_6H_3(NO_2)_3$	47.7
Picric acid (PA)	229	$C_6H_3N_3O_7$	227.61
2,4-dinitrotoluene	182	$C_7H_6N_2O_4$	78.24
2,6-dinitrotoluene	182	$C_7H_6N_2O_4$	19.66
m-nitrotoluene (MNT)	137	$C_7H_7NO_2$	47.77
Nitrosourea	105	$CH_3N_3O_3$	283.05
	123	$CH_5N_3O_4$	564.17
Pentaerythritol tetranitrate (PETN)	316	$C_5H_8N_4O_{12}$	541.28
Nitroglycerine (NG)	227	$C_3H_5N_3O_9$	370.83
Nitroglycol	152	$C_2H_4N_2O_6$	274.9
Ammonium nitrate	80	NH_4NO_3	365.51
Sodium nitrate	85	$NaNO_3$	467.44
Potassium nitrate	101	KNO_3	494.09
Ammonium perchlorate	117.5	NH_4ClO_4	293.72
Potassium perchlorate	138.5	$KClO_4$	437.23
Water (gas)	18	H_2O	241.75
Water (liquid)	18	H_2O	286.06
Carbon monoxide	28	CO	112.67
Carbon dioxide	44	CO_2	395.43
Nitric oxide	30	NO	−91.37
Nitrogen dioxide (gas)	46	NO_2	−51.04
Nitrogen dioxide (liquid)	46	NO_2	−12.97
Ammonia	17	NH_3	46.02
Methane	16	CH_4	76.57
Acetylene	26	C_2H_2	−223
Ethylene	28	C_2H_4	−48.53
Paraffin[a]	254	$C_{18}H_{38}$	558.56
Wood powder[a]	986	$C_{39}H_{70}O_{28}$	5690.24
Asphalt[a]	394	$C_{30}H_{18}O$	594.13
Light diesel[a]	224	$C_{16}H_{32}$	661.07

[a] Constant-volume formation heat

Therefore, the explosion heat of PTEN can be calculated according to the triangle graph of PTEN explosion heat as $Q_{2,3} = Q_{1,3} - Q_{1,2}$.

As listed in Table 3.4, formation heats of H_2O, CO_2, CO, and N_2 are 241.75, 395.43, and 112.47 kJ/mol and 0, respectively.

So, we can obtain $Q_{2,3} = 4 \times 241.75 + 3 \times 395.43 + 2 \times 112.47 - 541.28 = 1836.95$ kJ/mol where the used formation heat are the constant-pressure heat effect at 18 °C; therefore, the calculated heat is the constant-pressure thermal effect Qp at 18 °C. However, the explosion heat should be constant-volume thermal effect Qv, which should be corrected in accordance with Eq. 3.11 (Qv = Qp + 0.577n), where $n = 4 + 3 + 2 + 2 = 11$ mol.

Therefore, explosion heat of PTEN is:

$$Q_v = 439.04 + 0.577 \times 11 = 1863.55 \text{ kJ/mol}$$

or

$$Q_v = 1863.55 \times 1000/316 = 5897.31 \text{ J/g}$$

According to Kirchhoff Law, formation heats of material with different reference temperature (15, 18, 25 °C) are different. But, in engineering calculations, the calculation error caused by different reference temperature is relatively small, so, generally, the further correction is not needed.

For example, the calculation of explosion heat of explosive Amatol 80/20 is the following. Its explosion reaction equation is,

$$11.35NH_4NO_3 + C_7H_5(NO_2)_3 \rightarrow 7CO_2 + 25.2H_2O + 12.85N_2 + 0.425O_2 + Q_v$$
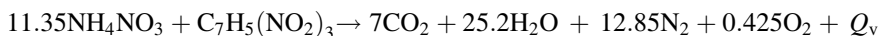
As listed in Table 3.4, formation heat values of ammonium nitrate and TNT are 365.5 and 73.22 kJ/mol, respectively.

According to the triangle diagram, we can obtain:

$$\begin{aligned} Q_{2,3} &= Q_{1,3} - Q_{1,2} \\ &= 7 \times 94.51 + 25.2 \times 57.78 - (11.35 \times 87.36 + 17.5) \\ &= 2117.63 - 1009.04 = 4638.41 \text{ kJ} \end{aligned}$$

which can be turned into constant-volume thermal effect Q_v as:

$$\begin{aligned} Q_v &= 1108.58 + 0.577 \times (7 + 25.2 + 12.85 + 0.425) \\ &= 1108.59 + 26.29 = 4748.34 \text{ kJ}. \end{aligned}$$

This value is the constant-volume explosion thermal effect of a mixture of ammonium nitrate (11.35 mol) and TNT (1 mol).

With J/g as the unit, constant-volume explosion heat of Amatol is the following:

$$Q_v = \frac{4748.38 \times 1000}{11.35 \times 80 + 227} \approx 4183.56\,\text{J/g}$$

3.2.1.2 Factors Affecting Explosion Heat

(1) Effect of charging density

Explosion heat is different with different explosive charging density. And the influence of charging density of oxygen-negative explosive is relatively significant, such as picric acid, tetryl, nitromethane/kerosene. With explosives having zero or positive oxygen balance, no increase of explosion heat was observed with the increase of charging density though in a strong enclosure, such as PTEN, EG, nitric acid/nitrobenzene, nitric acid/o-ethylbenzene, etc., because dissociation rates of explosion products (CO_2 and H_2O) of oxygen-zero explosive or oxygen-positive explosive are relatively small, and the momentary secondary reaction during the explosion is relatively small too or almost does not exist.

$$2CO \rightleftharpoons CO_2 + C + 172.38\,\text{kJ}$$

$$CO + H_2 \rightleftharpoons H_2O + C + 131.38\,\text{kJ}$$
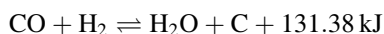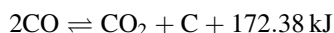
However, the explosion pressure of oxygen-negative explosive would be increased with the increase of the density; thus, the above-mentioned two secondary reaction equilibriums are moved to the right, leading the volume reduce of gaseous products and increase of the relative amount of CO_2, thus leading the increase of explosion heat. The influence of charging density of condensed explosive on explosion heat was shown in Table 3.5.

(2) Influence of the shell

Experiments showed that, when oxygen-negative explosive were detonated in high-density and strong shell, its explosion heat was increased significantly. For example, as shown in Table 3.6, when the TNT is charged and detonated in a brass shell, the released energy is 25 % than that within a thin glass shell.

However, the impact of shell was not very significant on the explosion heat of explosives with low negative oxygen balance, positive oxygen balance, and zero oxygen balance.

With a certain explosive charging density, explosion heat was also increased if the shell thickness was increased. While its thickness reached to a certain value, the explosion value reached its limit without any further increase. For example, in the brass shell with a thickness of 3–4 mm, the limit was reached. With the maximum charging density, the increase of shell thickness and the corresponding prolonged residence time of explosion products under high pressure at high temperature no longer had any effect on the explosion heat. Therefore, the explosion heat can be

Table 3.5 Influence of charging density on the measured explosion heat

Parameters	RDX					TNT			
ρ_o (g/cm^3)	0.5	1.0	1.8	0.95	1.1	1.5	0.85	1.0	1.5	1.62
Q_v (J/g)	5355.52	5773.92	6317.84	5313.68	5355.52	5397.36	3389.04–3556.40	3598.4–3681.92	4225.84	4853.44

Table 3.6 Influence of charging shell on explosion heat

Explosive	Charging density ρ_o (g/cm^3)	Q_v (J/g) (water gas)	Explosion conditions
RDX	1.78	5313.68	Inside of 2-mm-thick glass shell
RDX	1.78	5941.28	Inside of 4-mm-thick brass shell
TNT	1.60	3514.56	Inside of 2-mm-thick glass shell
TNT	1.60	4518.72	Inside of 4-mm-thick brass shell

regarded as a certain fixed value. In the absence of impact of the shell, Q_p has a linear relationship with the charging density ρ.

$$Q_v = A + B\rho; \quad B = \frac{dQ}{d\rho} \tag{3.14}$$

In RDX,

$$Q_v = 1,090 + 180\rho \tag{3.15}$$

In TNT,

$$Q_v = 550 + 340\rho \tag{3.16}$$

Because there is a part of the energy is released from the secondary reaction during the expansion of explosion products, the shell thickness has influence on the explosion heat of explosive. Therefore, without any shell or with relatively thin shell, the expansion of explosion products is not restricted, the pressure drops rapidly. Thus, balances of the above reactions ① and ② trend to move to the left, and the heat absorption reduces the explosion heat. Additionally, with the rapid expansion of these gaseous explosion products, some of the unreacted materials are also scattered leading to energy lose. The shell may hinder the gas product expansion, reduce the drop rate of pressure, and prolong the secondary reaction time of charged explosives inside of the shell, resulting in the formation of solid carbon and the decrease of rightward movement of the secondary reaction of explosion gas products. The shell also restricts the scattering of unreacted explosive, thus to increase the explosive heat.

(3) Influence of additive

The addition of an inert liquid can play the same role as the increase of explosive density to increase the explosion heat. The effect of added water on the explosive properties was shown in Table 3.7.

Table 3.7 in the dry explosive is pure explosive without added water, and explosive mixture is a mixture of explosive and water with the percentages listed in Table 3.7. It could also be found that the explosion heat with a certain amount of water added in the explosive was lower than that without added water. For example, with water of 35.6 % and TNT of 64.6 %, its explosion heat was 2719.60 J/g,

Table 3.7 Influence of water content on explosion heat of explosive

Explosive	Water content of the loaded explosive (%)	Oxygen balance (%)	Charging density ρ_0 (g/cm^3)	Explosion heat Q_v (J/g)		Change of explosion heat (%)
				Anhydrous	Hydrate	
NG	0	−3.5	1.6	6,213	–	
NG	20	−3.5	1.48	–	–	
NM	0	−39.3	1.130	4539.6	–	
NM	10	−39.3	1.117	–	4196.2	7.56
PETN	0	−10	1.395	5773.92	–	
PETN	29.1	−10	1.280	5815.76	4142.16	0.725

equivalent to a explosion heat of 4225.84 J/g of TNT, which was increased by 34 % compared with measured explosion heat of pure TNT. Furthermore, as listed in the table, the relatively significant impact of water content on the explosive with negative oxygen balance indicated that inert material, such as water, played a role of shell invisibly, and this impact is particularly important to explosives with negative oxygen balance. In addition to water, the added kerosene and organic reagents in the liquid explosive could play the same role. It should also be worth mentioning that the addition of inorganic oxidizer and combustible agent could not only play the role as mentioned previously, but also improved the explosive density, which was favorable to improve the explosion velocity and heat.

3.2.1.3 Methods to Improve Explosion Heat

Explosion heat of explosive is an important indicator to measure its explosion properties, and the improvement of explosion heat means the improvement of its explosion energy. According to the design calculations of explosion heat, it could be improved through these following methods.

(1) Improving the oxygen balance of explosive

This method is to make oxidant in the explosive can just completely oxidize its combustible agents to reach or be close to zero oxygen balance. In explosives of $C_aH_bO_cN_d$, if oxygen in the molecule can completely oxidize carbon and hydrogen into CO_2 and H_2O, the released energy should be the highest. However, different explosives with the same zero oxygen balances might release different explosion energies. Generally, explosive with relatively high hydrogen content has relatively large explosive energy because the complete oxidation of hydrogen into water releases relatively large explosion heat.

In explosive molecule, some oxygen atoms in the molecular structure are connected to the combustible element atoms, such as C–O, C=O, C–H bonds, these oxygen atoms are called "ineffective oxygen" because they are ineffective or partially ineffective in the explosion reaction. The explosive with many of these bonds, the explosion energy is not high although it has zero oxygen balance. Since part of

the energy is lost in the process of formation of molecule, its formation heat is relatively large. Therefore, the structure of explosive molecule has significant impact on its explosion energy.

(2) Introduction of some high-energy elements into the explosive molecule

Generally, combustible agent boron (B) or oxidant fluorine (F) are introduced in the explosive to form new compounds. The influence of introduced high-energy elements can be figured out roughly from that data listed in Table 3.8, in which energy of the boron-containing compound is the highest.

(3) Addition of fine metal powder of high-calorie oxide, such as aluminum powder, magnesium powder, and boron powder

A right amount of aluminum powder is added into RDX, its explosion heat can be increased by 50 % because the added aluminum not only can react with oxygen with large amount of released heat as the following:

$$2Al + 1.5O_2 \rightarrow Al_2O_3 + 1669.42 \, kJ \text{ or } 16401.28 \, J/g$$
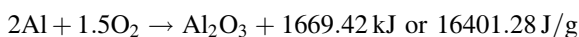
but also react with explosion products CO_2 and H_2O secondarily as the following:

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO + 593.29 \text{ kJ/mol}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 + 943.91 \text{ kJ/mol}$$
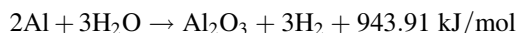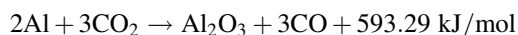
Because there is large amount of heat released, it can continue to maintain its explosion pressure.

The reaction level of aluminum depends on its particle size and the scattering conditions of explosion products. The decrease of aluminum powder grain size can increase the stability of explosive detonation, but it can cover other particles to hinder the reaction transmission if its size is too small. The typical used aluminum particle is 3–200 μm in diameter. Since aluminum are oxidized during its secondary reaction with oxygen-containing gas products from the first stage of explosion, the temperature of gas explosion products, the distribution of unreacted aluminum particles in the product, and the extended phase-contacting time all play important roles in the reaction level of aluminum powder.

Generally, influence of the aluminum powder added into explosive components on the explosion velocity is not significant. However, because aluminum powder

Table 3.8 Thermochemistry data of products from combustion and explosion

Product	Explosion heat Q_f (kJ)	Formula weight	Heat per unit mass (J/g)
B_2O_2(s)	1263.57	69.6	18744.32
HF(g)	268.60	20	13430.64
H_2O(g)	239.66	18	13430.64
CO_2(g)	395.43	44	8995.6
CF_4(g)	679.90	88	7740.4
CO(g)	112.47	28	4016.64

can greatly increase the explosion energy and the following secondary reactions enhanced the effect of released heat, it has been used relatively widely in military explosives and industrial explosives.

Metal element not only can capture the oxygen in carbon oxides and water, but also generate the corresponding metal nitride with nitrogen gas in the explosion products, such as,

$$Mg + N_2 \rightarrow MgN_2 + 463.17 \text{ kJ/mol}$$

$$Al + 0.5N_2 \rightarrow AlN + 241 \text{ kJ/mol}.$$
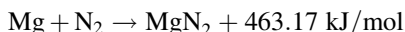
It can be found that these reactions are highly exothermic reactions, thus to increase the explosion heat.

3.2.2 Explosion Formation Heat of Explosive

The calculation of explosion heat of explosive involves its formation heat, therefore, its explosion heat not only depends on element composition of the explosive, but also has a great relationship with its formation heat.
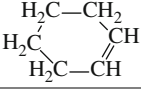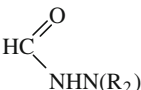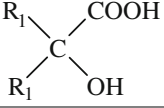
Formation heat is expressed with $-\Delta H_f$ or Q_f usually and their relationship is $-\Delta H_f = Q_f$, with unit of kJ/mol.

Formation heat is a basic parameter in the thermochemical calculation, which can be calculated from combustion heat of a compound according to Hess's law. The measurement accuracy of combustion heat has reached a very high level. In the design of a new explosive, in order to know its explosion properties and thermochemical properties, its formation heat can be calculated first, which is necessary to design and decide the formulation of explosive.

Electron transfer method is the basic method to calculate the combustion heat, which can also be used to calculate the formation heat. Assumed that the designed explosive or organic material is an aliphatic n-alkane, wherein one or more hydrogen atoms have been substituted with other atoms or atom group. Thus, its combustion is the transferring process of electrons from carbon and hydrogen atoms to oxygen atoms. It was found in experiments that, when the electron of 1 mol of atom is transferred to oxygen atom under constant pressure to 1 mol of atom, the substance will release 108.99 kJ of heat.
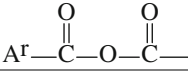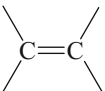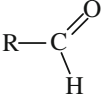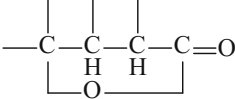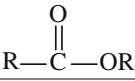
When any substituent is introduced in hydrocarbon molecules to saturate double bond or triple bond, the electronic structure of molecule will be changed, thus the thermal effect of electron transfer of 1 mol atom will have some change. According to the impact of change in molecule structure, the explosion heat of explosive can be calculated based on the corresponding corrected thermochemical data of some groups and the corrected data are listed in Table 3.9. The combustion heat of $C_a H_b O_c N_d$ compounds under constant pressure can be calculated as the following equation:

Table 3.9 Corrected thermochemical data of some groups

No.	Group and bond	Structure	Correct value Δ_f (kJ/mol)
1	Sulfur-containing groups in aromatic hydrocarbon	Ar–SO$_3$H	−98
2	Fused nucleus of aromatics		−84
3	Nitro atom group in aliphatic and aromatic compounds	R–NO$_2$	−54.4
	Carboxyl atom group in aromatic acids	Ar–COOH	−54.4
4	Nitro atom group in gem-dinitro chemicals	R–CH(NO$_2$)$_2$	−41.8
5	Aromatic radical bonding	Ar:Ar	−27.2
	Aromatic radical and olefin radical	Ar:C=C	−27.2
	Aromatic radical and alkyne radical	Ar:C≡C	−27.2
	Nitro atom group in trinitromethane	R–C(NO$_2$)$_3$	−27.2
	Aromatic radical and nitrile group	Ar:CN	−27.2
	Urea atom groups	C=ON=	−27.2
6	Aromatic and aliphatic radicals	Ar:ALK	−14.6
	Aromatic radical and nitrogen (ammonia-type)	Ar–N=	−14.6
	Quaternary carbon atom	(R)$_4$C–	−14.6
	Amides	R–CONH$_2$	−14.6
7	Carboxyl atom groups in acid	ALK–COOH	0
	Nitrates	R–ONO$_2$	0
	Nitro atom group in tetranitromethane	C(NO$_2$)$_4$	0
8	Tert-alcohol	(R)$_3$C–OH	+14.6
	Phenols	Ar–OH	+14.6
	Nitro amines	R–NHNO$_2$	+14.6
9	Secondary alcohol	R$_2$CH–OH	+27.2
	Ethylene bond in the ring		+27.2
	Aliphatic and aromatic ketones	R$_2$C=O	+27.2
	Amide with substituted group		+27.2
	Aromatic radical and chlorine	Ar:Cl	+27.2
	Oxyacids		+27.2

Table 3.9 (continued)

No.	Group and bond	Structure	Correct value Δ_f (kJ/mol)
10	Aromatic esters	Ar=COO=Ar	+41.8
	Carboxylic anhydride	$$\begin{matrix} & O & & O \\ & \| & & \| \\ A^r - & C - & O - & C - \end{matrix}$$	+41.8
11	Secondary alcohol	R–OH	+54.4
	Ethylene bond	$$\begin{matrix} \diagdown & & \diagup \\ & C = C & \\ \diagup & & \diagdown \end{matrix}$$	+54.4
	Aliphatic and aromatic aldehydes	$$R - C \overset{\displaystyle O}{\underset{\displaystyle H}{\Big\langle}}$$	+54.4
	Aliphatic primary amines	Al_k–NH$_2$	+54.4
	Aromatic secondary amine	Ar–NH–Ar	+54.4
	Lactone	$$-C - C - C - C = O$$ $$\quad\; H \; H$$ $$\;\; \rule{0pt}{0pt}\, O \, \rule{0pt}{0pt}$$	+54.4
	Aliphatic radical and chlorine (bromine)	Al_k–Cl(Br)	+54.4
	Aromatic radical and bromine	Ar:Br	+54.4
	Aromatic esters	Ar–COO–Ar	+54.4
12	Aliphatic esters	$$\begin{matrix} & O & \\ & \| & \\ R - & C - & OR \end{matrix}$$	+69.1
	Aliphatic radical and nitrile group	Al_k–CN	+69.1
13	Ethers	R$_1$–O–R$_2$	+91.6
	Aliphatic secondary amine	(Al$_k$)NH	+91.6
	Aromatic tertiary amine	Ar$_3$N	+91.6
14	Aliphatic tertiary amine	(Al$_{k)3}$N	+108.6
15	Alkyne bond (completely substituted)	R–C≡C–R	+138.5
	Isonitriles in the aliphatic series	R–N=C	+138.5
16	Derivatives of aliphatic iodine	R:I	+167.8
17	Alkyne bond	H–C≡C–H(R)	+192.9

$$Q_{pm} = 26.05(4a + b - p) + \sum \zeta_j \Delta_j \qquad (3.17)$$

where,

a, b   the molar numbers of carbon atom and hydrogen atom in 1 mol (or 1 kg) of the material,

p   number of electrons of carbon and hydrogen atoms connected to oxygen atoms, i.e., the number of C–O and H–O bonds;

ζ_j j-type substituents in the molecule including the number of short covalent bond,

Δ_j thermochemical corrected value of j-type substituent.

This equation is good to calculate, relatively accurately, the combustion heat of liquid explosives. While, in the calculation of combustion heat of solid explosives, the right part of equation must be deducted off its fusion heat. If the substance is gas, the vaporization heat should be added. In this method, the standard temperature used is T_b = 298.15 K.

Therefore, the formation heat can be calculated according to the substance formula and combustion heat of final products after the complete combustion. The calculation method is still explained with the triangular diagram, which is similar to that to obtain explosion heat (Fig. 3.4).

In Fig. 3.4, State 1 corresponds to a stable state of a simple element, State 2 corresponds to the explosive, and State 3 corresponds to the combustion products of explosive, thus, the following can be obtained.

$$Q'_{1,2} + Q'_{2,3} = Q'_{1,3}$$

And the formation heat of explosive $Q'_{1,2}$ can be obtained from the following equation:

$$Q'_{1,2} + Q'_{1,3} = Q'_{2,3}$$

Fig. 3.4 The *triangle* diagram to calculate combustion heat
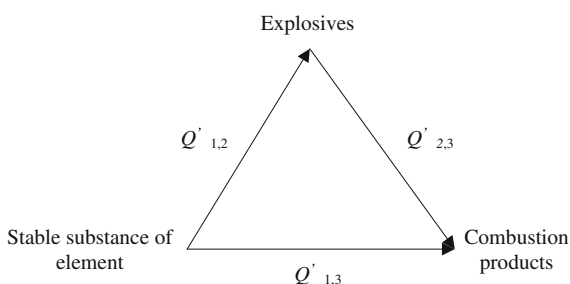
where, $Q'_{1,3}$ is the total of formation heat of all products from the complete combustion, $Q'_{2,3}$ is combustion heat of the explosive, which is the calculated value from Eq. 3.17, i.e., Q_{pm}.

In order to calculate the fusion heat and evaporation heat of the material, the following approximate method can be used to calculate.

Fusion heat of some explosives can be calculated as the following:

In organic explosives (or compounds),

$$q_{fus} = 0.0135T_{fus} \tag{3.18}$$

Inorganic explosives (or compounds),

$$q_{fus} = 0.006T_{fus} \tag{3.19}$$

Simple material,

$$q_{fus} = 0.0025T_{fus} \tag{3.20}$$

Vaporization Heat of some explosives can be obtained as the following:

In nonpolar liquid,

$$q_{vap} = 0.213T_{bp} \tag{3.21}$$

where,

T_{fus} melting point, K,
T_{bp} boiling point, K.

In order to further show the formation heat of liquid explosives, combustion heat and formation heat of nitroglycerine will be calculated in detail as an example.

The formula of nitroglycerin is known as $C_3H_5(ONO_2)_3$, where, $a = 3$, $b = 5$ and $p = 3$. As listed in Table 3.9, the correct value of R-ONO_2 is 0. Therefore, according to Eq. 3.17, the combustion heat of nitroglycerine is,

$$Q_c = 26.05 \times (3 \times 4 + 5 - 3) + 0 = 26.05 \times 14 = 1525.9 \, kJ$$

Then, formation heat of nitroglycerine can be calculated according to Hess's law.

The combustion reaction equation of nitroglycerine is,

$$C_3H_5(ONO_2)_3 \rightarrow 3CO_2 + 2.5H_2O + 1.5N_2 + 1525.9 \, kJ$$
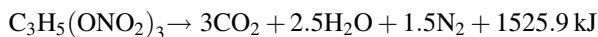
Thus, the formation heat of nitroglycerine is,

$$Q'_{1,2} = Q'_{1,3} - Q'_{2,3} = 94.5 \times 3 + 68.4 \times \frac{5}{2} - 364.7 = 454.5 - 364.7$$
$$= 375.72\,\text{kJ/mol}$$

3.2.3 Design of Explosion Temperature of Explosive

3.2.3.1 Explosion Temperature of Explosive

The highest temperature of explosion products heated by the explosion energy is the explosion temperature, which is an important characteristic factor of explosive. Because temperature change is extremely fast and high and can be up to several thousand degrees during the explosion, calculation of explosion temperature theoretically would have a very important practical significance in the formulation design of explosive.

Measuring method of explosion temperature is to determine the color temperatures of instant explosion products. The spectra are used to study the distribution of energy in the spectra, and this energy distribution is compared with that in absolute blackbody spectrum to obtain explosion temperature data. However, because the actual radiator explosion product is not an ideal blackbody, the calculated temperature is called color temperature, and this color temperature is generally slightly higher than the actual temperature. And measured explosion temperatures of some explosives are listed in Table 3.10.

Theoretical calculation of explosion temperature:

The application of explosives has certain requirements. For example, combusting agents are required to have higher combustion temperatures, and mining explosives are required to have lower explosion temperature that guarantees to avoid firedamp explosion accidents during the mine explosion.

In order to simplify the theoretical calculation of explosion temperature, the following three assumptions are made first and these assumptions, whether in theory or in practice, are allowed and do not cause large deviation in the calculation. These assumptions are

a. the explosion is approximately regarded as a constant-volume process,
b. the explosion process is adiabatic, all of the released heat from explosion is used to heat the explosion products,

Table 3.10 Measured explosion temperatures of several explosives

Explosive	Nitroglycerine	RDX	PETN	TNT	Tetryl
Density (g/cm^3)	1.6	1.79	1.77	–	–
Explosion temperature (K)	4,000	3,700	4,200	3,010	3,700

c. thermal capacity of explosion product is only a function of temperature, and is independent of the pressure (or density) during the explosion.

These assumptions could cause relatively large error in the calculation of explosion temperature of high-density explosives.

A. Explosion temperature calculated from the average thermal capacity of explosion products

Based on the above assumptions, the following relationship can be obtained,

$$Q_v = \overline{C_v} t \tag{3.22}$$

where,

Q_v explosion heat of explosive,

$\overline{C_v}$ the average thermal capacity of all explosion products at temperatures from 0 to t °C,

t the required explosion temperature, °C.

The general relationship of thermal capacity with temperature is,

$$\overline{C_v} = a + bt + ct^2 + dt^3 + \cdots \tag{3.23}$$

Generally, in calculations that are not too complicate, only the first two are chosen, which means that thermal capacity and temperature have a linear relationship, thus,

$$\overline{C_v} = a + bt \tag{3.24}$$

According to Eq. 3.22, the following can be obtained,

$$\begin{aligned} Q_v = \overline{C_v} t = (a + bt)t \\ bt^2 + at - Q_v = 0 \end{aligned} \tag{3.25}$$

Therefore, the explosion temperature is,

$$t = \frac{-a + \sqrt{a^2 + 4bQ_v}}{2b} \tag{3.26}$$

When this method is used to calculate explosion temperature, explosion reaction equations, ingredients of explosion products and thermal capacity of explosion products must be known. In the calculation, thermal capacity of explosion products can be that of their gas molecules as listed in Table 3.11.

Thermal capacity values in Table 3.11 are good at 4,000 °C or below, but the experimental temperature for these data is 2,500–3,000 °C. Thus, its extrapolated temperature is too high and the necessary correction should be done. Additionally, Al_2O_3 is only useful at a temperature of 0–1,400 °C.

Table 3.11 Average molecular thermal capacity parameters

Atomic state	Thermal capacity parameter
Two-atom gas	$\overline{C_v} = 4.8 + 4.5 \times 10^{-4}\,t$
Water vapor	$\overline{C_v} = 4.0 + 21.5 \times 10^{-4}\,t$
Three-atom gas	$\overline{C_v} = 9.0 + 5.7 \times 10^{-4}\,t$
Four-atom gas	$\overline{C_v} = a + bt$
Five-atom gas	$\overline{C_v} = 12 + 4.5 \times 10^{-4}\,t$
Carbon	$\overline{C_v} = 6.0$
Salt	$\overline{C_v} = 28.3$
Aluminum oxide	$\overline{C_v} = 23.86 + 67.3 \times 10^{-4}\,t$

Now, with TNT as an example, the explosion temperature is calculated, and TNT explosion reaction equation is,

$$C_6H_2(NO)_2CH_3 \rightarrow 2CO_2 + CO + 4C + H_2O + 1.2H_2 + 1.4N_2 + 0.2NH_3 + 1113.28\,\text{kJ/mol}$$
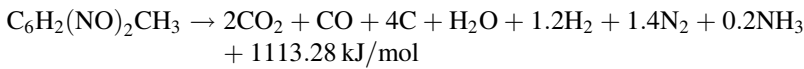
The thermal capacity of TNT explosion products is the following:
In two atomic gas, $\overline{C_v} = (1 + 1.2 + 1.4)(4.8 - 0.00045\,t) = 17.28 + 0.00162\,t$;
In water, $\overline{C_v} = 1 \times (4.0 + 0.00215\,t) = 4.0 + 0.00215\,t$;
In CO_2, $\overline{C_v} = 2 \times (9.0 + 0.00058\,t) = 18.0 + 0.00116\,t$;
In NH_3, $\overline{C_v} = 0.2 \times (10.0 + 0.00045\,t) = 2.0 + 0.00009\,t$;
In C, $\overline{C_v} = 4 \times 6 = 24$.
Thermal capacity of all explosive products, $\sum \overline{C_v}t = 65.28 + 0.00502t$
So, $a = 65.28$ and $b = 0.00502$ are introduced into Eq. 3.26, then,

$$t = \frac{-65.28 \pm \sqrt{65.28^2 + 4 \times 0.00502 \times 266.08 \times 1000}}{2 \times 0.00502} = 3{,}260\,°C$$

or

$$T = 3{,}260 + 273 = 3{,}533\ \text{K}$$

From the average molecular thermal capacity parameters, the calculated value is slightly low, thus the calculated explosion temperature t are slightly large.

B. Explosion product internal energy method

Internal energy of explosion product ingredients is another method to calculate the explosion temperature. The change of internal energy of explosion product with temperature has been calculated accurately as shown in Table 3.12.

In the explosion, Eq. 3.7 is believed to be a constant-volume process, i.e., $dV = 0$, while all of the released heat are used in the internal energy transition of explosion products, namely, $\Delta E = -Q_v$. Therefore, with energy data of explosion product change in Table 3.12, explosion temperature can be calculated.

Table 3.12 Internal energy values of some gases and graphite (C_solid) at 291–5,000 K (kJ/mol)

Temperature (K)	H_2	O_2	N_2	CO	NO	OH	CO_2	H_2O	NH_3	Graphite (C_{solid})
291	0	0	0	0	0	0	0	0	0	0
300	0.188	0.188	0.188	0.188	0.192	0.192	0.259	0.226	0.251	0.079
400	2.264	2.33	2.276	2.28	2.347	2.335	3.364	2.791	3.138	1.114
500	4.356	4.556	4.381	4.402	4.54	4.452	6.832	5.439	6.318	2.446
600	6.452	6.887	6.535	6.581	6.795	6.577	10.602	8.192	9.791	4.025
700	8.56	9.314	8.745	8.832	9.544	8.699	14.619	11.083	13.598	5.799
800	10.682	11.82	11.025	11.155	11.527	10.845	18.845	14.092	17.698	7.799
900	12.824	14.393	13.372	13.552	14.004	13.021	23.238	17.213	22.05	9.765
1,000	15.025	17.025	15.778	16.008	16.544	15.464	27.778	20.456	26.736	11.878
1,200	19.445	22.418	20.769	21.083	21.769	19.799	37.208	28.083	36.736	16.292
1,400	24.066	27.957	25.937	26.338	27.163	24.556	46.999	34.472	47.53	20.945
1,600	28.853	33.614	31.242	31.711	32.673	29.476	57.003	42.066	59.078	25.79
1,800	33.811	39.359	36.66	37.192	38.246	34.564	67.308	50.02	71.17	–
2,000	38.92	45.2	42.158	42.752	43.894	39.786	77.697	58.258	83.722	35.748
2,200	44.162	51.141	47.727	48.367	49.589	45.124	88.249	66.731	96.65	–
2,400	49.526	57.17	54.187	54.036	55.338	50.576	98.889	75.396	109.872	48.593
2,600	54.999	63.279	59.015	59.739	61.124	56.12	109.629	84.216	123.386	–
2,800	60.572	69.488	64.722	64.722	66.948	61.747	120.441	93.165	137.11	–
3,000	66.229	75.781	70.454	71.25	72.789	67.446	131.302	102.366	150.959	61.898
3,200	71.965	82.14	76.22	77.044	78.655	73.207	142.248	111.525	165.059	–
3,400	77.764	88.575	82.019	82.86	84.534	79.04	153.306	28.868	179.159	–
3,500	–	–	–	–	–	–	–	–	186.230	75.454
3,600	83.626	93.199	87.835	88.697	90.433	84.931	164.406	31.114	193.384	–

(continued)

Table 3.12 (continued)

Temperature (K)	H₂	O₂	N₂	CO	NO	OH	CO₂	H₂O	NH₃	Graphite (C_solid)
3,800	89.546	101.65	93.667	94.554	96.374	90.876	175.506	33.387	207.777	–
4,000	95.512	108.257	99.508	100.429	102.332	96.86	186.669	35.679	222.17	89.387
4,200	101.533	114.934	105.382	106.307	108.315	102.918	197.886	37.959	236.731	–
4,400	107.587	121.662	107.089	112.207	114.324	109.01	209.162	40.243	251.249	–
4,600	113.692	128.436	117.181	118.131	120.365	115.16	220.442	42.537	265.893	–
4,800	119.83	135.219	123.085	124.085	126.436	121.374	231.706	44.839	280.537	–
5,000	126.014	142.018	129.035	129.583	132.545	127.6	243.166	47.182	295.265	–

The temperature range listed in the table is 291–5,000 K. Calculation detail is in the following paragraph.

First, a explosion temperature is assumed. According to this explosion temperature and data in Table 3.12, all internal energy of explosion product ΔE is calculated, and compared with the explosion heat Q_v. If the deviation is very large, then another temperature is assumed to recalculate ΔE. If this ΔE is very close to Q_v, the assumed temperature can be considered as the explosion temperature.

With ammonium/TNT explosive mixture as an example, the explosion temperature is calculated now. Explosive reaction equations of TNT/ammonium nitrate explosive mixture is the following,

$$11.35NH_4NO_3 + C_7H_5(NO_2)_3 \rightarrow 7CO_2 + 25.2H_2O + 12.85N_2 + 0.425O_2 \\ + 4748.84\,kJ$$
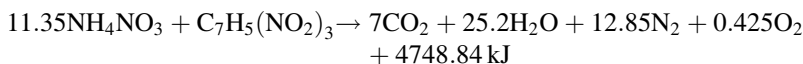
Assuming its explosion temperature is 3,200 K, we can obtain according to Table 3.12:

$$\Delta E_{CO_2} = 142.25\,kJ/mol$$
$$\Delta E_{H_2 0} = 111.52\,kJ/mol$$
$$\Delta E_{N_2} = 76.22\,kJ/mol$$
$$\Delta E_{O_2} = 82.14\,kJ/mol$$

Thus, the total internal energy is:

$$\Delta E = 7 \times 142.25 + 111.52 \times 25.2 + 76.22 \times 12.85 + 82.14 \times 0.425 \\ = 4862.23\ kJ/mol$$

This number is larger than $Q_v = 4748.84$, indicating the assumed temperature is a little bit high. Therefore, the explosion temperature is reassumed as 3,000 K and the following total internal energy can be obtained according to Table 3.12:

$$\Delta E = 7 \times 131.30 + 25.2 \times 102.37 + 12.85 \times 70.45 + 0.425 \times 57.78 \\ = 4436.30\,kJ/mol$$

This result shows that the assumed temperature is too low. Thus, explosion temperature of this explosive mixture is between 3,000 and 3,200 K. Assumed that ΔE value has a linear relationship with temperature within this temperature range, we can obtain:

$$T = 3200 \frac{-\frac{4862.23-4748.84}{4862.23-4436.30}}{200} = 3{,}163\ K$$

or

$$t = 3163 - 273 = 2{,}890\,°C$$

3.2.3.2 Influence Factors and Ways of Explosion Temperature of Explosives

According to the actual needs of application, the explosion temperature of the explosive need be adjusted usually.

The general equation to calculate explosion temperature is

$$t = \frac{Q_v}{C_v} = \frac{Q_{t\ \text{explosion production}} - Q_{t\ \text{explosive}}}{C_v} \tag{3.27}$$

where,

$Q_{t\ \text{explosion production}}$ the sum of formation heat of explosion products, and
$Q_{t\ \text{explosive}}$ the formation heat of explosive.

According to Eq. 3.24, in order to increase the explosion temperature t, you need to (1) increase the formation heat of explosion products $Q_{t\ \text{explosion production}}$, (2) reduce the formation heat of explosive itself $Q_{t\ \text{explosive}}$, and (3) reduce the thermal capacity of explosion products. The first two are to increase explosion heat, such as adjusting the oxygen balance to complete oxidization to produce large amounts of CO_2 and H_2O with relatively large formation heat, or adding some metal powders with high thermal value. In liquid explosives, the addition of hydrazines and increasing the amount of the oxidizer urea perchlorate are effective ways to increase the explosion temperature. When the heat was increased, we must take into account whether the thermal capacity of explosion products can be increased or not. Thermal capacities of CO_2 and H_2O (gas) are larger than that of two-atom gas. Thus, specific conditions should be considered in the calculation, otherwise, the desired effect cannot be obtained. Therefore, when the explosion temperature is increased, the combined effect of these three factors should fully be taken into account at the same time.

The addition of metal powders with a high thermal value, such as aluminum, magnesium, titanium, boron, etc. Because the formation heats of their explosion products are relatively large and their thermal capacities are not increased very much, their addition is beneficial to the increase of explosion temperature.

Metal powders and hydrogen can significantly improve the explosion temperature with the typical reaction as:

$$2Al + 1.5O_2 = Al_2O_3 + 1669.42\,kJ, \ C_v = 125.52\,J\ (3{,}000\,K).$$

$$3Mg + 1.5O_2 = 3MgO + 1820.04\,kJ,\ C_v = 150.62\,J\ (3{,}000\,K).$$

$$1.5C + 1.5O_2 = 1.5CO_2 + 592.04\,kJ,\ C_v = 75.31\,J\ (3{,}000\,K).$$

$$3H_2 + 1.5O_2 = 3H_2O + 725.5\,kJ,\ C_v = 112.97\,J\ (3{,}000\,K).$$
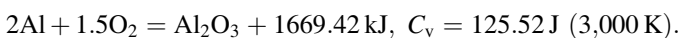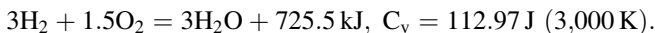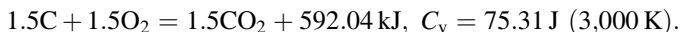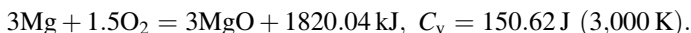
Although thermal capacity of combustion products of aluminum and magnesium is slightly higher than that of C and H_2, energy released from the oxidation of aluminum and magnesium is much larger than that from the oxidation of C and H_2, thus adding aluminum and magnesium can increase the explosion temperature.

In order to reduce the explosion temperature, complements or additives are generally added into the explosive. These additives can change the ratio between oxygen and combustible elements to cause incomplete oxidation products and thus to reduce the formation heat of explosion products. Some additives are not involved in the explosion reaction and only increase the total thermal capacity of explosion products.

In order to eliminate the muzzle flame and reduce erosion, usually hydrocarbons, resins, fatty acids and their esters, and nitro derivatives of aromatics esters with low nitration level are added into the explosive.

In the industrial safety explosive, the following materials are added: sulfate, chloride, nitrate, bicarbonate, oxalate, etc., and sometimes these salts with crystallized water can be used as a suppressing agents.

3.2.4 Comprehensive Parametric Design of Liquid Explosives [5]

Neat solution-type liquid explosives are molecular mixture of all components with the best dispersion, mixing homogeneousness, and density consistency. Liquid explosives with suspended solid particles has the liquid primary explosive as the continuous media to form a sol–gel with the help of thickening agents, and their solid phase is suspended homogeneously in the system to form a mixture system. And the solid particles are surrounded by the liquid phase solution, and there are relatively ideal dispersion and uniformity of every component. Therefore, both of these two liquid explosive mixtures have sufficient explosion thermochemical reaction conditions, which makes almost all chemical potentials of the explosive system can be released in the explosion reaction zone. And the calculation of liquid explosives with the dispersion of solid particles can be done according to the explosion property parameters of general explosive mixtures.

Example 1 Calculate explosion parameters of liquid explosive with 72 % of nitric acid (mass concentration of 98 %) and 28 % of nitrobenzene. The explosive density is known to be 1.40 g/cm^{-3}.

Table 3.13 Formation enthalpy of 100 g of explosive

Component	Mass (100 g/g)	The amount of material (mol)	Formation enthalpy (J mol^{-1})
HNO$_3$	70.56	1.12	−173.0
C$_6$H$_5$NO$_2$	28.0	0.2276	11.2
H$_2$O	1.44	0.08	−285.9

Solution:

Let $M = 100$, then, these basic data as listed in Table 3.13 can be obtained according to the known conditions.

Composition of each element in the 100 g liquid explosives is $C_{1.366}H_{2.418}N_{1.348}O_{3.895}$. And this explosive has a slightly negative oxygen balance and belongs to that of $c - b/2 - 2a < 0$. Thus, the following calculation can be done according to $c - b/2 - 2a < 0$ and Eqs. 3.9, 3.10 and 3.12,

$$Q = 5993.5 \text{ J g}^{-1}$$
$$\omega = 14.04$$
$$\Gamma_0 = 2.4526$$

Thus,

$$v_D = 33.0 \times (5993.5)^{0.5} + 243.2 \times 14.04 \times 1.40$$
$$= 7,335 \text{ m s}^{-1}$$

v (measured) $= 7,300$ m s^{-1}

$$r = 1.25 + 2.4526 \times \left(1 - e^{-0.5461 \times 1.4}\right)$$
$$= 2.56$$

$$P_{C-J} = \frac{1.40 \times (7335)^2 \times 10^{-6}}{1 + 2.56} = 21.16 \text{ (GPa)}$$

The calculated values and the measured values of several liquid explosives are listed in Table 3.14. The experimental data of explosion pressure are rarely reported and the measured data are related to experimental methods with significantly large error, therefore, only the explosion velocity data are listed in the table for comparison.

Table 3.14 Comparison of experimental explosion velocities of several liquid explosives to their calculated values

	Formula	ρ (g cm^{-3})	v_D (calculated) (m s^{-1})	v_D (experimental) (m s^{-1})	The relative error × 100
1	75C(NO$_2$)$_4$(98 %)/ 25C$_6$H$_5$NO$_2$(95 %)	1.47	7,698	7,510	+2.5
2	72HNO$_3$(98 %)/ 28C$_6$H$_5$NO$_2$	1.40	7,335	7,300	+0.48
3	65H$_5$N$_3$O$_3$/5N$_2$H$_4$/ 8NH$_2$CH$_3$/22H$_2$O	1.28	7,220	7,280	−0.79
4	80H$_5$N$_3$O$_3$/ 20N$_2$H$_4$·H$_2$O	1.421	8,542	8,491	+0.60
5	77TNEOF/ 23C$_2$H$_5$NO$_2$	1.496	7,421	7,440	−0.25
6	77.1TNEOF/ 22.9C$_2$H$_5$NO$_2$	1.533	7,544	7,545	−0.40
7	69.7TNEOC/ 30.3CH$_3$NO$_2$	1.480	7,324	7,350	−0.35

3.3 Design on the Uniformity and Stability of Liquid Explosives

Although the liquid explosives are multicomponent mixture systems, they have good component uniformity and density consistency. And the solution-type liquid explosive is an intermolecular mixed explosive with the uniformity of pure solution. Although another liquid explosive with suspended solid particles has not uniformity as the former does, it also has relatively good uniformity in components and density, and physical stability of the system.

3.3.1 Solution-Type Liquid Explosives

In the design of solution-type liquid explosives, miscibility among all components should be considered specially, and solubility data of all main components in the desired operating temperature range should be obtained first. If the component ratio, determined according to solubility, does not meet the requirements of zero oxygen balance within this temperature range, additives should be considered. For example, in the hydrazine nitrate–hydrazine system, adding a certain proportion of ammonia can significantly reduce the freezing point of the mixture system because ammonia is the freezing inhibitor in this system to enlarge the temperature range of hydrazine nitrate–hydrazine liquid solution. In some liquid explosives, water can play a very good role as solvent. In the liquid explosive with hydrazine nitrate and aliphatic amines as the main components, a small amount of water in the components can

significantly increase the amount of oxidizers, such as hydrazine nitrate, dissolved in fatty amine, and water played a cosolvent (or solubilizer) role. When solute components of the liquid explosive cannot be completely dissolved in the solvent, a variety of substances with similar properties can be considered to increase their total dissolving amount in the solvent. As proved in experiments, when a sensitizer explosive (e.g., TNT) is dissolved in nitromethane, it does not affect the dissolution of other ingredients (such as RDX, PETN), which means every nitro compound sensitizer can reach its own solubility without affecting each other in nitromethane.

3.3.2 Liquid Explosives with Small Solid Particles [8]

Suspension systems of sticky slurry and paste-like liquid explosives with solid particles, based on the dispersion of suspended solid particles, should belong to suspension or coarse multiphase systems in colloid chemistry. In these suspension systems, the main issue is its dynamic instability, because the density of the dispersed particles and the density of the dispersion medium are different (generally, the density particle is greater than that of the medium), settlement or floating can occur with the role of gravitational field to separate the system, resulting in unevenness in composition and density of liquid explosive. Stability is the ability to overcome the so-called sink-and-float separation of two-phase components, therefore, within a certain period of use, the composition and density of explosive and other physical parameters remained unchanged and its properties are stable and reliable.

Here, the method of increasing the viscosity of the suspension system to reduce settling velocity of suspended particles will be mainly discussed. The general method to increase the viscosity of suspending medium is to add tackifier. There are two types of tackifiers: (1) polymer and (2) some ultrafine inorganic materials, such as carbon black, silica, alumina, etc. Polymer tackifier is usually dissolved in the suspension medium, and polymer concentration is adjusted to achieve the desired viscosity and their roles are generally based on their dissolving or swelling in the liquid medium. Roles of ultrafine inorganic materials are based on the interaction between their huge surface areas and the liquid medium, and suspension systems with these dispersions usually have thixotropy and abnormal viscosity.

$$\eta = \eta' + \eta'' \tag{3.28}$$

wherein η' is Newton viscosity, η'' is structure viscosity, which can disappear due to the tangential stress changes or mechanical action. Advantages of this tackifier is to lead to a relatively high viscosity of the system at a static status, which is very conducive to the stability of suspension system; and the dynamic viscosity is not high, which does not affect the flow and transport of the material system. Therefore, this tackifier is often used in liquid explosive recipes. Most of tackifiers are inert,

Table 3.15 Effects of amounts of nitromethane and silica on viscosity and explosion velocity of explosive

Additives	Amount (%)	Viscosity (n)	Brisance (mm)	Explosion velocity (m/s)	Strength (mL)	Detonation transmission distance (cm)
White carbon black silica	2.5	125	26.3	5,960	398	20
	5.0	197	30.5	6,490	416	39
	8.0	310	41.7	7,310	479	65
PMMA	2.5	157	24.6	5,740	336	27
	5.0	262	27.4	5,930	297	48

thus high efficient material should be selected as tackifier that can achieve the necessary tackfying effect with only a small amount. As listed in Table 3.15, nitromethane explosive is added with 0.5 % of (Cab–O–Sil) silica gelling agent to improve its viscosity, thus to stabilize microparticles of aluminum and part of RDX to suspended in the system.

However, the other two slurry and pasty explosives stabilize aluminum powder and RDX particles in the mixture system through dissolving polymer nitrocellulose (1–2 %) in nitroalkanes.

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Chapter 4
Liquid Nitro Explosives

4.1 Introduction

Liquid nitro explosives are mainly liquid nitro-containing aliphatics, aromatics and alcohols. Among these compounds, nitro alkane is a very important liquid explosive, which has a certain explosive power. Thus, nitro alkane is an important energy-containing component to produce liquid nitro explosive mixtures and also an important raw material for other nitro derivatives. Additionally, liquid nitro compounds also have applications very widely in the solvent and chemical industries.

Hydrogen atoms on α-carbon of primary and secondary nitroalkane are very active to have many chemical reactions, whereby many derivatives can be produced. Because t-nitroalkane molecule does not have any α-hydrogen atom, some reactions could not take place [1]. Because α-hydrogen atoms in 1,1-dinitroalkane and trinitromethane are influenced by several nitro groups, their chemical properties are more active than those in mononitroalkane. Nitro alcohols are derivatives of nitro alkanes, which are important liquid explosives and the key intermediates of many nitro explosives and propellants; mono nitro aromatic compounds and a few dinitro compounds are liquid; because the electron withdrawing effect of $-NO_2$ decreases the electron density on other positions of the aromatic ring, hydrogen atoms turn to be particularly active and easy to be substituted. In this chapter, liquid nitro explosives are nitroalkanes, heteroatom-containing nitroalkanes, nitro alcohols and nitro or dinitro aromatic compounds; because nitrobenzene and nitrotoluene are two well-known nitro compounds, they not be discussed in this chapter again.

4.2 Properties of Liquid Nitro Explosives

Nitroalkane, nitrobenzene, nitrotoluene and nitro alcohol are common and the most-used liquid nitro explosives. Physical and chemical properties, and explosive performance of these liquid explosives are significantly different with different composition or structures.

4.2.1 Physical Properties of Liquid Nitro Compounds

Lower homologs of nitroalkanes are usually colorless and transparent liquid with density that is slightly larger than that of water, and fragrance. With the growth of carbon chain, boiling point is gradually increased, and the density is decreased. The boiling point of nitroalkane is much higher than that of its isomer-nitrite ester; the solubility of mononitroalkane in water is decreased with the growth of carbon chain, it can be dissolved easily in most organic solvents, and it is not soluble in aliphatic and alicyclic hydrocarbons; Lower aromatic nitro compounds are difficult to dissolve in water, and solubility of nitro alcohol in water is greater than that of nitroalkane and lower liquid aromatic nitro compound. Lower nitroalkane itself is a good solvent to dissolve cellulose acetate, cellulose propionate, butyrate, nitrocellulose, vinyl resins, dyes, oils, fats, waxes and others; Because nitro alcohol, cyclic nitroalkane and nitrobenzene can dissolve most organics, nitroalkanes and lower cyclic nitro compounds are not only widely used in the liquid explosive industry, but also have broad application prospects in chemical industry.

Heat of combustion ($-\Delta H$) and oxygen balance of nitroalkane have an linear relationship [2], obeying the enthalpy equation with an error within 1.8 %.

$$-\Delta H_c = 176.9 \left[\frac{2x + \frac{y}{2} - z}{M} \right] + 7,499 \, \text{J/g}$$

wherein x, y and z are the number of oxygen atoms, hydrogens and carbons of the molecule, respectively; M is relative molecular mass.

Nitroalkane has two characteristic UV absorption peaks, including relatively strong absorption peaks at 210 and 280 nm (K_{max} = 23–26). Regardless of the locations of nitro groups, the extinction coefficient of dinitro compound is almost doubled, thus, the number of nitro groups can be determined from the extinction coefficient of the absorption peak; when nitro group and amino group, two or more hydroxyl groups form intramolecular hydrogen bonds, red shift effect will occur compared to that of the original nitroalkane, with peak shift of 8–20 mm [3, 4]. Nitro in nitroalkane has two infrared absorption peaks, and Fig. 4.1 shows the infrared spectrum of typical liquid nitro compound measured in our group.

As shown in Fig. 4.1, similar nitro compounds with substituted carbon atoms at different positions have different infrared absorption peaks. Infrared absorption peaks of different nitro compounds are shown in Table 4.1.

Fig. 4.1 A typical infrared spectrum of liquid nitro compounds. **a** Nitromethane, **b** Nitrobezene, **c** O-Nitrotoluene, **d** Nitroalcohol
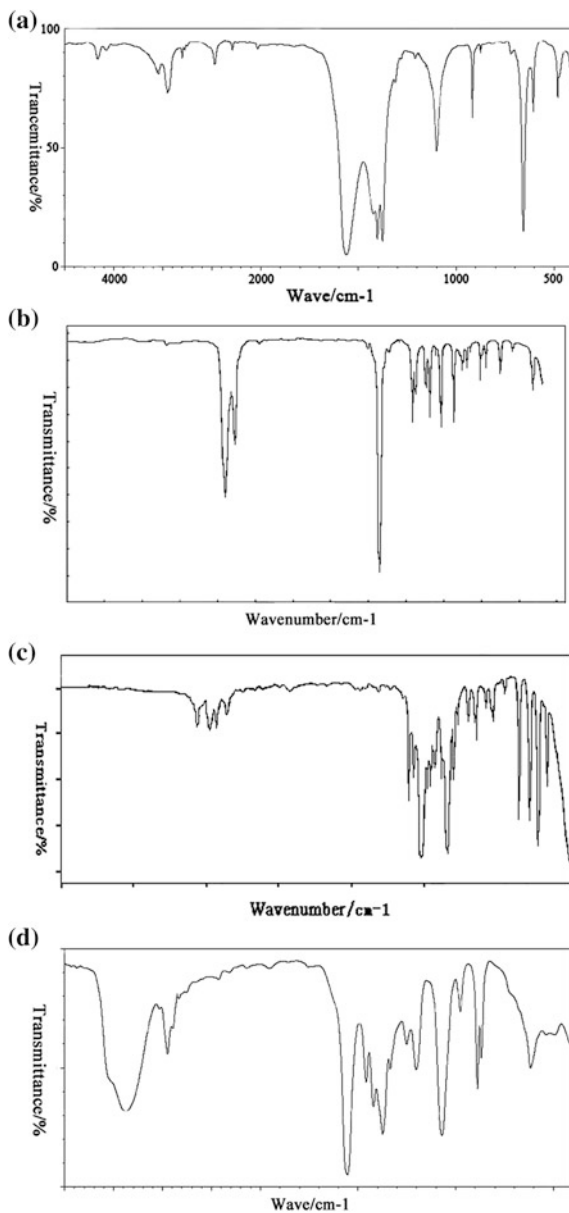
Table 4.1 Infrared
absorption peaks of nitro
groups [5]

Nitro compounds	σ_{as}/cm^{-1}	σ_s/cm^{-1}	$\Delta\sigma/cm^{-1}$
Primary nitroalkane	1,550–1,567	1,368–1,379	190
Secondary nitroalkane	1,545–1,565	1,360–1,383	180
Tertary nitroalkane	1,530–1,545	1,342–1,358	190
2,2-dinitropropane	1,575–1,587	1,327–1,337	250
Dinitromethane	1,538–1,550	1,375–1,389	150–200
1,1,1-trinitromethane	1,603	1,298–1,303	300
Nitrobenzene	1,510–1,540	1,345	200

Note $\Delta\sigma$ is the wavenumber of the two vibrations, therefore, the number of
nitro groups can be determined according to $\Delta\sigma$

4.2.2 Chemical Properties of Liquid Nitro Compounds

(1) Chemical Stability

Nitroalkanes have acidic isomers and tautomerism, in which primary and sec-
ondary nitroalkane are acidic because their α-hydrogen atoms are influenced by the
nitro group, and can be configured tautomerically into acidic structure.

$$RCH_2NO_2 \underset{}{\overset{K_i}{\rightleftharpoons}} RCHNO_2H$$

$$\Big\updownarrow K_a \qquad\qquad \Big\updownarrow K_{aci}$$

$$H^+ \qquad + \qquad RCHNO_2^-$$
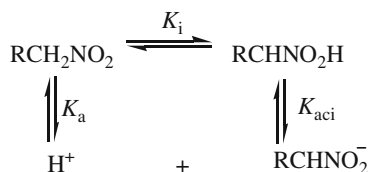
With the increase of the number of nitro groups in nitomethane, pKa is 10.2, 3.6
and 0.2, respectively [1]. The stability of nitroalkane salt is very poor, and can be
automatically decomposes with heat or long-term storage, and, especially, the dry
explosive nitro compounds salts are very sensitive to heat, impact, friction, static
electricity and flame; dry nitromethane salt may explode when it is getting wet, and
the sensitivity of salt of nitro group on aromatic ring is many times higher than that
of the corresponding nitro compounds; tert-nitroalkanes do not have any α-
hydrogen atom, thus, the above-mentioned tautomeric isomerization reaction could
not occur, and they could not react with bases to generate salts.

(2) Reaction with Acid

When equal amount of concentrated mineral acid and primary nitroalkane react,
a carboxylic acid and a hydroxylamine salt are generated, generally with yield of up
to 85–90 %. When sulfuric acid reacts with nitromethane [6], products are CO and
hydroxylamine sulfate. The mixture from the reaction between anhydride sulfuric
acid and a primary nitroalkane at 60 °C was poured into ice-water and then
treated with Ca(OH)$_2$, an intermediate, hydroxamic acid $\begin{smallmatrix} O \\ \parallel \\ (R\text{-}C\text{-}NHOH) \end{smallmatrix}$ between car-
boxylic acid and hydroxylamine can be produced with a yield of 55 %. Salt from

diluted mineral acid and primary nitroalkane or secondary nitroalkane can react as the following Nef reaction [7].

$$2R\text{-}CH{=}NOONa + 2H_2SO_4 \longrightarrow 2R\overset{\overset{\displaystyle O}{\|}}{C}H + 2NaHSO_4 + N_2O + H_2O$$

$$2 \ \overset{R'}{\underset{R}{\diagdown}}C{=}NOONa + 2H_2SO_4 \longrightarrow 2 \ \overset{R'}{\underset{R}{\diagdown}}C{=}O + 2NaHSO_4 + N_2O + H_2O$$
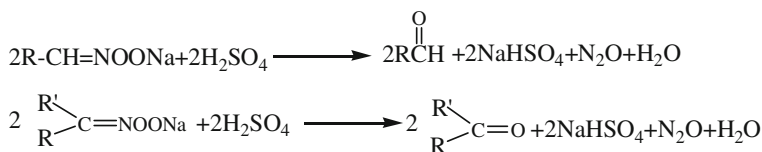
The yield of Nef reaction is generally up to 85 % (except for nitromethane). If the steric hindrance of this reaction is relatively large, the yield will be decreased significantly.

Primary and secondary nitroalkane react with nitrous acid, in which α-hydrogen atoms will be substituted.

$$RCH_2NO_2 + HNO_2 \longrightarrow R\overset{\overset{\displaystyle NO}{\diagup}}{\underset{\underset{\displaystyle NO_2}{\diagdown}}{C}}H \ \ +H_2O \longrightarrow R\text{---}\overset{}{\underset{\underset{\displaystyle NO_2}{}}{C}}{=}NOH$$

$$\underset{\text{1-nitroso-Nitroparaffin}}{} \qquad\qquad \underset{\text{Nitrosates}}{}$$

$$R_2CHNO_2 + HNO_2 \longrightarrow R_2\overset{\overset{\displaystyle NO}{\diagup}}{\underset{\underset{\displaystyle NO_2}{\diagdown}}{C}} \ + H_2O$$
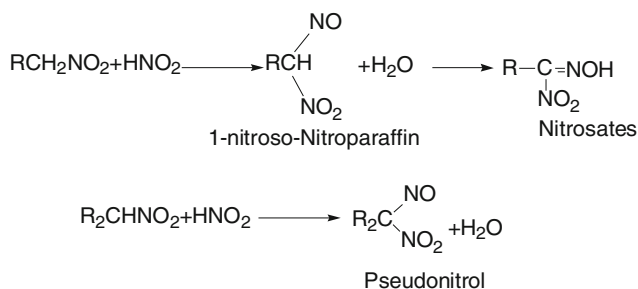
$$\underset{\text{Pseudonitrol}}{}$$

The neutralization of nitrolic acid and will generate crimson salt. Pseudonitrol from the reaction between nitrous acid and secondary nitroalkane does not have α-hydrogen atoms, cannot be rearranged and also have no color development reaction, which could be used to distinguish primary and secondary nitroalkanes.

Nitric acid (70 %) or the mixture of nitric acid and sulfuric acid or other mixed acids with catalytic function can nitrate secondary nitroalkanes directly into geminal dinitroalkane [8]. With the sodium alkoxide and tetranitromethane, primary nitroalkanes can be nitrated into dinitroalkanes and trinitroalkanes [9]. In a neutral or basic solvent, primary, secondary nitroalkane salts can be nitrated, step by step, into gem-dinitroalkanes by silver nitrate and sodium nitrite [10]. Alkali metal salts of aryl nitroalkanes can be nitrated, step by step, into dinitroalkanes and trinitroalkanes by dinitrogen tetroxide [11].

(3) Reaction with Base

Both nitroalkane and aromatic nitro compounds can react with bases to produce salts. Primary nitroalkane reacts with concentrated NaOH to generate trialkyl isoxazole [12].

$$4CH_3CH_2NO_2 \longrightarrow$$

$$+CH_3CN+2HNO_2+3H_2O$$
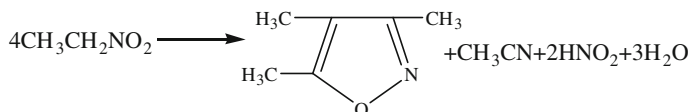
Primary and secondary nitroalkanes can react with sodium alcohol to form the adducts.
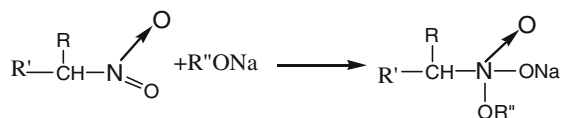
Dinitro compounds can be generated from slats of primary and secondary nitroalkanes, and secondary nitroalkane through α-**halogenation**, electrochemical reaction, oxidation or automatic decomposition [13–16].

(4) Reaction of an Oxidizing Agent and a Reducing Agent

Primary nitroalkanes react with oxidants to generate aldehydes, while ketones are generated from secondary nitroalkanes and oxidants. And this reaction can occur on nitro groups of aromatic ring [17].
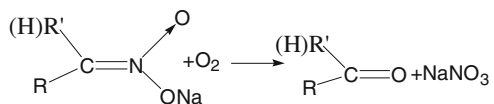
Nitrobenzene and nitro group on a aromatic ring can be reduced into hydroxylamine, oxime or amine. Only with a protective agent, it can be reduced nitroso compound, which is an intermediate reaction. If it starts from primary or secondary nitro compounds, oxime will be formed quickly through molecular rearrangement. When there is α-hydrogen atom, nitroso compounds can be obtained. When the reducing ability of agent is not enough, the product is a carbonyl compound, which will be rearranged into an oxime and further hydrolyzed into the corresponding aldehyde or ketone in acidic medium [18].

(5) Addition Reaction

Henry reaction can occur between nitroalkane and aldehyde to form β-nitroalcohol. Lower nitroalkanes can react with formaldehyde through addition reaction to form β-nitroalcohol.
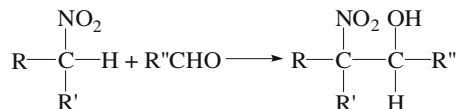
The first step of this reaction under basic catalysis is addition reaction of an nucleophilic reagent with a carbonyl group as the following:

$$R'CH_2NO_2 \longrightarrow R'\overset{-}{C}HNO_2 \xrightarrow{+R\text{-}CHO} R-\overset{\overset{O^-}{|}}{C}H-\overset{\overset{R'}{|}}{C}H-NO_2 \xrightarrow[-B^-]{+HB} R-\underset{\underset{OH}{|}}{C}H-\underset{\underset{R'}{|}}{C}H-NO_2$$
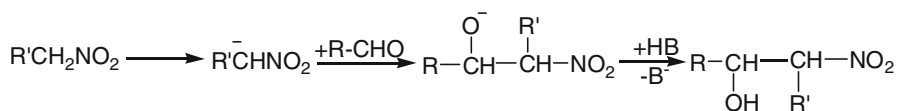
Acetal from the formed multi-nitro alcohol is the main energetic ingredient in liquid mixed explosives [19], and can be used as a rocket propellant. Formaldehyde and 2,2-dinitropropanol can generate acetal through addition reaction. The condensation reaction can be catalyzed by 96 % H_2SO_4, calcium chloride, zinc chloride, ferric chloride or boron trifluoride via catalytic polycondensation.

Mannich condensation reaction can occur between nitroalkanes and aldehydes with amines. t-nitroalkane does not have α-hydrogen atoms and can not have the Mannich condensation reaction.

$$\overset{\diagup}{\underset{\diagup}{C}}-H + HCHO + HN\overset{\diagup R}{\underset{\diagdown R'}{}} \longrightarrow \overset{\diagup}{\underset{\diagup}{C}}-CH_2-N\overset{\diagup R}{\underset{\diagdown R'}{}} + H_2O$$
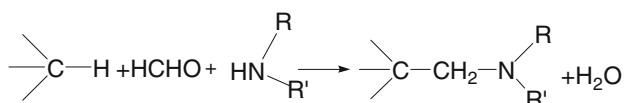
α-Hydrogen atoms in primary and secondary nitroalkanes are acidic, can make this reaction smoothly to generate an nitroalkylamine. A plurality of intermediates and many explosives can be synthesized through this reaction. Tertiary nitro compounds or tertiary amine can not have Mannich condensation reaction. In Mannich condensation reaction, in addition to formaldehyde, acetaldehyde and propionaldehyde also can be used.

Nitroalkane also can reacts with carbon–carbon double bonds via Michael nucleophilic addition reaction. And nitroalkanes with α-hydrogen atom can have such reaction under alkaline catalytic conditions.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NO_2 \ + H_2C{=}CHA \xrightarrow{Alkali} NO_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2A$$
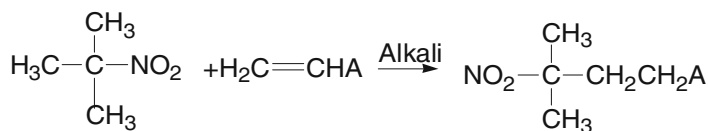
A in the equation represents a substituted aldehyde. An electron withdrawing group can activate the double bond and its the electron-withdrawing capability is related to the produced electronegativity, which are usually believed that nitro is the strongest followed by sulfonic acid group [20]. The double bond is between the substituted α, β carbons. α, β-Unsaturated carboxylic acids, carboxylic acid esters, nitriles, acids, ketones, sulfones, aldehydes, ethers, olefins and heterocyclic alkene can all react with nitroalkane via addition reactions to form the corresponding nitro-derivatives.

$$-NO_2 > -SO_3R > -CN > -COOR > -CHO > -COR$$
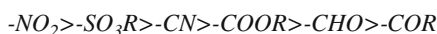
In the addition reaction, the used basic catalyst can be an alkali metal hydroxide, sodium carbonate and sodium alcohol. The addition reaction of multi-nitroalkane does not need a catalyst because it has a stable strong acidic anion.

In the addition of nitromethane with group containing a double bond, hydrogen atoms of nitroalkane are usually added to the atom of double bonds with less hydrogen atoms, but the opposite results will be obtained with the presence of unsaturated ethers. In the addition reaction between an unsaturated compound with conjugated double bonds and an nitroalkane, double bonds will be isomerized.

$$H_3CCH_2NO_2 + H_2C=CH\text{-}CH=CH\text{-}CN \longrightarrow H_3C\underset{\displaystyle \overset{|}{\underset{}{}}}{C}H\text{---}CH_2\text{---}CH=CH\text{---}NO_2$$

(with NO_2 on the CH carbon)

Nitroalkanes may also react with carbon-nitrogen double bond and nitrogen-nitrogen double bond via addition reaction to form nitroalkylamines and unsaturated nitro compounds [21].

$$\underset{R'\text{---}N}{\overset{R\text{-}CH}{\|}} + R''CH_2NO_2 \longrightarrow \underset{R'\text{---}C\text{---}NO_2}{\overset{R\text{-}CH}{\|}} + R'NH_2$$
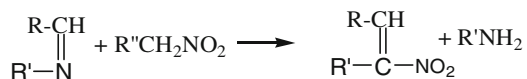
Most of these reactions only can take place under acidic medium. If the R group is an aromatic group, with an organic amine as catalyst, the reaction can take place with product of ω-nitrostyrene.

$$C_6H_5CHO + CH_3NH_2 \rightarrow C_6H_5CH = NCH_3 + H_2O$$
$$C_6H_5CH = NCH_3 + CH_3NO_2 \rightarrow C_6H_5CH = NCHNO_2 + CH_3NH_2$$
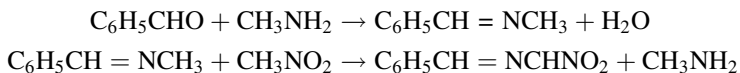
Nitroalkane and diazo salt can form the following product as:

$$\left[H_5C_6\text{-}\overset{+}{N}\equiv N\right]NO_2^- + H_3C\text{-}CH=N\underset{ONa}{\overset{O}{\diagup}} \longrightarrow H_5C_6\text{-}NH\text{-}N=\underset{NO_2}{\overset{}{C}}\text{-}CH_3 + NaNO_2$$
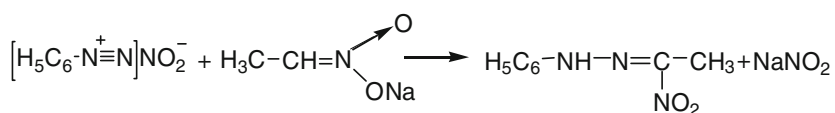
The product from this reaction can be dissolved in basic solution. With a secondary nitroalkane salt, the product was 2-nitro-2-phenylazopropane that is not dissolved in basic solution.

$$\left[H_5C_6\text{-}N\equiv N\right]^+ Cl^- + (H_3C)_2\text{-}CH=N\underset{ONa}{\overset{O}{\diagup}} \longrightarrow H_5C_6\text{-}N=N\text{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}NO_2 + NaCl$$
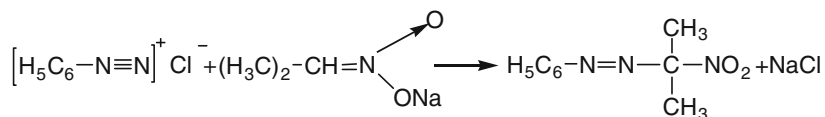
It is worth mentioning that, the addition product from nitroalkane and –N=N– double bond is not very stable and may explode or decompose to obtain the original

product. Nitroalkane, in the presence of boron trifluoride, reacts with potassium acetate to form the corresponding acetate [22].

$$CH_3NO_2 + (CH_3CO)_2O \xrightarrow{BF_3} CH_3-\overset{\overset{\textstyle O}{\|}}{C}-OCH_3$$
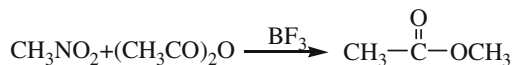
And a secondary nitroalkane reacts with aqueous solution of sodium azide and concentrated sulfuric acid to form an amide. The product from nitrocyclohexane is caprolactam with conversion of 59–86 %.

4.2.3 Explosion Properties of Liquid Nitro Compounds

In general, the lower nitro aromatic compound only is flammable and not explosive. Only nitro aromatic compounds with two or more nitro groups are explosive, and the explosive capability increases the increase of the number of nitro groups; the explosive capability is weakened with the increase of the number of carbon atoms in nitro aliphatic compounds; with the increase of nitro number on the same carbon atom, explosive capability is increased dramatically.

Mechanical sensitivity of the liquid aromatic nitro compounds is very lower and increased with the increase of the number nitro; mechanical sensitivity of liquid nitro aliphatic compound is decreased with the increase of carbon atoms, and the mechanical sensitivity is dramatically increased with the increase of nitro group number on the same carbon atom; for example, in nitromethane, its explosion limit is 7.3 % (volume) and its impact sensitivity is 0–8 % (hammer is 10 kg and characteristic drop height is 50 cm); mechanical sensitivity of nitro alcohol is lower than that of nitroalkane and aromatic nitro compounds.

4.3 Liquid Aliphatic Nitro Compounds

The simplest aliphatic nitro compound is nitromethane. Liquid aliphatic nitro compounds also include nitroalkanes including multi nitro groups and carbon atoms.

4.3.1 Properties and Preparation of Nitromethane

4.3.1.1 Properties of Nitromethane [23]

Formula: CH_3NO_2

Structure: $H-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}-NO_2$

Molecular weight: 61.04
Oxygen balance: −39.3 % (calculated according to the produced CO_2)
Content of nitrogen: 23 %

Nitromethane (NM) is a colorless and transparent liquid explosive with aromatic odor, a relative density of 1.1376, boiling point of 101.2 °C, freezing point of −28.55 °C, flash point of 43 °C (open cup) and refractive index of 1.3818^{20}. It is soluble in water, ethanol and basic solution, and its aqueous solution is acidic. Nitromethane is miscible with many organic matters to form azeotrope liquid. Itself is a good solvent and can be thickened after a small amount of nitrocellulose is added. Additionally, concentrated acid can decompose into nitromethane into ammonia, hydroxylamine and carbon oxides.

Further treatment with a base can generate a nitro acetic acid. At 50 °C, nitromethane was added dropwise into 50 % sodium hydroxide solution, followed by boiling and cooling, nitro sodium acetate can be obtained, which can be turned into nitro acetic acid with hydrogen chloride gas going through the suspended ether system.

$$CH_3NO_2 \xrightarrow[+H_2O]{H_2SO_4(thick)} HCOOH + NH_2OH \cdot H_2SO_4$$

$$HCOOH \rightarrow CO + H_2O$$

$$CH_3NO_2 \xrightarrow{H_2SO_4(thick)} NH_3 + H_2O$$
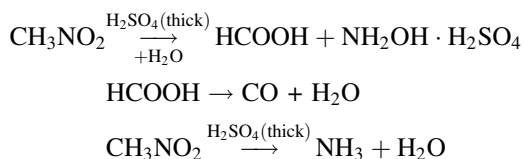
Nitromethane are particularly sensitive to base, and the reaction with base is different from that of other nitroalkanes, hydrazone acid can be formed through condensation reaction at low temperature (40–50 °C).

$$CH_2=NO_2H \longrightarrow H_2O_2N\text{-}CH_2\text{-}CH_2NO_2 \xrightarrow{-H_2O} ON\text{-}CH_2\text{-}CH_2\text{-}NO_2 \longrightarrow HO\text{-}N=CH\text{-}CH_2\text{-}NO_2$$
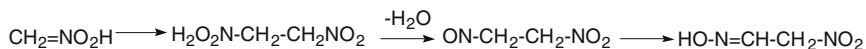
4.3.1.2 Thermal and Explosion Properties of Nitromethane

Standard heat of formation: −112.97 kJ/mol or −1850.75 J/g
Heat of combustion: −709.17 kJ/mol or −11618.1 J/g
Standard Gibbs free energy: −14.4 kJ/mol
Entropy: 171.8 kJ/mol
Heat capacity: 106.6 kJ/mol
Explosion limit: the low limit is 7.3 % (volume)
Explosion velocity: 6,320 m/s (ρ = 1.13 g/cm^3)
Explosion heat: 4539.6 J/g
Explosion volume: 1,092 mL/g
Specific volume: 936 cm^3/g
Explosion enthalpy: −5150 J/g
Explosion point: 420 °C
TNT equivalent: 470 mL

P_{c-J}: 13 GPa

Hit (impact) sensitivity: 0–8 % (drop weight of 10 kg, characteristic drop height of 50 cm)

Heat or vacuum stability: At 300 °C, the half-life of nitromethane is 30 days, it decomposes completely at 350–400 °C slowly, and its autocatalytic decomposition at above 400 °C generates explosion detonation.

At room temperature, the 8th detonator can detonate nitromethane, and the minimum shock energy to detonate nitromethane is 8–9 GPa. With the increase of temperature, explosion detonation sensitivity increases and the critical diameter decreases, but the explosion velocity is reduced, and the explosion velocity is 6,380 m/s at 4 °C, $\Delta D/\Delta T = -3.964 \pm 0.18$ m/s °C. At 25 °C, the maximum stable explosion velocity of nitromethane is 6,320 m/s.

4.3.1.3 Applications of Nitromethane

Nitromethane is active chemically, can have many chemical reactions as a chemical reagent or synthesis intermediate. It also can be used as solvents for cellulose nitrate, cellulose acetate, cellulose acetate, vinyl resin, polyacrylate coating, beeswax, etc.; base or other materials can be added into nitromethane for generate explosives; when nitromethane is mixed with strong oxidant hydrogen peroxide or N_2O_4, it can be used as liquid rocket propellants and fuel; nitromethane can also be used in medicine, dyes, insecticides, fungicides, stabilizers and surfactants.

4.3.1.4 Preparation of Nitromethane

Nitro Methane is the simplest nitro aliphatic compound with strong explosion properties, thus, it is a very important liquid explosive. Nitromethane can be produced directly through methane gas phase nitration [24, 25]. In the methane direct method, methane gas as a raw material reacts with nitric acid at 300–500 °C through gasification reaction followed by rough separation and distillation to obtain nitromethane. The advantage of this process is the wide sources of raw materials, and its disadvantage is that rich gas resources and relatively good production facilities are needed to build the production line, which has certain restrictions on the practice and poor selectivity. Because nature gas purity is not high, many byproducts will be produced. In addition to the methane direct method, tmethods to prepare nitromethane include nitrite slat substitution method [26], sodium nitrite halogenated alkyl method [27], refluxing nucleophilic displacement between dimethyl sulfate and sodium nitrite [28]. Liquid methane and its derivatives can be liquid-nitrated at about 200 °C, in which the nitration rate depends on the concentration of nitric acid and the reaction temperature. With nitric oxide as catalyst, special attention should be paid to controlling the explosion limit concentration of nitric oxide and hydrocarbons. The main reactions are:

$$4CH_4 + 3N_2O_4 \rightarrow 4CH_3NO_2 + 2NO + 2H_2O$$
$$2H_2O + 3N_2O_4 \rightarrow 4HNO_3 + 2NO$$
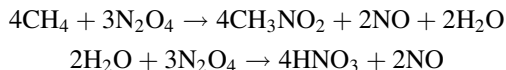
When there is dehydrating agent in the reaction mixture, the formation of nitric acid can be prevented. Therefore, increasing the reaction temperature, shortening the reaction time and increasing oxygen can increase the conversion rate of nitration. In the preparation of nitromethane from sodium nitrite and alkyl halide, sodium sulfite is added into an autoclave with a mixture of water and acetonitrile as the solvent and ammonium chloride as catalyst, and methyl chloride is pressed into the autoclave. After 4–6 h at room temperature, nitromethane is prepared, and this process has advantages of relatively low temperature and good production safety; but the large investment in equipment, very low conversion of sodium nitrite or chlorine methane (usually only of 15–36 %) and difficult separation of the crude product from the solvent are its drawbacks.

In sodium nitrite and acid salt replacement method [29, 30], ammonium chloroacetate as a raw material reacts with sodium nitrite mainly through the following reactions.

$$ClCH_2CO_2NH_4 + NaNO_2 \rightarrow NO_2CH_2CO_2NH_4 + NaCl$$
$$NO_2CH_2CO_2NH_4 + H_2O \rightarrow CH_3NO_2 + NH_4HCO_3$$
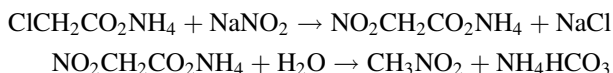
The advantages of this process include the following: The byproducts can be used as industrial raw materials and agriculture fertilizer, therefore the production process does not have industrial pollution, the investment in production equipment is low, there is no security risk, and the product purity is high. Its disadvantages are the high production costs and the reduced yield of nitromethane. In China, this technology method is generally adopted, but some European and American countries have this preparation process with product yield of 40–70 %.

However, the replacement reaction between sodium nitrite and dimethyl sulfide to prepare nitromethane is very moderate and the reaction principle is:

$$(CH_3)_2SO_4 + 2NaNO_2 \rightarrow CH_3NO_2(much) + CH_3ONO(little) \uparrow + NaSO_4$$
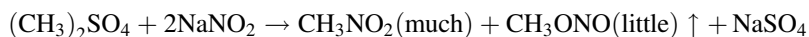
In this reaction, the yield of nitromethane can be up to 55–78 %. Its advantages are: raw materials are cheap with wide source, equipment investment is low, operation is simple, production cost is low, and it is easy to implement industrial production. However, the toxicity of dimethyl sulfate in this production process is high, and the produced methyl nitrite should be absorbed with basic solution, etc. The disadvantage of lye. Nevertheless, in China and most Asian countries, this process route has been adopted to produce nitromethane.

Therefore, the important and urgent issues are: how to optimize nitromethane process to reduce pollution, improve product yield, reduce production costs, simplify the operation, and achieve the environmental and friendly green process.

Based on the sodium nitrite and dimethyl sulfate replacement reaction to produce nitromethane, Some [31] used tetrabutylammonium bromide as a catalyst to achieve nucleophilic substitution to improve the conversion. And the obtained purity of nitromethane can be up to 99.9 % with methyl nitrite as the byproduct. The main raw materials are dimethyl sulfate and sodium nitrite with a feeding molar ratio of 1:2, and its synthesis mechanism is:

$$(CH_3)_2SO_4 + 2NaNO_2 \rightarrow CH_3NO_2 + CH_3ONO \uparrow + Na_2SO_4$$
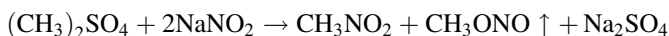
This overall chemical reaction can be explained step by step as the following: The first methylation step:

$$(CH_3)_2SO_4 + NaNO_2 \rightarrow CH_3NO_2(much) + CH_3ONO(little) \uparrow + CH_3NaSO_4$$
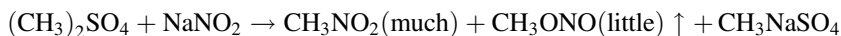
The second methylation step:

$$CH_3NaSO_4 + NaNO_2 \rightarrow CH_3NO_2(much) + CH_3ONO(little) \uparrow + Na_2SO_4$$
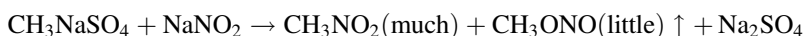
The hydrolysis of dimethyl sulfate under basic or acidic conditions:

$$(CH_3)_2SO_4 \begin{cases} \xrightarrow{OH^-} 2CH_3OH + SO_4^{2-} \\ \xrightarrow{H^+} 2CH_3OH + H_2SO_4 \end{cases}$$

$$CH_3NaSO_4 \begin{cases} \xrightarrow{OH^-} CH_3OH + Na_2SO_4 \\ \xrightarrow{H^+} CH_3OH + NaHSO_4 \end{cases}$$
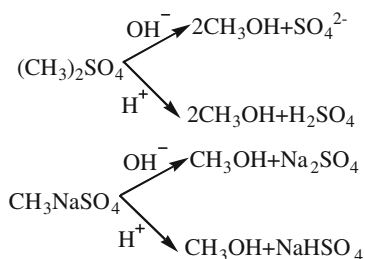
Reactions of nitromethane with acid and base:

$$CH_3NO_2 + HCl \rightarrow NH_2OH \cdot HCl + CO \uparrow$$
$$CH_3NO_2 + NaOH \rightarrow CH_3OH + NaNO_2$$
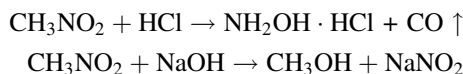
Reactions of nitrous acid:

$$N_2O + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} ONO + H^+$$

$$ONO + (CH_3)_2SO_4 \begin{cases} \nearrow CH_3ONO \\ \searrow CH_3NO_2 \end{cases}$$
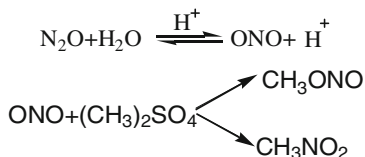
Based on the analysis and comparison of the mentioned chemical reactions, it can be known that: ① In the main reaction, it is easy to produce methyl nitrite, which makes it difficult to increase the total yield; ② the product is not stable under acidic conditions; ③ dimethyl sulfate is very easy to decompose into methanol under acidic and basic conditions; ④ dimethyl sulfate reacts with sodium nitrite through two steps, in which the first step is the conversion of dimethyl sulfate into the intermediate methyl sulfonate followed by the higher energy-required reaction between methyl sulfonate and sodium nitrite, thus, in this step, the formation of byproduct methanol should be minimized through the hydrolysis of acid and base.

In order to improve the yield of nitromethane, the first step hydrolysis damage of dimethyl sulfate should be avoided, and decreasing reaction temperature is favorable to the reaction; because the hydrolysis of dimethyl sulfate is related to the pH value, strict controlling on the pH can avoid the damage on dimethyl sulfate, sodium sulfide, nitromethane; catalyst can further accelerate the reaction, reduce the side reaction hydrolysis and significantly improve the yield and quality of product. The reaction is:

$$(CH_3)_2SO_4 + 2NaNO_2 \xrightarrow[\text{pH6-9}]{\text{Na}_2\text{CO}_3\text{aq}} CH_3NO_2(\text{much}) + CH_3ONO(\text{little}) \uparrow + Na_2SO_4$$
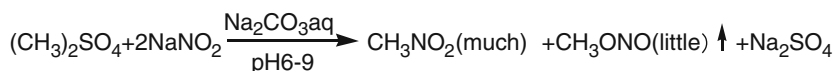
According to this equation, the synthesis process of nitromethane is shown in Fig. 4.2.

As shown in Fig. 4.2, when the ratio of dimethyl sulfate over sodium nitrite is 1:1.25, effects of various factors during the synthesis on yields is listed in Tables 4.2, 4.3, 4.4, 4.5 and 4.6.

The systems to synthesize nitromethane is shown in Fig. 4.3.

Based on these results, the optimum process controlling conditions and raw material parameters are: Dimethyl sulfate: sodium nitrite is 1:1.29, the reaction temperature is from room temperature to 53–57 °C, distillation temperature is
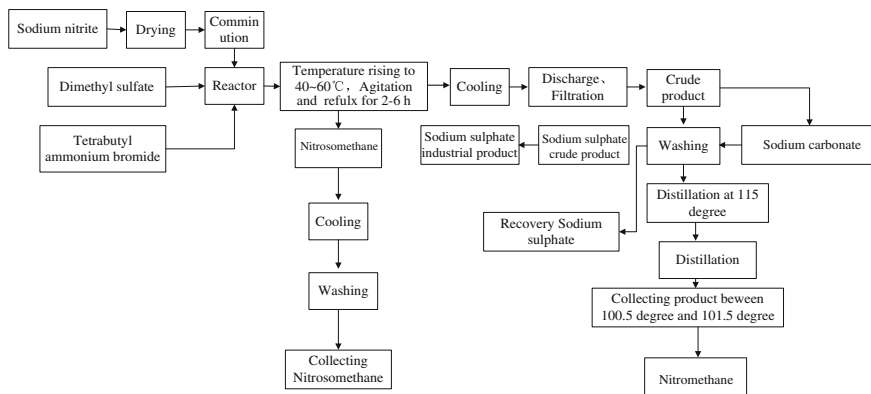
Fig. 4.2 Process of sodium nitrite replacement method to produce nitromethane

50–120 °C, the amount of sodium carbonate is 4.0–5.5 % (pH should be kept at 6.5–7.5 during its addition), reaction time is 4.5–5.5 h, catalyst is tetrabutylam-monium bromide, the amount of catalyst is 0.5 %, the water and methanol liquid after nitromethane distillation is reused, the yield is 79.8 %, and the purity is ≥99.9 % (Table 4.7).

Table 4.2 The relationship between the mass ration of dimethyl sulfate over sodium nitrite and nitromethane

Dimethyl sulfate: sodium nitrite	1:0.5	1:0.75	1:1	1:1.25	1:1.5	1:1.75	1:2.0
Yield of nitromethane (%)	48.71	56.22	65.27	73.53	76.43	77.32	79.88

Table 4.3 Effects of temperature on the yield of nitromethane

Reaction temperature (°C)	25	35	45	55	65	75	85	95
Yield of nitromethane (%)	49.87	56.44	65.49	78.47	74.31	70.67	63.40	55.63

Table 4.4 Effects of reaction time on the yield of nitromethane

Reaction time (h)	1	1.5	2.5	3.5	4.5	5.5	6.5	8
Yield of nitromethane (%)	30.20	38.42	56.87	71.37	79.67	81.83	74.12	61.39

Table 4.5 Effects of dosage of tetrabutylammonium bromide on the yield of nitromethane

Dosage of tetrabutylammonium bromide (%)	0.05	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5
Yield of nitromethane (%)		49.7	59.2	71.6	80.3	79.1	82.6	87.8	89.7	91.3

Table 4.6 Effects of dosage of sodium carbonate on the yield of nitromethane

Dosage of sodium carbonate (%)	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Yield of nitro-methane (%)	40.3	49.8	56.2	61.6	89.7	84.6	86.3	59.1	53.7	49.9	44.6

Fig. 4.3 Instrument of
sodium nitrite replacement
method to produce
nitromethane

4.3.1.5 Toxicity of Nitromethane

Nitromethane is a volatile liquid with high toxicity; its vapor has stimulating effects
on the lungs, long-term exposure to it can result in decreased appetite, nausea and
diarrhea with damage on liver and kidney. The maximum allowable concentration
is 250 mg/m^3, 50–200 ppm. Experimental results on rats show that the lethal dose is
1.44 g/kg (body weight), the allowed nitromethane concentration in the workplace
air is 100 ppm. In the place with high concentration of nitromethane, activated
carbon can not be used as adsorbents to adsorb nitromethane, because the
adsorption heat is large and it may cause a fire. Good safety protective equipments
should be used during the nitromethane production process, for example, chemical
safety goggles can be worn to protect the eyes, and wearing gas masks can avoid
inhalation. Workplace should also have good ventilation.

4.3.1.6 Storage and Transportation of Nitromethane

Nitromethane should be stored in a cool and ventilated place, isolated from oxi-
dants, can not be stored in hazardous area with ignition, fire or easily oxidized
materials, and be suitable to store at low temperature; it should be stored and
transported according to the standard of toxic and flammable materials.

4.3.2 Properties and Preparation of Dinitromethane

4.3.2.1 Properties of Dinitromethane [23]

Formula: $CH_2N_2O_4$

Structure:

$$H - \underset{\underset{H}{|}}{\overset{\overset{NO_2}{|}}{C}} - NO_2$$
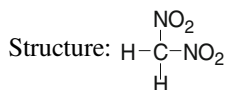
Table 4.7 Influences of different catalysts on the yield of nitromethane

Catalyst (%)	0.05	0.10	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Tetrabutylammonium bromide	49.7	59.2	63.3	67.7	71.6	79.7	80.3	81.6	79.1	81.7	82.6	84.8
Ammonium chloride	31.1	39.6	42.7	47.3	52.2	57.9	61.1	58.7	53.6	55.7	53.9	52.5
Ammonium sulfate	26.2	29.1	33.2	39.7	41.3	45.2	45.6	47.5	48.3	49.1	48.9	49.3
Ammonium phosphate	27.9	28.3	29.7	34.3	39.6	43.3	46.7	49.2	50.4	51.3	50.9	52.1
Trolamine	39.3	47.6	51.3	55.6	58.7	61.2	69.7	76.8	81.2	80.1	81.4	81.9
Rare earth	46.2	58.1	62.2	67.3	70.7	73.3	79.2	80.1	81.0	74.3	70.6	70.9

Molecular weight: 106.0
Oxygen balance: 15.1 % (calculated according to the produced CO_2)
Content of nitrogen: 26.4 %

Dinitromethane is liquid at room temperature and yellower needle at a lower temperature (-20 °C) with aromatic odor; its relative density is 1.501, the freezing point is <-15 °C, boiling point is 100 °C, and it is soluble in alcohol and ether.

4.3.2.2 Thermal and Explosion Properties of Dinitromethane

Dinitromethane is an extremely explosive and highly sensitive liquid compounds. It standard heat of formation is: -105.44 kJ/mol or -994.72 J/g.

4.3.3 Properties and Preparation of Trinitromethane

Trinitromethane is also known as nitroform.

4.3.3.1 Properties of Trinitromethane [23]

Formula: CHN_3O_6

Structure:

$$H-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-NO_2$$

Molecular weight: 151.04
Oxygen balance: 37.1 % (calculated according to the produced CO_2)
Content of nitrogen: 27.83 %
Oily liquid or white crystals
The relative density: 1.479
Melting point: 22 °C
Boiling point: 48 °C (2,266 Pa)
Refractive index: 1.4451
Soluble in water, ethanol and acetone.

4.3.3.2 Thermal and Explosion Properties of Trinitromethane

Trinitromethane is a weak explosive with explosion enthalpy of $-3,120$ J/g. Its standard heat of formation is -38.58 kJ/mol or -255.46 kJ/kg.

4.3.3.3 Preparation of Trinitromethane

Trinitromethane have two tautomers. The colorless nitro type tautomer is present in an acidified solution and solution of diethyl ether or carbon disulfide; the yellow acid type one is present in aqueous (without strong acid) or basic solution, pKa = 0.2.

The preparation of nitromethane at laboratory is the nitration of cyanide acid with mixed acid at 10–30 °C to obtain trinitro acetonitrile, and then trinitromethane after hydrolysis and acidification. You can also obtain trinitromethane salt after treatment of tetranitromethane with basic solution. In industry to produce trinitromethane catalyzed by mercuric nitrate, acetylene is nitrated with fuming nitric acid, and the resulting trinitromethane is dissolved in excess nitric acid, then concentrated sulfuric acid was added; trinitromethane is nitrated into tetranitromethane; because tetranitromethane is insoluble in acid mixture, trinitromethane and tetranitromethane can be separated [32]. The separated liquid is treated with base to generate trinitromethane salt, and trinitromethane can be produced after acidification. Main reactions mechanism are:

$$HC \equiv CH \xrightarrow{HNO_3} HC(NO_3)_3 + H_2O$$

$$HC(NO_2)_3 + HNO_3 \longrightarrow C(NO_2)_4 + H_2O$$

$$C(NO_2)_4 + 2KOH \longrightarrow KC(NO_2)_3 + KNO_3 + H_2O$$

$$KC(NO_2)_3 + H^+ \longrightarrow HC(NO_2)_3 + K^+$$
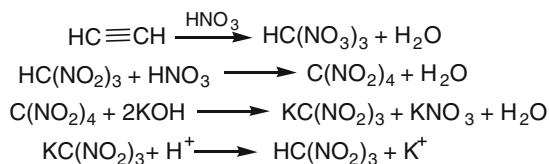
The main side reaction is:

$$C(NO_2)_4 + 6KOH \rightarrow 4KNO_2 + K_2CO_3 + 3H_2O$$

This method is relatively cumbersome, the yield is only about 40−50 % with a purity of 99.9 %.

4.3.4 Properties and Preparation of Tetranitromethane

4.3.4.1 Properties of Tetranitromethane [23]

Formula: CN_4O_8

Structure:
$$O_2N-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-NO_2$$

Relative molecular weight: 196.03
Oxygen balance: 49.0 % (calculated according to the produced CO_2)
Content of nitrogen: 29 %

Tetranitromethane (TNM) is a colorless to pale yellow oily liquid with odor similar to nitrogen dioxide, the relative density of 1.6377, melting point of 14.2 °C, boiling point of 126 °C and refractive index of 1.4382225. Tetranitromethane is

insoluble in water, soluble in many organic solvents such as ethanol, ether, acetone, toluene, nitrobenzene.

4.3.4.2 Thermal and Explosion Properties of Tetranitromethane

Tetranitromethane is positive oxygen balance explosive, but it is not sensitive to detonation. Even with 10 g of tetryl explosive can not make it fully detonated.

Standard heat of formation: 38.40 kJ/mol or 195.89 kJ/kg
Heat of Combustion: −434.7 kJ/mol or −2217.5 J/g
Explosion velocity: 8,000 m/s
Explosion heat: 2,259 J/g
Explosion pressure: 1.44×10^7 Pa
Explosion capacity: 685 mL/g
Enthalpy explosion: −1,890 J/g
Flash point: 225 °C (5 s)
Heat or vacuum stability: No gas is released from 2.5 g sample for 6 h at 90 °C
Friction sensitivity: Two explosions from 10 times of friction pendulum experiments
Sand test: 7.5 g
Lead cast test: 21.4 TNT
Hit (impact) sensitivity: 2 kgf.m, at least one explosion from ten dropping trials with 2 kg hammer, characteristic drop height of 100 cm (2 kg dropping hammer).

4.3.4.3 Applications of Tetranitromethane

Tetranitromethane can be used as explosive energetic component of liquid and liquid mixed explosives, rocket fuel oxidizer, and the raw material of nitromethane. It can be used as nitrating agent and chemical reagent with analytic grade in the laboratory.

4.3.4.4 Preparation of Tetranitromethane

The main chemical reaction to prepare tetranitromethane:

$$4(CH_3CO)_2O + 4HNO_3 \rightarrow C(NO_2)_4 + 7CH_3COOH + CO_2 \uparrow$$
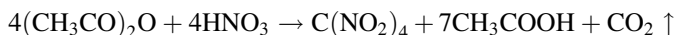
Tetranitromethane can be prepared through the following four steps: 31.5 g of anhydrous nitric acid (d > 1.53) was added into the reaction flask; the temperature is controlled below 5 °C with ice bath; 51 g of acetic anhydride was slowly added under a nitrogen atmosphere dropwise; after the adding, the system is cooled down to room temperature naturally. The mixture is added to a flask containing 300 ml of water and steaming distilled, and tetranitromethane are distilled out with the first 20 ml distilled-out solution; the upper layer of water is removed, washed first with

diluted basic solution, washed with water and dried over anhydrous sulfate. 16 g of product is obtained with a yield of 65 %.

4.3.4.5 Toxicity of Tetranitromethane

Tetranitromethane is highly toxic, its vapor has a similar smell of nitrogen dioxide with a strong irritant to mucosal tissues (such as the eyes, nose, upper respiratory tract). With a small amount of tetranitromethane vapor inhaled, the initial poisoning symptom is the increase of salivation, and then upper respiratory tract irritation. Chronic poisoning symptom is headache, weight loss, lethargy, slower pulse, the formation of methemoglobin and damage on the body circulation. Long-term exposure to tetranitromethane can damage the central nervous system and heart, and sometimes also cause anemia.

4.3.4.6 Storage and Transportation Conditions of Tetranitromethane

Tetranitromethane should be stored in a cool and well-ventilated place, should be isolated from oxidants, is toxic, should not be transported with the storage tank and be transported and stored according to the standard of toxic and flammable materials.

4.3.5 Properties of Nitroethane

4.3.5.1 Properties of Nitroethane [23]

Molecular formula: $C_2H_5NO_2$

Structure:
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-NO_2$$
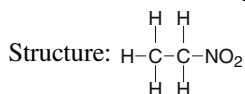
Molecular weight: 75.07
Oxygen balance: -95.9 % (according to the produced CO_2)
Content of nitrogen: 19 %

Nitroethane is colorless transparent liquid with a relative density of 1.05, melting point of -89.52 °C, boiling point of 114–115 °C, flash point of 40–41 °C (open cup), refractive index of 1.3719. It is insoluble in water, and miscible with acetic acid, ethyl ether, chloroform and basic solution.

4.3.5.2 Thermal and Explosion Properties of Nitroethane

Standard heat of formation: -143.93 kJ/mol or -1917.28 J/g
Heat of Combustion: -1362.35 kJ/mol or -18147.68 J/g

Explosion heat: 3,889 J/g
Heat capacity: 134.4 kJ/mol
Explosion limits: 3.0–5.0 % (volume).

4.3.5.3 Applications of Nitroethane

Nitroethane can be used as solvents of cellulose nitrate, cellulose acetate, resins, waxes, fats and dyes, and rocket fuel.

4.3.5.4 Toxicity of Nitroethane

Nitroethane is toxic and seriously damage the kidney and liver, the maximum allowable concentration is 310 mg/m^3, and operator should wear chemical safety goggles to protect the eyes and wear a gas mask at high concentrations in order to avoid excessive inhalation of toxic gases.

4.3.5.5 Storage and Transportation Conditions of Nitroethane

Nitroethane can not be stored in a place with strong oxidant, areas having open fire danger, and the container should be sealed at low temperature with label. It can be directly shipped with tanks and storage tanks, the steel storage container is generally used, but not exceeding 200 L. The container should marked as flammable and explosive.

4.3.6 Properties of 1,1-Dinitropropane

4.3.6.1 Properties of 1,1-Dinitropropane (DNP) [23]

Molecular formula: $C_3H_6N_2O_4$

$$\begin{array}{ccc} H & H & NO_2 \\ | & | & | \\ H-C-C-C-H \\ | & | & | \\ H & H & NO_2 \end{array}$$

Structure: as above
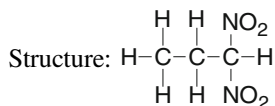
Relative molecular weight: 134.092
Oxygen balance: −59.66 % (calculated according to the produced CO_2)
Content of nitrogen: 21 %
DNP relative density: 1.261
Melting point: −42 °C
Boiling point: 184 °C
Refractive index: 1.4339
Solubility: soluble in base.

4.3.6.2 Thermal and Explosion Properties of 1,1-Dinitropropane

Standard heat of formation: −170.70 kJ/mol or −1273.01 J/g
Heat of combustion: −1872.76 kJ/mol or −13966.23 J/g.

4.3.7 Properties of 1,3-Dinitropropane

4.3.7.1 Properties of 1,3-Dinitropropane [23]

Molecular formula: $C_3H_6N_2O_4$

Structure:
$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ NO_2- & C- & C- & C- & NO_2 \\ & | & | & | & \\ & H & H & H & \end{array}$$
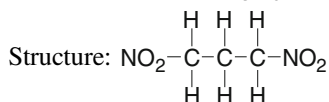
Molecular weight: 134.09
Oxygen balance: −59.66 % (calculated according to the produced CO_2)
Content of nitrogen: 21 %

   1,3-dinitropropane is yellow liquid with a pungent odor, and extremely unstable in nature, with a relative density of 1.353, melting point of −21.4 °C, boiling point of 103 °C, refractive index of 1.465420. It is soluble in ether and insoluble in water.

4.3.7.2 Thermal and Explosion Properties of 1,3-Dinitropropane

Standard heat of formation: −223.89 kJ/mol or −1670.45 J/g
Heat of Combustion: −1817.91 kJ/mol or −13557.4 J/g.

4.3.7.3 Toxicity of 1,3-Dinitropropane

1,3-Dinitropropane has strong irritation on the skin, eyes, mucous membranes and upper respiratory tract, and can cause cyanosis after it is absorbed into the body.

4.3.7.4 Storage and Transportation Conditions of 1,3-Dinitropropane

1,3-Dinitropropane should be stored in a cool, dry and well-ventilated non-combustible warehouse to keep away from fire and heat sources. The storage temperature should not exceed 30 °C. The container should be sealed. It should be stored separately from oxidants, reducing agents, acids and food chemicals, and must avoid the mixing storage. During the transportation, the tank cars should be grounded. Some partition holes can be used in the tank to reduce static electricity shocks.

4.3.8 Properties of 2-Methyl-2-Nitropropane

4.3.8.1 Properties of 2-Methyl-2-Nitropropane [23]

Molecular formula: $C_4H_9NO_2$
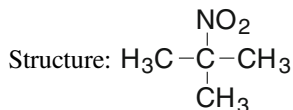
Structure:
$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{NO_2}{|}}{C}} - CH_3$$

Molecular weight: 103.12
Oxygen balance: −163 % (calculated according to the produced CO_2)
Content of nitrogen: 14 %

   The relative density of methyl-2-nitropropane is 0.95 with boiling point of 126 −127 °C. It is soluble in alcohol, ether, acetone and benzene.

4.3.8.2 Thermal and Explosion Properties of 2-Methyl-2-Nitropropane

Standard heat of formation: −229.8 kJ/mol or −2228.47 J/g.

4.3.9 Properties of 1-Nitrobutane

4.3.9.1 Properties of 1-Nitrobutane [23]

Molecular formula: $C_4H_9NO_2$
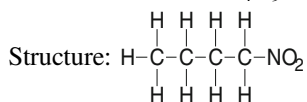
Structure:
$$H - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - NO_2$$

Molecular weight: 103.12
Oxygen balance: −163 % (calculated according to the produced CO_2)
Content of nitrogen: 14 %

   1-Nitrobutane is a colorless liquid. Its relative density is 0.971 with melting point of −81.0 °C, boiling point of 152–153 °C and refractive index of 1.430320. It can be soluble in most organic solvents, such as ethanol, ether and others.

4.3.9.2 Thermal and Explosion Properties of 1-Nitrobutane

Standard heat of formation: −200.8 kJ/mol or −1947.25 J/g
Heat of combustion: −2667.98 kJ/mol or −25872.58 J/g.

4.3.9.3 Applications of 1-Nitrobutane

The explosion of 1-nitrobutane is very weak and it can not be used alone as the liquid explosive. But it be the energetic component in a liquid explosive mixture, the liquid propellant fuel, and also a gasoline additive. In the chemical industry, it is mainly used as intermediate and solvent of organic synthesis.

4.3.9.4 Toxicity of 1-Nitrobutane

Except that nitroalkanes stimulate the mucosa, they also damage the central nervous system. Animal experiments indicate that it maybe damage the liver too.

4.3.9.5 Storage and Transportation Conditions of 1-Nitrobutane

1-Nitrobutane should be stored in a cool and ventilated warehouse, which is far away from fire, heat. The container should be sealed. It should be stored separately from oxidants, reducing agents, acids and food chemicals, and must avoid the mixing storage.

4.4 Liquid Nitro Explosives with Heteroatoms

4.4.1 Properties of Fluorodinitromethane

4.4.1.1 Properties of Fluorodinitromethane [23]

Molecular formula: CHN_2O_4F

Structure:
$$H-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-F$$

Molecular weight: 124.028
Oxygen balance: 25.8 % (calculated according to the produced CO_2)
The relative density: 1.595
b.p.: 123 °C.

4.4.1.2 Thermal and Explosive Properties of Fluorodinitromethane

Standard heat of formation: −278.24 kJ/mol or −2243.36 J/g.

4.4.2 Properties of Fluorotrinitromethane

4.4.2.1 Properties of Fluorotrinitromethane

The fluorotrinitromethane is also known as trinitrofluoromethane.

Molecular formula: CN_3O_6F

Structure: $O_2N-\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{C}}-F$

Molecular weight: 169.0

Content of nitrogen: 25 %

Oxygen balance: 37.9 % (calculated according to the produced CO_2)

Fluorotrinitromethane is a colorless liquid with a relative density of 1.785, melting point of −29 °C, and boiling point of 84.2 °C.

4.4.2.2 Thermal and Explosive Properties of Fluorotrinitromethane [23]

Standard heat of formation: −220.70 kJ/mol or −1305.92 J/g

Heat of Combustion: −3336.74 kJ/mol or −19744.02 J/g.

4.5 Nitroalcohol

Among derivatives of nitroalkanes, nitro alcohol is one of the important compounds. Since the nitro-alcohol is suitable solvents for a variety of cellulose ester, polyacrylonitrile, and their copolymers and aminoplast modifier, it is widely used [33]. Among nitro alcohols, 2-nitroethanol, 2-methyl-2-nitro-1-propanol and 2-nitro-1-propanol are the most widely used ones. 2,2-Dinitro, namely, gem-dinitro, is a class of characteristic energetic group, and gem-dinitro compounds have moderate energy with suitable stability and are important liquid explosives, also are important intermediates of energetic plasticizers and energetic adhesives of propellant components [34, 35]. The typical liquid dinitro alcohol compounds is 2,2-nitro-1-propanol (DNPOH); it is not only the important intermediate material to synthesize energetic plasticizer BDNPF/A (bis-2,2-dinitropropanol formaldehyde/bis-2,2-dinitropropanol acetal); and it is a variety of key intermediate of nitro explosives and propellant components. DNPOH, as a nitrosating agent, can nitrosate morpholine into nitrosomorpholine [36].

The preparation of nitroalkane is very difficult, and it is more difficult to prepare nitro alcohols. In most of the early nitroalcohol preparation methods, oxidation nitration method was used to obtain the target products, DNPOH [37, 38] was also produced with oxidation nitration method and chlorination nitration method [39]. Disadvantages of these nitro alcohol preparation methods is: The oxidized nitration

need to use silver nitrate, thus the production cost is high with environmental pollution; in the chlorination nitration method for nitro alcohols, the risk of produced intermediate potassium salt is large, and production safety risk is high because a large amount of chlorinated solvents and chlorine are used in the process. Polysulfide in America, Grakauskas and others [40–42], proposed the oxidation nitration method to alleviate effectively the problem in safety and environmental protection [43, 44].

Problem in the synthesis of DNPOH in polysulfide company is [45–49] that the amount of required nitrite in the process is very high. Therefore, a large amount of salt and water will be produced in the process, which not only increases the processing costs, but also result a certain degree of impacts on environment. American "Strategic Environmental Research and Development Planning Office" (SERDP) [50] proposed the electrochemical synthesis of DNPOH; From the view of protecting environment and reducing the cost, the impact on the environment is expected to improve.

4.5.1 Properties and Preparation of 2,2-Dinitropropanol

2,2-dinitropropanol (DNPOH), also known as gem-nitropropanol, is an important liquid nitro compound.

4.5.1.1 Properties of DNPOH

Formula: $C_3H_6N_2O_5$

Structure: $H_3C-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2\text{-OH}$

Molecular weight: 150.092

Oxygen balance: −42.6 % (calculated according to the produced CO_2)

Content of nitrogen: 18.66 %

2,2-Nitro-1-propanol is a highly explosive colorless liquid with an aromatic odor, melting point of −21.4 °C, boiling point of 103 °C, refractive index of 1.465420. It is soluble in ether, but insoluble in water. It has five hydrogen bond acceptors, topological molecular polar surface area of 112, heavy atom number of 10, rotatable bond number of one, the number of hydrogen bond donor of 1, and the number of covalent bond units of one.

4.5.1.2 Applications of DNPOH

(1) Antibacterial inhibitor: DNPOH can be used to prepare bacteria inhibitors and fungicides [35, 36, 52].

(2) Energetic material: DNPOH itself is explosive and can be used in explosives. Of course, its most important application is a key intermediate in the synthesis of some important energetic materials [53–57], such as BDNPF/A, and then can be assed in the solid propellant and propellant explosive formulations, as the energetic component.

(3) Energetic plasticizer: DNPOH is used by many people to develop many excellent energetic plasticizers. For example, Rai et al. [58], Adolph [59] used DNPOH and DNBOH (2,2-dinitrobutanol) to react with formaldehyde (or formaldehyde polymer) under the action of concentrated sulfuric acid, from which F/F mixture tis prepared, namely DNPBH (2,2-butyl-2,2-dinitropropyl formal)/BDNBF (bis-2,2-dinitrobutyl formal); Through adjusting the molar ratio of DNPOH over DNBOH, that ratio of each component in F/F is assigned to be rational, and chemical and thermal stabilities of products are increased and the production cost is reduced. F/F mixture is a very potential energetic plasticizer.

(4) Energetic binders: Seuk et al. [60] used DNPOH and acryl chlorosulfonate to prepare 2,2-dinitro-propyl glycidyl ester, and this compound can form polymer through ring-opening polymerization. Thermal degradation temperature of the obtained polymer is up to 200 °C, which can be used as an excellent energetic adhesive in high-performance plastic explosives [61].

(5) Applications in the eutectic mixture: Seuk et al. [61], Rai et al. [62] also proposed a new binary eutectic mixture F/DF, namely BDNPF/BDNPDF (bis-2,2-dinitropropyl dimethyl acetal), can be prepared from DNPOH and formaldehyde with concentrated sulfuric acid added to the raw material at a low temperature. F/DF has good chemical and thermal stability with low cost, and does crystallize for long-term storage even at −20 °C.

(6) Important intermediate of energetic materials: The most main application of DNPOH is in the synthesis of BDNPF/A. It also is used to some extent in the syntheses of other energetic plasticizers, adhesives and bacteria-containing inhibitors. Due to the low cost and limited waste production, it is a promising environment-protection industrial synthesis method.

4.5.1.3 Preparation of DNPOH

(1) Early synthesis process of DNPOH

Early DNPOH synthesis methods include nitrification oxidization method, chlorination nitration method and electrochemical method. In 1961, Kaplan et al. [37] proposed a reaction with a redox process to synthesize gem-dinitro compounds, in which nitro ethane, as the raw materials, reacts with formaldehyde in the presence of sodium hydroxide, followed by the synthesis of DNPOH through the nitration reaction of silver nitrate and sodium nitrate. The reaction mechanism is:

$$CH_3CH_2NO_2 \xrightarrow{NaOH.HCHO} CH_3CH(NO_2)CH_2OH \xrightarrow{AgNO_3.NaNO_2} CH_3C(NO_2)_2CH_2OH$$

$$DPNOH$$
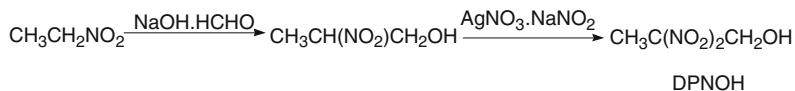
In the company Aerojet, based on the TerMeer method [37], DNPOH was synthesized from as the starting material nitroethane in dichloroethane (EDC), through the chlorification with sodium chloride, substitution of chlorine atom with nitro, and finally reaction with formaldehyde under the action of sulfuric acid. The reaction mechanism is:

$$CH_3CH_2NO_2 \xrightarrow[2.Cl_2]{1.NaOH.EDC} CH_3CHClNO_2 \xrightarrow[EDC]{NaOH.NaNO_2}$$

$$CH_3C(NO_2)=NO_2Na \xrightarrow[EDC]{H_2SO_4.H_2O.HCHO} CH_3C(NO_2)_2CH_2OH$$
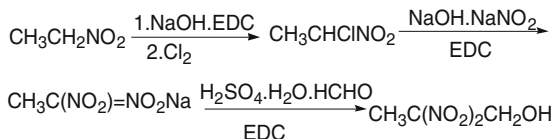
Wright et al. used silver as a medium to electrolyze and oxidize salts of polynitro compounds to prepare gem-polynitroalkanes [64]. The reaction mechanism is:

$$R\text{-}NO_2 + Ag^+ \rightarrow RC\text{-}NO_2 + Ag$$
$$RC\text{-}NO_2 + NO_2^- \rightarrow RC\text{-}(NO_2)_2^-$$
$$RC\text{-}(NO_2)_2^- + Ag^+ \rightarrow RC\text{-}(NO_2)_2 + Ag$$
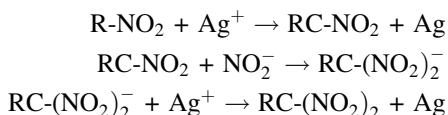
The electrolytic oxidation of silver electrode generate silver ions, which then react with nitrite and nitroethane to produce 1,1-dinitroethane and metal silver. The initial electron transfer reaction stage is a free radical ions generating from nitro-alkanes, and nitrite attacks free radical to generate polynitro intermediate which is oxidized to the gem-dinitro compound; after the continuing electrolysis, a small amount of silver is produce on the bottom of electrolysis groove, and a certain consumption of the silver electrode can also be found.

The advantage of chlorination nitrification process is the low raw materials cost, which is suitable for continuous production and mass production, but the yield of the synthesized BDNPF/A is low with relatively large amount of impurities, and the production process is relatively complex; the advantage of oxidation nitration is the synthesized BDNPF has high yield and high purity, which is suitable for batch operation, the production process has been effectively controlled and simplified, but the cost of production process with silver nitrate, low chlorine content and sodium hydroxide is significantly high [39]. According to the raw material costs, equipment costs, operating costs, labor costs and other factors, chlorination nitration is suitable for the industrial continuous production, while oxidation nitration method is suitable for the batch preparation of a small amount of high-purity products. Electro-lytic production of DNPOH silver is mainly used in laboratory research and not suitable for industrial production because the required consumption of silver.

In Ter Meer method, due to the use of chlorine and a large amount of chlorinated solvents, a large amount of waste will be generate from the production process, which has heavy pollution on environment. Additionally, there are many problems

in the production of BDNPF/A from the early-produced DNPOH, such as the low product purity, short storage and service periods, aging, etc. It is necessary to further optimize the DNPOH production process.

In the early oxidation nitration preparation of DNPOH, the yield is relatively low (59–63 %), the product needs further purification, there is formaldehyde condensation reaction and other serious problems. Jeong et al. [63] modified the oxidation nitration process to optimize the oxidation nitration conditions of silver nitrate, in which aqueous formaldehyde solution (mass fraction of 35 %) was used for hydroxymethylation and its reaction conditions were optimized, and a yellow solid DNPOH was obtained after extraction with methylene chloride and distillation. The average yield of DNPOH was more than 90 % and the mass fraction was more than 97 %. Based on these results, Grakauskas et al. [40–42, 65] used potassium ferricyanide as catalyst and potassium persulfate as oxidant to synthesize DNPOH. In this method, with potassium(sodium) ferricyanide and over potassium(sodium) persulfate, nitrite substitution reaction of nitroethane with sodium nitrite occurred, and then further reacted with formaldehyde under basic conditions, and finally DNPOH was extracted out with ethyl acetate under acidic conditions. Product was obtained through potassium distillation. The reaction mechanism is:

$$CH_3CH_2NO_2 \xrightarrow[\text{NaNO}_2]{\text{K}_3\text{Fe(CN)}_6.\text{Na}_2\text{S}_4\text{O}_8} CH_3CH(NO_2)_2$$

$$\xrightarrow[\text{H}^+,\text{CH}_3\text{COOCH}_2\text{CH}_3 \text{ extraction}]{\text{HCHO.NaOH}} CH_3C(NO_2)_2CH_2OH$$
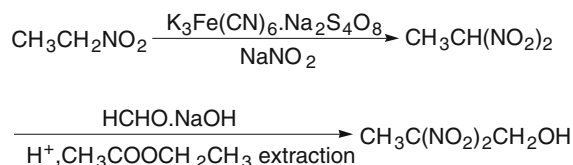
It was found that polar organic solvents, as the extraction agents, could be selected to extract DNPOH from the aqueous phase as shown in Table 4.8. According to Table 4.8, the choice of ethyl acetate, butyl acetate, methyl tert-butyl ether, cyclohexane and other polar reagents are beneficial to extraction. The concentrated crude product from the extraction agent does not need further purification, and the purity can be up to 98–99 % that can be directly used in the synthesis of BDNPF/A. In this reaction, the key factors to affect the product yield are pH of the reaction mixture and the oxidation time. Rely on the fine controlling on these key factors, the final yield of DNPOH can be up to 80 %. Comparison of impacts of several different process to produce DNPOH on environment is shown in Table 4.9. In Table 4.9, the inexpensive sodium persulfate is used as oxidant, and potassium ferricyanide as catalyst. The cost is relatively low. Compared to Ter Meer method, it has limited environmental pollution. Compared with the earlier process, the improved DNPOH production, ferricyanide method developed in polysulfide company, has lower cost with small environmental pollution, which is suitable for industrial production.

Although ferricyanide method to produce DNPOH has many advantages, a large amount of oxidants is used in this process, and a large amounts of waste is produced, in which contains a large amount of salt and pollution on environment, and the treatment costs is increased.

Table 4.8 Comparison of selectivities of organic solvents in the extraction of DPNOH from aqueous phase

Solvent	Ratio of solvent over water	Number of extraction	Extraction efficiency (%)	Purity of product after treatment
Methanol	1:1	2	61	94.62
Acetone	1:1	2	52	95.37
Ether	1:0.5	2	73	92.91
Ethyl acetate	1:0.5	1	97.5	99.18
Butyl acetate	1:0.5	1	98.3	99.06
DME	1:0.5	1	89.7	98.9
DMF	1:0.5	2	93.9	99.25
Methyl tert-butyl ether	1:0.5	1	98.1	99.52
Toluene	1:0.5	2	91.9	98.80
Cyclohexane	1:0.5	1	95.3	98.90

(2) New green synthesis process of DNPDOH

In the improvement of DNPDOH (2,2-dinitro-1,3-propanediol) [66], used sodium nitrite was reduced from 4 times to the equal amount, the amounts of sodium persulfate and potassium ferricyanide were adjusted, which reduced the impact of carbon emission pollution on the environment, and the cost of synthesis was reduced. The synthesis yield was 68 % after improvement, and lower than the production cost is much lower than that of silver nitration method. Major improvement in electrochemical synthesis of DNPOH is that: In the first step, sodium hydroxide solution was added to an aqueous solution of 2-nitropropanol; after 45 min of stirring at room temperature, lithium perchlorate solution and sodium nitrite solution were added to prepare the deprotonated 2-nitropropanol solution; in the second step, deprotonated 2-nitro-propanol solution is added into the working electrode chamber and the reference electrode chamber of the electrolytic cell, and electrolytic reaction is continued for about 1 h under nitrogen for 20 min. Finally DNPOH will be obtained with a yield of about 40 %. The reaction mechanism is:
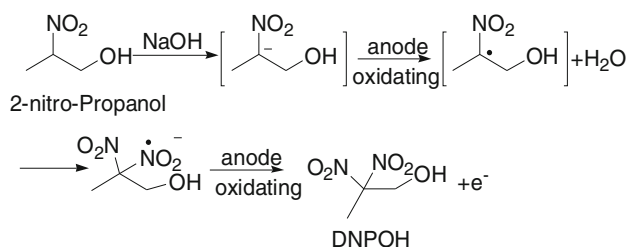
Although the yield is low, the yield can be increased to 70 % after the electrolysis conditions are optimized. Electrochemical DNPOH synthesis method is greener and cheaper than the traditional chemical synthesis method, because, in electrochemical processes, sodium nitrite consumption can be reduced from 10

Table 4.9 Comparison between Grakauskas method and TerMeer method in the production of DNPOH

Method	Starting material	Intermediates (Catalysts, oxidizing agents, etc.)	Controlling conditions	Production cost	Final yield (%)	Extent of environmental pollution
Grakauskas method	Nitroethane	Ferricyanide, potassium persulfate, $NaNO_2$, Ethyl acetate	pH value oxidation time	Relatively lower	78	Very small
TerMeer method	Nitroethane	Cl_2, NaOH, EDC, H_2SO_4	Refluxing time, extraction temperature	Lower	83	Large amount of wastewater
Electrolysis	Nitropropanol	Lithium perchlorate, sodium nitrite, electrolysis, electrode	Current voltage concentration of electrolyte	Very high	70	Very small

equivalents to 4 equivalents, the amount of water is drastically reduced while the ethyl acetate loss will be reduced and the waste liquid is also dropped significantly. It can be expected that, if 1,000 g of DNPOH is produced, the amount of generated waste is 14.26 kg; the cost of raw materials and waste handling can be reduced to $8.59 (reduced by 56 %). In the production, if nitroethane is used as a starting material instead of 2-nitropropanol, two different electrolytic pathways to synthesize DNPOH have been designed as shown in Figs. 4.4 and 4.5.

After many years of development, the U.S. Department of Defense-funded project WP-1460 [67] was made a significant progress. In 2007, Idaho National Laboratory completed a continuous process of electrochemical synthesis of the key intermediate 2,2-nitroethyl potassium (KDNE) of DNPOH in the laboratory [68] from nitroethane. It was believed that the electrochemical process to produce DNPOH could reduce more than 92 % of the waste, carbide or nickel alloy rods was used as electrodes instead of silver rods according to the U.S. patent [69]. With different voltages, anode oxidizes inactive chemical intermediates (such as ferro-cyanide ion) into active intermediates or oxidant (such as iron cyanide ion). Oxidants and nitro compounds react with nitrite ions to form a gem-dinitro product. Anode can oxidize ferrous cyanide continuously to produce lively iron cyanide ions, thus to provide enough iron cyanide ions for reaction. The scheme of synthesis is shown in Fig. 4.6.

In the technical report of 2011 [67], Alexander Paraskos et al. on the basis of synthetic route in a small test, amplified and completed the pilot test of KDNE. The results confirmed that, in the pilot test of KDNE electrochemical synthesis, [Fe $(CN)_6]^{3-}/^{4-}$ is an excellent reaction medium, leading very good operating
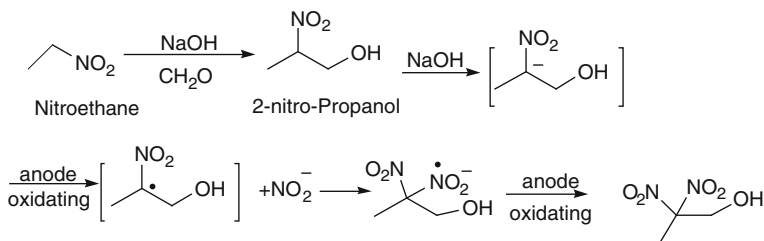
Fig. 4.4 Electrochemical synthesis route 1 of DNPOH
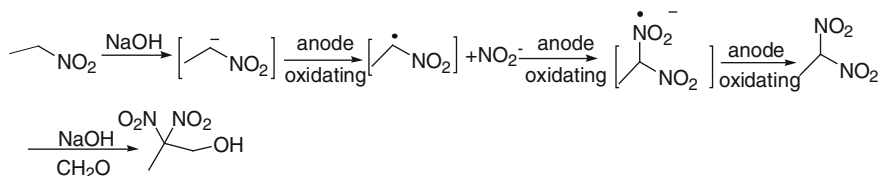
Fig. 4.5 Electrochemical synthesis route 2 of DNPOH

Fig. 4.6 Electrochemical
synthesis route of KDNE
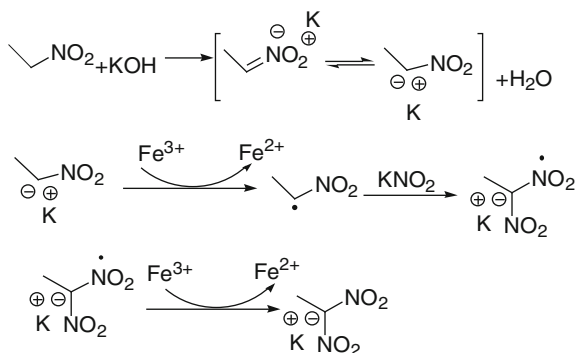
conditions with the combination of electrochemistry and crystallization process to
produce KDNE cleanly. It was also confirmed that the electrochemical production
of KDNE can be achieved kg/h scale, and it is easy to transform DNPOH into
KDNE with existing equipments. Electrochemical synthesis KDNE is shown
schematically in Fig. 4.7.

After the electrochemical production of KDNE, it is very easy to convert KDNE
into DNPOH on the industrial equipments. The conversion equipment is shown in
Fig. 4.8.

In 2002, the cost of raw materials to synthesize DNPOH at ATK with traditional
production method ferricyanide was $17.5 per 1,000 g of BDNPF/A, while it is
only $8.34 with electrochemical synthesis route, which can be significant cost
savings.

Fig. 4.7 Scheme of KDNE
electrochemical synthesis
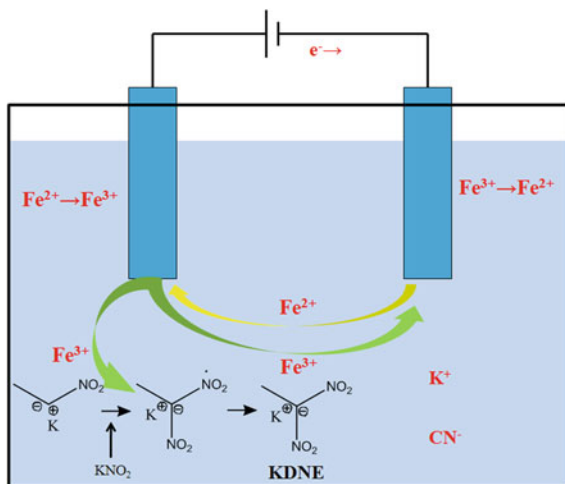
Fig. 4.8 Industrial equipments for the conversion of KDNE to DNPOH

4.5.1.4 Toxicity

DNPOH has some toxicity and can inhibit the growth of bacteria [51].

4.5.2 Properties of 2-Nitroethanol

4.5.2.1 Properties of 2-Nitroethanol

Molecular formula: $C_2H_5NO_3$

Structure:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$
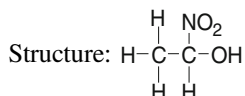
Molecular weight: 91.07

Oxygen balance: −61.5 % (calculated according to the produced CO_2)

Content of nitrogen: 15.37 %

2-Nitroethanol is a pale yellow liquid and miscible in water, with melting point of −80 °C, boiling point of 194 °C (65 mmHg), density of 1.27 g/ml (25 °C), refractive index (n_{20}^{D}) of 1.445, flash point of >230 °F, molar refractive index of 18.87, molar volume (m^3/mol) of 71.8, isotonic hematocrit (90.2 K) of 187.0, surface tension (dyne/cm) of 45.9, polarization ratio (10^{-24} cm^3) of 7.48.

4.5.2.2 Toxicity

2-Nitroethanol is slightly toxic with mice acute poisoning (peritoneum) LD50 of 2,100 mg/kg. Because salt LD50 is 3,000 mg/kg, the acute toxicities of BPA and salt are the same.

4.5.2.3 Method for Storage

2-Nitroethanol should be stored in a sealed container and kept in a cool dry place. It cannot be stored together with strong acidic and basic materials. It should be kept far away from the acid chloride and acid anhydride.

4.5.3 Properties of 2-Nitro-1-Propanol

Properties 4.4.3.1 2–nitro-1-propanol C3H7NO3
   Structure:

4.5.3.1 Properties of 2-Nitro-1-Propanol

Molecular formula: $C_3H_7NO_3$

Structure: $O_2N-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2OH$

Molecular weight: 105.09

Oxygen balance: $-99.0\ \%$ (calculated according to the produced CO_2)

Content of nitrogen: 13.32 %

   2-Nitro-1-propanol is a slightly yellow liquid with boiling point of 72–74 °C (1 mmHg), density of 1.185 g/mL (25 °C), refractive index of (n_{20}^D) 1.439 and flash point of 212 °F.

4.5.3.2 Method for Storage

2-Nitro-1-propanol should be stored in cylinders and stored in well-ventilated and dry environment at 2–8 °C. It cannot be stored together with acidic/basic materials, and must be far away from the fire, acidic chloride and acid anhydride.

4.5.4 Properties of 2-Methyl-2-Nitro-1-Propanol

Molecular formula: $C_4H_9NO_3$

Structure: $O_2N-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2OH$

Molecular weight: 119.2

Oxygen balance: $-127.5\ \%$ (calculated according to the produced CO_2)

Content of nitrogen: 11.74 %

2-Methyl-2-nitro-1-propanol is a colorless liquid with a strong combustion performance. When it is combusted under confined conditions, an explosion will occur. It density is 1.135 g/cm^3 with melting point of −1 °C, boiling point of 204.4 °C (760 mmHg), flash point of 92.1 °C, vapor pressure of 0.0634 mmHg (25 °C) and refractive index of 1.553.

4.6 Liquid Nitro Aromatic Compounds

4.6.1 Properties and Preparation of Nitrobenzene

Nitrobene is also known as secret spot oil, almond oil.

4.6.1.1 Properties of Nitrobenzene

Molecular formula: $C_6H_5NO_2$

Structure:
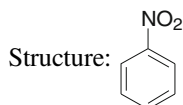
Molecular weight: 123.11
Oxygen balance: −162.5 % (calculated according to the produced CO_2)
Content of nitrogen: 11.37 %

Nitrobenzene is pale yellow liquid with a bitter almond flavor. It is insoluble in water with a density larger than water, and soluble in alcohol, ether, benzene and oil. In the case of fire, it will be burnt and explode after the heat at high temperature, and can reacts violently with nitric acid. The relative density is 1.205 (15 °C) with melting point of 5.7 °C, boiling point of 210.9 °C, flash point of 87.78 °C, ignition point of 482.22 °C, vapor density of 4.25 and vapor pressure of 0.13 kPa (1 mmHg, 44.4 °C).

4.6.1.2 Applications of Nitrobenzene

Nitrobenzene is an important basic organic intermediates. Sulfonation of nitro-benzene with sulfur trioxide gives m-nitrobenzene sulfonic acid, which can be used to produce dye intermediates, mild oxidants, resist salt S, and dye and medicine intermediates. Chlorification of nitrobenzene gives m-nitrochlorobenzene, which is widely used in the production of dye and pesticide, and m-chloroaniline can be obtained after reduction. Dye orange-base GC is also intermediate of pharmaceu-ticals, pesticides, fluorescent brighteners and organic pigments. The further nitri-fication of nitrobenzene can give m-dinitrobenzene, and m-phenylenediamine can be obtained after reduction, which can be used as dye intermediates, epoxy curing

agents, oil additives, cement accelerators. Partial reduction of m-dinitrobenzene with NaS can give nitroaniline as well. It can also be Orange-base R of dye, which is the intermediate of organic dyes and pigments.

4.6.1.3 Toxicity

LD50: 489 mg/kg (rat oral); 2,100 mg/kg (rat skin); 150 mg/kg (the minimum lethal dose of dog intravenous); 200 mg/kg person (the minimum toxic dose of female oral, hematologic toxicity); 5 mg/kg, (the minimum toxic dose for unpleasantness, human oral). It has mutagenic and reproductive toxicity.

4.6.1.4 Method for Storage

Nitrobenzene should be sealed and stored in a cool dark environment, while far away from fire.

4.6.2 Properties of o-Nitrotoluene

4.6.2.1 Properties of o-Nitrotoluene

Molecular formula: $C_7H_7NO_2$

Structure:
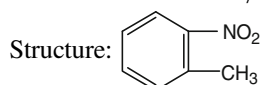
Oxygen balance: -180.8 % (calculated according to the produced CO_2)
Content of nitrogen: 10.21 %

o-Nitrotoluene is yellow flammable liquid, insoluble in water, soluble in chloroform and benzene, miscible with alcohol and ether, and can be evaporated with water, with melting point of -9.5 °C, boiling point of 221.7 °C, relative density of 1.163 (20 °C), refractive index of 1.5474, flash point of 106 °C and lighting point of 420 °C.

4.6.2.2 Preparation of o-Nitrotoluene

Nitration of toluene with mixed acid gives mixed nitrotoluenes, which are mainly o-nitrotoluene (about two thirds) and p-nitrotoluene (about one third); the pure chemicals can be obtained through separation. After toluene is added to a reactor and cooled to 25 °C, the previously mixed acids were added (25–30 % of nitric acid, 55–58 % of sulfuric acid and 20–21 % of water) and the temperature adjusted to less than 50 °C. After 1–2 h of stirring and then 6 h of static storage, the

produced nitrotoluene is separated. The unreacted aliphatic compounds and toluene was washed away with water and base, and the crude nitrotoluene product includes 55–60 % of *o*-nitrotoluene, 2–5 % of m-nitrotoluene and 35–40 % of *p*-nitrotoluene. The yield is 90–95 %. Based on the difference between their boiling points and melting points, crude distillation and crystallization can be used to separate isomers. The majority of *o*-nitrotoluene is separated from the crude nitrotoluene through vacuum distillation; the most of residual nitrotoluene fractions is distilled and separated out under vacuum, and final product can be obtained after cooling and crystallization. The tarry substances with high boiling point was left in the distillation pot. m-Nitrotoluene is contained in the mother liquor after the separation of *p*-nitrotoluene, and can be obtained through distillation after repeated accumulation. The purities of ortho- and para-nitrotoluene are 98 and 99 %, respectively. In China, manufacturing process with a series of two pot is used, and the temperature of the main pot is 40–45 °C, and it is 50–55 °C at the second pot. Substantially, it is similar to prepare mixed acid as the following: 26–28 % of nitric acid, 56–57 % of sulfuric acid, 16–18 % of water. Consumptions of raw materials are: 800 kg/t of toluene (98 %), 470 kg/t of nitric acid (98 %), 450 kg/t of sulfuric acid (92.5 %), 100 kg/t of caustic soda (42 %).

4.6.3 Properties and Preparation of 3-Nitrotoluene

4.6.3.1 Properties of 3-Nitrotoluene

Molecular formula: $C_7H_7NO_2$
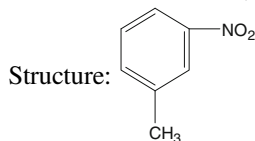
Molecular weight: 137.14
Oxygen balance: −180.8 % (calculated according to the produced CO_2)
Content of nitrogen: 10.21 %

   m-Nitrotoluene is a yellow liquid, insoluble in water, ethanol and ether, with melting point of 15.1 °C, boiling point of 231.9 °C, relative density of 1.16, relative vapor density of 4.72, saturated vapor pressure of 0.13 kPa (50.2 °C), partition coefficient in octanol/water of 2.4–2.45 and flash point of 101.67 °C.

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Chapter 5
Preparation and Properties of Liquid Nitrate Ester

Nitrate esters are sorts of liquid compounds, which were first discovered and had powerful explosion strength [1]. As one of early well-known liquid explosives, nitroglycerine was the first explosive to be used in mining and military [2]. It played a great role in the World War I and II [3, 4]. In the past half a century, the alternatives for nitroglycerine, including glycol dinitrate, diethyleneglycol dinitrate, triethyleneglycol dinitrate, mannitol nitrate, nitrodiethanolamine, nitroisobutylnitroglycerine, butanetriol trinitrate, nitroerythrite, butylenes glycol dinitrate, pentaetriol trinitrate, pentaerythritol trinitrate, nitro-sugar, and nitro-starch, have been developed one and another in many countries [3]. Among them, triethylene glycol dinitrate, butanetriol trinitrate, pentaetriol trinitrate, and their mixtures have been especially studied in reference [5]. The preparation process and performance of those nitrate esters, which have been widely applied in aviation, aerospace, propellant, military, and natural science and technology, are similar with those of nitroglycerine [6–8].

The nitrate esters have also been used in human health and medicine fields [9, 10]. For example, single alkane nitrates play an important role in clearance and purification of energy and environment [11, 12]. There are about 20 liquid nitrate esters with most bright potential in application and production over the world. They will be introduced in the following sections.

5.1 Characteristics of Nitrate Esters

5.1.1 Structure of Nitrate Esters

The basic feature of nitrate esters is the nitroxyl group of $-C-O-NO_2$. The ester group in nitrate esters is of an oxygen atom connecting with a carbon atom, that is, the nitrate esters belong to *O*-nitro compounds. This was confirmed by the hydrolysis or reduction of nitrate esters to alcohols [3, 13, 14], as the following reaction equation.

$$R-O-NO_2 \xrightarrow{\text{[H]}} R-OH + NH_3$$
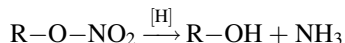
The essential difference between nitrate esters and nitro compounds can be found in the reaction. In the same reaction conditions, nitro compounds would be converted to amines. Though the structure of ester group ($-NO_2$) is the same as the nitro group ($C-NO_2$) in nitro compounds, the reactivity of nitrate esters is higher and the product distribution after hydrolysis reaction is more complicated. It indicates that nitrate esters might have the structure of hyperoxide group $-R-O-O-NO$.

However, the hyperoxide structure was not found in nitrate esters after multiple chemical structure analysis techniques [1, 3, 15]. The only structure of nitrate esters is:

$$R-O\!-\!NO_2$$
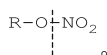
The structure of nitrate esters was further characterized by techniques of Raman spectroscopy, Infrared spectroscopy, Electron Diffraction, dipole moment, and X-ray. The results supported the finding of no hyperoxide structure in nitrate esters. Symmetrical structure was demonstrated for nitrate esters.
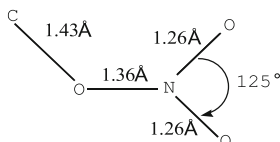
The bond length and bond angle of nitrate esters are similar with those of nitro compounds [3, 16].

5.1.2 Physical Properties of Nitrate Esters

Lower alcohol esters formed through the reaction between nitric acid and alcohol –OH are usually liquid with a slightly higher boiling point than the corresponding alcohols. However, the boiling point of the corresponding nitrous esters is much lower than the alcohols. The *C*-nitro compounds have higher boiling point than the corresponding nitrate esters. The boiling points of monohydric alcohols and esters are listed in Table 5.1.

The highly associated structure, mainly through hydrogen bonds, of liquid alcohols can be used to explain why the boiling points of alcohols are lower than the corresponding nitrate esters. Because of the molecular association, the viscosity of alcohols is higher than that of the corresponding nitrate esters. On the other hand, semipolar bonds of nitro groups are existed in nitrate esters, like nitro compounds.

Table 5.1 Boiling point of alcohols, esters, and nitro compounds (°C)

Alkyl	Alcohols	Nitrate esters	Nitrous esters	Nitro groups
Methyl	65	65	−12	101
Ethyl	78	88	17	114
N-propyl	96	111	47	131
Isopropyl	82	102	45	120
N-butyl	117	136	75	151

Table 5.2 The physical constants of nitrate esters

Compounds	ε_{20}	n^{20}_{∞}	d^{20}_4	η_{20}
N-butyl nitrate	13.10	1.39526	1.0156	0.87
Glycol dinitrate	28.26	1.43235	1.4918	4.61
1,3-propylene glycol dinitrate	18.97	1.43476	1.3952	5.8
1,2-propylene glycol dinitrate	26.80	1.42720	1.3774	4.65
1,3-butanediol glycol dinitrate	18.85	1.43259	1.3167	6.00
2,3-butanediol glycol dinitrate	28.84	1.42754	1.3061	4.7
Nitroglycerine	19.25	1.45731	1.5931	37.8
3-chloro-1,2-propylene glycol dinitrate	17.50	1.45850	1.5323	12.4
1,3-dichloro-2-propylene glycol dinitrate	13.28	1.46032	1.4630	4.8
Tribromopropane	6.45	1.56190	2.4360	
Glycerol triacetate	7.19	1.410929	1.1596	

Thus, nitrate esters have higher vapor pressure and are easier to be volatilized than the corresponding alcohols.

The physical constants of nitrate esters, such as dielectric constants ε_{20}, refractive index n^{20}_{∞}, density d^{20}_4, and viscosity η_{20}, have been measured [3, 17]. Those constants are listed in the Table 5.2.

The data of tribromopropane and glycerol triacetate are listed in the Table 5.2 for the comparison with the corresponding derivatives.

The difference of viscosity among analogue compounds of 1,3-propylene glycol dinitrate, 1,2-propylene glycol dinitrate, 1,3-butanediol glycol dinitrate, and 2,3-butanediol glycol dinitrate is due to the optical isomerism. Anomers, which should have higher viscosity, would be formed because of free rotation. This explanation supports that the viscosity of 1,3-propylene glycol dinitrate and 1,3-butanediol glycol dinitrate are higher than the other nitrate esters.

With increasing studies and knowledge to nitrate esters [3, 18], more physical constants of nitroglycerine and some glycol dinitrates have been obtained, as listed in Table 5.3.

Table 5.3 Constants for five nitrate esters

Esters	Viscosity (η)		Density d_{16}^{16}	Refractive index $n_D^{21.2}$
	Temperature (°C)	Poise		
Nitroglycerine	5.1	1.033	1.5985	1.472
	20.0	0.352		
	55.0	0.0875		
Ethanediol dinitrate	7.1	0.0633	1.4918	1.446
	20.0	0.0423		
	54.4	0.0198		
1,3-propylene glycol dinitrate	6.3	0.0940	1.4053	1.448
	20.4	0.0550		
	54.4	0.0275		
Diethylene glycol dinitrate	6.0	0.133	1.3890	1.4505
	20.4	0.0727		
	54.4	0.0337		
Triethylene glycol dinitrate	6.0	0.257	1.3291	1.4542
	20.3	0.119		
	54.2	0.015		

5.1.2.1 Dipole Moment

Dipole moment (μ) is one of the main parameters to judge the stability of constants. In general, the dipole moment of alkyl nitrates is relatively easy to be measured. The μ of methyl nitrate is 2.73 Debye. It seems no distinct connection between the chain lengths of alkyl nitrates with their μ values. The dipole moment of some nitrate esters can be calculated through their ε and η_∞^{20}. The calculation results are shown in Table 5.4.

Based on the point of view, the discrimination of the dipole moments between pure materials and benzene solution is due to the formation of trans optical isomers in benzene solution.

Through the study of dipole moments [19], pentaerythritol tetranitrate might have optical anomers. The general formula of nitrate esters can be given by Infrared adsorption spectroscopy as:

$$\underset{\underset{ONO_2}{|}}{R-CHX-CH-R'}$$

.

If $X = ONO_2$, NO_2, CN, I, Br, or Cl, the nitrate esters have optical anomers.

5.1.2.2 Spectroscopic Features of Nitrate Esters

A band at 270 nm in UV spectra can be observed for *O*-nitro groups, similar with the band of *C*-nitro groups. Though there are few studies on UV spectroscopy of

Table 5.4 The dipole moment of some nitrate esters

Compounds	Dipole moment μ (Debye)		Compounds	Dipole moment μ (Debye)	
	Pure	Benzene solution		Pure	Benzene solution
N-butyl nitrate	2.90	2.98	Nitroglycerine	3.82	3.16
Glycol dinitrate	4.00	3.28	3-chloro-1,2-propylene glycol dinitrate	3.46	3.05
1,3-propylene glycol dinitrate	3.50	3.14	1,3-dichloro-2-propylene glycol dinitrate	2.86	2.59
1,2-propylene glycol dinitrate	4.24	3.72	Tribromopropane	1.63	1.58
1,3-butanediol glycol dinitrate	3.74	3.45	Glycerol triacetate	2.50	2.58
2,3-butanediol glycol dinitrate	4.72	4.12			

nitrate esters, it has been demonstrated that the UV absorptivity of the esters that do not include other luminophores is even lower than aliphatic nitro compounds (ε = l0–20) (Table 5.5).

Besides the UV spectroscopy of nitrate esters [20], researchers [21] have studied infrared absorption characteristics of a series of nitrate esters from methyl nitrate to *n*-butyl nitrate. Raman spectroscopy of nitrate esters and nitro compounds of aliphatic or aromatic nitrate has been investigated [22].

In the IR spectra of 20 nitrate esters, including monohydric alcohol nitrate, dihydric alcohol nitrate, nitroglycerine, dipentaerythritol, and tripentaerythritol [23–26], the characteristic stretching frequency of $-ONO_2$ is at the following positions.

$$\text{Asymmetric} \quad 1{,}639 \ \pm 13 \, \text{cm}^{-1}$$
$$\text{Symmetric} \quad 1{,}279 \pm 7 \, \text{cm}^{-1}$$

The stretching frequencies of glycol dinitrate and pentaerythritol tetranitrate are at 1,650–1,610 and 1,300–1,250 cm^{-1}, respectively [27].

The results are in agreement with Raman spectra, in which two frequencies of NO_2 characteristic vibration are at 1,640 and 1,290 cm^{-1} [28, 29].

The author [15, 30] studied more than 40 nitrate esters by spectroscopic method to obtain their stretching vibration frequency range.

Table 5.5 UV absorption parameters of nitrate esters [7, 8]

Compounds	Solvent	Maximum absorption	
		Wavelength (nm)	Absorptivity (ε)
$C_2H_5ONO_2$	–	270	10
$C_2H_5ONO_2$	Ethanol	265	14.8
α-methylglucose-6-nitrate esters	Water	265	19.0
2,3,4-trimethyl-α-methylglucose-6-nitrate esters	Ethanol	265	21.4

$$
\begin{aligned}
&\text{Asymmetric stretching } \nu_{as}(NO_2) && 1{,}675-1{,}621\,\text{cm}^{-1}\\
&\text{Symmetric stretching } \nu_a(NO_2) && 1{,}301-1{,}268\,\text{cm}^{-1}\\
&\text{Stretching } \nu(C-O) && 1{,}100-950\,\text{cm}^{-1}\\
&\text{Stretching } \nu(O-N) && 880-816\,\text{cm}^{-1}\\
&\text{Vibrating } \gamma_w(NO_2) && 760-737\,\text{cm}^{-1}\\
&\text{Bending } \delta(NO_2) && 710-640\,\text{cm}^{-1}\\
&\text{Sway } \gamma_r(NO_2) && 580\,\text{cm}^{-1}
\end{aligned}
$$

If R in R–ONO_2 molecular was substituted, the frequency of the asymmetric vibration of NO_2 would be changed. The frequency of $\nu_{as}(NO_2)$ would be decreased or increased by the positive or negative induction effect of R group. It can be used to discriminate primary, secondary, and tertiary alkyl nitrate.

If –ONO_2 group is close to other big groups, the asymmetric and symmetric bands of NO_2 group will be blue shifted. Optical isomerism can be distinguished by this phenomenon. Because of the optical isomerism, both stretching vibrations of NO_2 group will be split to two distorted peaks

$$
\begin{aligned}
&\text{Asymmetric} && 1-25\ \text{cm}^{-1}\\
&\text{Symmetric} && 10-35\ \text{cm}^{-1}
\end{aligned}
$$

There are intramolecular hydrogen bonds, which cannot be detected by instrument, between OH and ONO_2 groups. It might be because ONO_2 restrains the formation of intermolecular hydrogen bonds with OH groups.
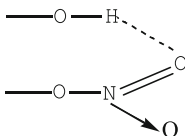
5.1.3 Hydrolysis of Nitrate Esters

Monohydric alcohol and polyhydric alcohol nitrate would be hydrolyzed in weak alkaline or weak acidic agents, but they are relatively difficult to be hydrolyzed in neutral agents. The hydrolysis process is shown in the following equation.

$$RONO_2 + H_2O \rightarrow ROH + HNO_3$$
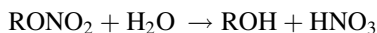
Besides the main products of alcohols and acids, other compounds, including aldehyde, ketone, hydroxycarboxylic acid, unsaturated hydrocarbons, and nitrous acid, can be obtained in the hydrolysis process of nitrate esters [31].

In general, the corresponding alcohols can be obtained in the hydrolysis process of esters, but rather a series of other compounds.

$$C_3H_4(ONO_2)_2 + 5KOH \rightarrow KNO_2 + 2KNO_3 + CH_3COOK + HCOOK + 3H_2O$$

This equation cannot stand for all hydrolysis process of esters [32, 33]. In the same conditions, the hydrolysis products of different nitrate esters include phenolic resin, oxalic acid, and ammonium. In alkaline agents, glycerol is not found in the hydrolysis products [34].

If thiophenol is involved in nitroglycerine, glycerol is formed in hydrolysis in alkaline agents.

Nitrous acid is only produced in the hydrolysis of nitrate esters with peroxide structure. Under the influence of hydrolytic reagent, the structure of nitrate esters would be changed to peroxide structure. Thus, nitrous acid would be produced in the process.

$$ROONO + H_2O \rightarrow ROOH + HNO_2$$
$$RCH_2ONO_2 + H_2O \rightarrow RCH_2OOH + HNO_3$$
$$RCH_2OOH \rightarrow RCHO + H_2O$$
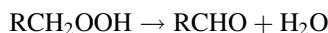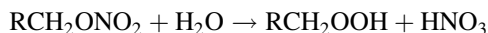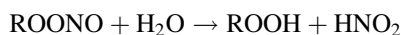
When nitrate esters are hydrolyzed in neutral agents and ethanol is treated by potassium nitrate solution, the ethanol will not be oxidized even under boiling solution [35]. Olefin is produced in the hydrolysis of tertiary alcohol nitrate. Under the circumstance, besides the corresponding alcohols, a certain amount of isobutylene is produced:

$$C_4H_9ONO_2 + 2H_2O \rightarrow C_4H_9OH_2H_3O^{\oplus} + NO^{\ominus}$$
$$C_4H_9ONO_2 + H_2O \rightarrow C_4H_8 + H_3O^{\oplus} + NO_3^{\ominus}$$
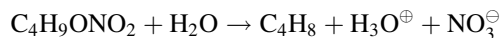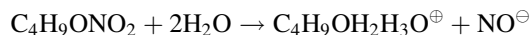
In the hydrolysis of benzyl nitrate, both benzyl alcohol and benzaldehyde are produced:

$$C_6H_5CH_2ONO_2 + 2H_2O \longrightarrow C_6H_5CH_2OH + H_3O^{\oplus} + NO_3^{\ominus}$$

$$C_6H_5CH_2ONO_2 \xrightarrow{H_2O} C_6H_5CHO + HNO_2$$
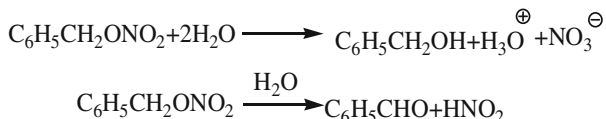
Based on the hydrolysis of those nitrate esters, it can be obtained that there are three paths for nitrate ester hydrolysis [36].

$$RCH_2CH_2ONO_2 + Y^{\ominus} \rightarrow RCH_2CH_2Y + NO_3^{\ominus}$$
$$RCH_2CH_2ONO_2Y^{\ominus} \rightarrow RCH{=}CH_2 + NO_3^{\ominus} + HY$$
$$RCH_2CH_2ONO_2 + Y^{\ominus} \rightarrow RCH_2CHO \quad + NO_2^{\ominus} + HY$$
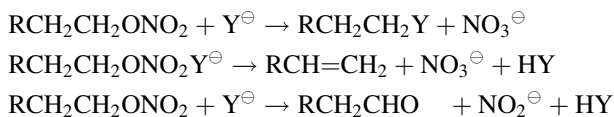
where Y is hydrolytic reagent.

The first path of hydrolysis is the nucleophilic substitution reaction. In the second path, a hydrogen atom at β position is eliminated. In the third path, α-H atom is supposed to be removed.

Those reactions only happen in the alcohol aqueous solution of monohydric alcohol nitrates. It should be noted that methyl nitrate cannot be reacted in the first path, while tert-butyl nitrate cannot be hydrolyzed in the third path. The product amount of methyl nitrate hydrolysis through the third path is very small. Only 4 % ethyl nitrate is hydrolyzed in the first and second paths. The other nitrate esters would be completely hydrolyzed in the first path. The ratio of the reaction velocity for three reaction paths is 70:7:1.

If sodium sulfhydrate, equal to basicity of pH 10–11, is used in hydrolysis, 93 % N-ester group of nitrate esters is hydrolyzed to nitrous acid ions and 7 % is hydrolyzed to ammonium. If ammonium sulfhydrate is used, the concentration of nitrous acid ions will be increased to a maximum first and then decreased to zero because of the reduction of ammonium sulfhydrate. The reduction effect would be increased with increasing pH value, especially at pH over 10. The reaction can be expressed as following chemical equations.

$$C_4H_9ONO_2 + 2NaHS \rightarrow C_4H_9OH + NaNO_2 + NaHS_2$$
$$C_4H_9ONO_2 + 4NH_4HS + 3H_2O \rightarrow C_4H_9OH + 4S + 4NH_4OH$$
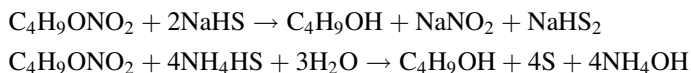
In the hydrolysis process of cellulose nitrate by sodium sulfhydrate [37], the products are formed in regenerated cellulose.

$$C_6H_8O_3(ONO_2)_3 + 2NaHS \rightarrow C_8H_{10}O_5 + 2NaNO_2 + 2S$$
$$2NaHS + 2S \rightarrow Na_2S_3 + H_2S$$
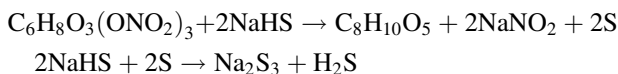
The reduction mechanism of cellulose nitrate hydrolysis in sodium sulfhydrate can be expressed as:

$$RONO_2 + HO^{\ominus} \rightarrow ROH + NO_3^{\ominus}$$
$$NO_3^{\ominus} + 2HS^{\ominus} \rightarrow NO_2^{\ominus} + HS_2^{\ominus} + HO^{\ominus}$$
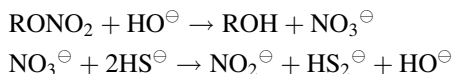
In the condition of dilute sodium hydroxide solution, the hydrolysis of cellulose nitrate and primary monohydric alcohol nitrate would be hydrolyzed very slowly. For example, only 10 % of 0.1 mol butyl nitrate, which was mixed with the solution of 0.2 mol sodium hydroxide and ethanol (60 %), was hydrolyzed at 27 °C for 16 days. Even the temperature was elevated to 60 °C and the reaction time lasted for 100 h, still only 10 % butyl nitrate was involved in the reaction. However, if sodium sulfhydrate was added to the reaction system, the butyl nitrate can be completely hydrolyzed in 4 h.

Compared with nitrous acid ions, nitric acid ions can be slowly reduced in sodium sulfhydrate. The nitrous acid ions are produced from the hydrolysis of nitrate esters, other than from the reduction of nitric acid ions. Thus, the nitrous acid ions are formed, most likely, by the breakage of bonds between oxygen and nitrogen atoms. The effect of sulfhydrate on the hydrolysis of nitrate esters is to reduce the reactants, as expressed in the following reaction mechanism equations.

$$RONO_2 + S_x^{2\ominus} \longrightarrow RO^{\ominus} + NO_2S_x^{\ominus}$$
$$NO_2S_x^{\ominus} + HS^{\ominus}(S^{\ominus}) \longrightarrow NO_2^{\ominus} + HS_{x+1}^{\ominus}(S_{x+1}^{\ominus})$$
$$HS_{x+1}^{\ominus} + H_2S^{\ominus} \rightleftharpoons HS_x^{\ominus} + HS_2^{\ominus}$$
$$RO^{\ominus} + HS_x^{\ominus} \rightleftharpoons ROH + S_x^{2\ominus}$$
$$HO^{\ominus} + HS_x^{\ominus} \rightleftharpoons H_2O + S_x^{2\ominus}$$
$$RONO_2 + S_x^{2\ominus} \longrightarrow ROS_x^{\ominus} + NO_2^{\ominus}$$
$$ROS_x^{\ominus} + HS^{\ominus} \longrightarrow RO^{\ominus} + HS_{x+1}^{\ominus}$$
$$HS_{x+1}^{\ominus} + H_2S^{\ominus} \rightleftharpoons HS_x^{\ominus} + HS_2^{\ominus}$$
$$RO^{\ominus} + HS_x^{\ominus} \rightleftharpoons ROH + S_x^{2\ominus}$$
$$HO^{\ominus} + HS_x^{\ominus} \rightleftharpoons H_2O + S_x^{2\ominus}$$
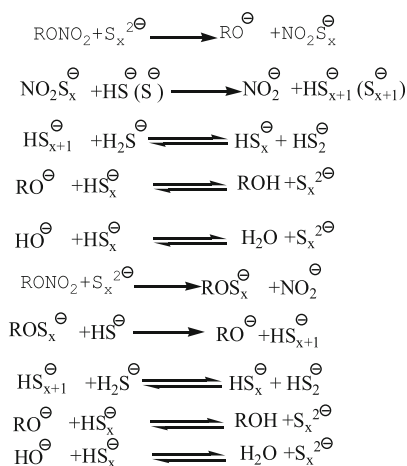
Because of the activity of sulfions and polysulfide ions, O–N bonds would be broken to form alkoxy and thionitrate ions or polythionitrate ions. The effect of sulfides on the reduction of oxygen atoms should be considered in other same type reactions. It would form nitrous ions, which cannot be produced from nitrate reduction.

If hydrazine is involved, nitrate esters act as oxidizers in the explosion reaction.

At high temperature, ethyl nitrate would react with hydrazinobenzene to produce aminobenzene, ammonium nitrate, and ammonium. If sodium ethoxide is used in the reaction, even at high temperature, the products would not include nitrous acid ions, nitrogen, benzene, phenyl azide, azobenzene, nitrobenzene, aminobenzene, acetic acid, and aldehyde.

In the presence of palladium or platinum, nitric acid would react with hydrazine to produce hexyl alcohol, nitrous oxide, and nitrogen.

$$2C_6H_{13}ONO_2 + 2N_2H_4 \rightarrow 2C_6H_{13}OH + N_2O + 3H_2O + 2N_2$$

If hydrazine is substituted by methyl hydrazine, hexyl nitrate would be converted to hexyl alcohol, but rather hexyl methyl ether.

In the products of the reaction between alkyl nitrate and hydrazine, the compounds, including nitric ions, nitrous ions, alcohols, alkyl hydrazine, nitrogen oxide, ammonium, and trace aldehyde, can be detected. If the reaction runs in solvent-free or excess hydrazine solvent, a reduction reaction would be happened [38].

In the hydrolysis process of β-chloro ethyl nitrate, 1,3-dichloro-2-propyl nitrate, nitroglycerine, or glycol dinitrate, the gas products are released more violently than the hydrolysis reaction of nonsubstituted aliphatic nitrate.

In the reaction of nitrate esters and hydrazine or its derivatives, such as methyl hydrazine and ethyl nitrate, the products are methane and nitrogen, rather than ethane. It indicates that methyl diamide is the intermediate product.

$$CH_3HNNH_2 + C_2H_5ONO_2 \rightarrow CH_3N{=}NH + C_2H_5OH + HNO_2$$
$$CH_3N{=}NH \rightarrow CH_4 + N_2$$
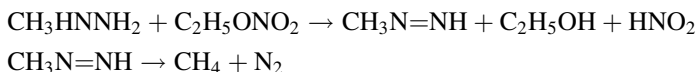
The concentration of nitrous acid product is gradually decreased by the reduction of hydrazine.

$$HNO_2 + N_2H_4 \rightarrow NH_3 + N_2O + H_2O$$
$$HNO_2 + N_2H_4 \rightarrow NH_3 + 2H_2O$$
$$HNO_2 + HN_3 \rightarrow N_2N_2O + H_2O$$
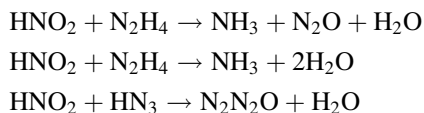
A series of products, including $C_6H_5CH_2HNNH_2$, $(C_6H_5CH_2)_2NNH_2$, $(C_6H_5CH_2)_2NNHCH_2C_6H_5$, and $(C_6H_5CH_2)_2NN(CH_2C_6H_5)_2$, can be obtained in the reaction between benzyl nitrate and hydrazine. If benzyl hydrazine is used, benzal dibenzyl hydrazine, $(C_6H_5CH_2)_2N{-}N{=}CHC_6H_5$, is produced.

Tribenzyl hydrazine is likely to be oxidized in air. In the presence of hydrazine, the C–O bonds of tert-butyl nitrate would be broken only to produce isobutene and hydrazine nitrate. Isopropyl nitrate is hydrolyzed in basic condition to produce 70–80 % isopropanol, 11–14 % propylene, and 8–14 % acetone. The hydrolysis process can be expressed as the following equation.

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!\!CHONO_2 + OH^{\ominus} \longrightarrow \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!\!CHOH + NO_3^{\ominus}$$

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!\!CHONO_2 + OH^{\ominus} \longrightarrow CH_2=CH\text{-}CH_3 + NO_3^{\ominus} + H_2O$$

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!\!CHONO_2 + OH^{\ominus} \longrightarrow \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}\!\!\!C=O + NO_2^{\ominus} + H_2O$$
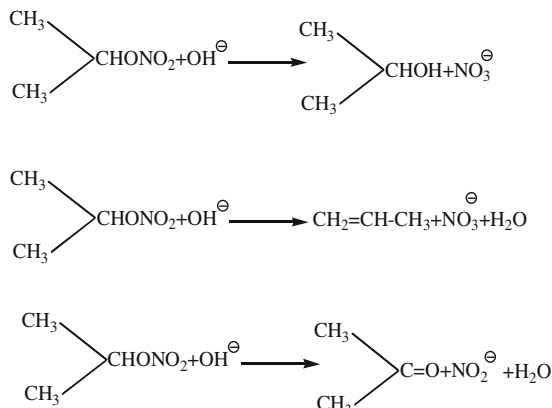
Only alcohol can be produced in the hydrolysis process of isopropyl nitrate in neutral condition.

If sodium ethoxide is used, only butyl ethyl ether and sodium nitrate are produced in the reaction between tert-butyl nitrate and benzyl cyanide. Transesterification reaction would not happen in this circumstance.

In the mixture of secondary alcohol or primary alcohol with tertiary esters, the products of secondary alcohol esters or primary alcohol esters would be further chemically combined immediately. A hydrogen atom in the raw esters would react with α-carbon atom to form alcohols, which would not be oxidized. Transesterification reaction would happen for tert-butyl nitrite because of the instability of NO.

5.1.4 Reduction of Nitrate Esters

There are many methods to reduce nitrate esters from ester groups to alcoholic hydroxyl groups, most likely to obtain the corresponding alcohols. The oldest, also the most common, reduction method is the reductive hydrolysis by alkali sulfide or alkali sulfhydrate, such as sodium sulfide, ammonium sulfide, or corresponding sulfhydrate [39]. Transesterification reaction would happen in the hydrolysis of nitrate esters by sulfuric acid to form sulfate esters [40].

The corresponding alcohols can be obtained in several reaction conditions for nitrate esters. For examples, in acetic acid solvent, iron is used as a reducer for nitrate esters [41]. In pressure condition, iron and zinc are used to reduce nitrate esters in acetic acid solvent, and palladium is used as a catalyst in the hydrogenation process. By using palladium or platinum catalysts, nitrate esters is reduced by hydrazine. The yield of reduction is up to 60–80 %. Some gases, such NO, N_2, and H_2O, are also obtained in the reduction process.

Nitrate esters can be reduced in acetic anhydride if zinc is used in the reaction, or reduced by electrolysis. They are prone to be reduced if lithium aluminum hydride is used. The reaction is finished in ether solution and the corresponding alcohols are

stoichiometrically obtained. NO_2 and ammonium are also found in the products. 1 mol ONO_2 groups need 3.4 mol $LiAlH_4$. In boiling solution, uronic nitrate is reduced by the method. However, the reaction goes very slowly, usually to be finished in 40–50 h with products of pure acetal alcohols.

5.1.5 Other Reactions of Nitrate Esters

In the presence of sodium ethoxide or potassium ethoxide, nitrate esters can be reacted with active methylene compounds to produce isonitro salt compounds (–(HO)ON=). The esters are hydrolyzed in the condition.

Similar to nitrite esters, alkyl nitrate would react with excessive Grignard reagent to produce N-dialkyl hydroxylamine.

A remarkable special property of nitrate esters is the ability to catalyze some additional polymerization reactions [42]. In nitroglycerine, both styrene and methyl methacrylate can be self-polymerized. If the amount of nitroglycerine is up to 5–20 portion (weight fraction), equals to 10 % of polymers, the polymerization rate will be fastened. The molecular weight of polymers is less than that obtained through slowly polymerization or in situ anionic polymerization.

For the typical polymerization between methyl methacrylate and glycol nitrate [43], their molar ratio is in the range of 0.07–5.9. The reaction temperatures are 25, 60, 80, and 90 °C. Glycol nitrate will be partly decomposed to produce radicals for initiating polymerization.

5.1.6 Chemical Stability of Nitrate Esters

Stability is usually called as chemical stability, which is referred to as either the stability of a chemical, or the stability of the product which is obtained by stability treatment of the chemical.

Stability of nitrate esters is a factor to decide if they can be long-term stored [44]. Because of their structure, they could be decomposed by hydrolysis and spontaneously burned to cause explosion. The higher the purity of esters is, the lower the risk of decomposition is. The stability depends on the chemical structure of nitrate esters. For example, the stability for most pure nitrate esters, such as methylene glycol dinitrate, nitroglycerine, glycol dinitrate, 1,3-propanediol dinitrate, pentaerythritol tetranitrate, and cellulose nitrate, is acceptably high.

Thermal decomposition of nitrate esters is very important in application [44]. It is related to long-term storage of weapons and industrial products, and safety and security in operation in military.

The relationship between the decomposition rate and temperature can be expressed as the following equation.

$$V = K_t + C$$

where V is reaction velocity, mg ammonium/g nitrate ester; t is temperature; K and C are constants, related to purity and nitration degree of materials, and their properties, respectively.

For alkyl nitrate esters, the relationship can be expressed as the following equation.

$$\log N = a + b \times 0.9932\,t$$

where N is the amount of nitrogen released by 2.5 g nitrate esters at a certain temperature for 15 min, mg; a and b are constants; t is temperature.

The constants for cellulose nitrate with nitrogen of 13.55 % are $a = 8.8842$ and $b = 22.86$.

Nitrate esters can be autocatalyzed to accelerate the decomposition [45]. The trace nitroxides, which are formed in the decomposition process of nitrate esters, could combine with trace water to form nitric acids or nitrous acids. Those acids would accelerate the decomposition reaction of nitrate esters.

5.2 Properties and Preparation of Monohydric Alcohol Nitrate

Monohydric alcohol nitrate is referred to as the esters with one $-ONO_2$ and alkyl monohydric alcohol group.

5.2.1 Properties and Preparation of Methyl Nitrate [46]

Methyl nitrate, CH_3ONO_2, is the simplest nitrate ester and one of the strongest liquid explosives. It is obtained from the nitration of methanol as following equation.

$$CH_3OH + HNO_3 \rightarrow CH_3ONO_2 + H_2O$$
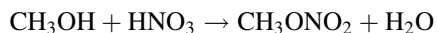
Methyl nitrate, with high volatility and low boiling point, mixes with H_2O_2 or dinitrogen tetroxide to be as liquid explosive or liquid propellant. The mixture of methyl nitrate and gasoline can be as heating agent. For example, the heating power or the total work capacity of gasoline can be increased by 6.2 % by adding 1–2 % methyl nitrate. Methyl nitrate is also used as a foaming agent in gas bags.

5.2.1.1 Chemical–Physical Properties of Methyl Nitrate

Molecular formula: CH_3NO_3
   Chemical structure:

$$H-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-ONO_2$$
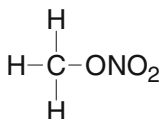
   Molecular weight: 77.02
   Oxygen balance: -10.4 % (CO_2-based)
   Nitrogen content: 18.18 %
   Methyl nitrate is a transparent colorless oily liquid with a sweetish odor. Its
density is 1.21 and boiling point is 65–66 °C. The viscosity is lower than water,
thus its fluxility is good. It is miscible with alcohols. About 385 g methyl nitrate can
be dissolved in 100 mL water at 25 °C. The dissolving capacity of methyl nitrate for
collodion and high-nitrogen cellulose nitrate is strong. The vapor of methyl nitrate
is flammable and would be exploded at 150 °C. In closed condition, methyl nitrate
would be vapor exploded by spark or ultraviolet irradiation at 250–300 °C.

5.2.1.2 Explosion Property and Thermal Decomposition of Methyl Nitrate

The explosion heat of methyl nitrate is 6732.1–6744.15 J/g, higher than nitro-
glycerine by 1.02 %. Its shock sensitivity is lower than nitroglycerine. The
explosion height for 2,000 g falling weight is 400 mm. Its burning velocity is about
four times higher than nitroglycerine, about 0.12 cm/s in a glass tube. Even under
pressurized condition of 0.15 MPa, it can be continuously burnt. At higher pressure,
it will be in pulsation combustion. The combustion will be turned to detonation at
the pressure of 0.4 MPa.
   The decomposition of methyl nitrate will cause spontaneous explosion [47]
because of the exothermal property of the reaction.

$$2CH_3ONO_2 \rightarrow CH_3OH + CH_2O + 2NO_2$$
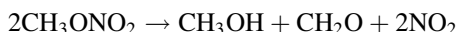
   The explosion of methyl nitrate induced by spark at 25 °C [48] is different from
the heat-induced explosion. The mechanism of the spark-induced explosion is
shown as the following steps.
   Induced reaction

$$CH_3ONO_2 \rightarrow CO + NO + H_2O + \frac{1}{2}H_2$$

Explosive reaction

$$CH_3ONO_2 \rightarrow \frac{1}{2}CO + \frac{3}{2}H_2O + \frac{1}{2}CO_2 + \frac{1}{2}N_2$$
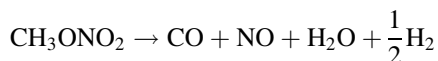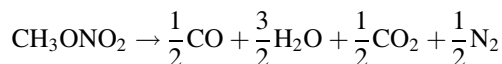
Oxidation and reduction reactions alternately happen among products to form gases of nitrous oxide and carbon monoxide. Methyl nitrate would be oxidized through spontaneous decomposition path at 300 °C.

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2NO + 2CO \rightarrow 2CO_2 + N_2$$
$$2NO + 2H_2 \rightarrow 2H_2O + N_2$$
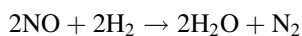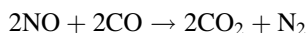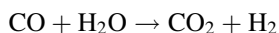
The overall reaction is expressed as

$$CH_3ONO_2 \xrightarrow{Q} 0.95NO + 0.025N_2 + 0.75CO + 0.25CO_2 + 0.7H_2 + 0.8H_2O$$
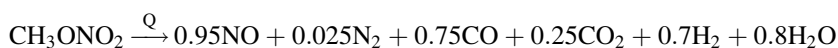
For the spark-induced reaction, the reaction can be given as

$$CH_3ONO_2 \xrightarrow{Spark} 0.175NO + 0.41N_2 + 0.49CO + 0.51CO_2 + 0.175H_2 + 1.31H_2O$$
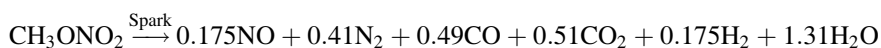
The decomposition of methyl nitrate under ultraviolet is different from other decomposition pathway.

$$CH_3ONO_2 \xrightarrow{h\gamma} 0.30NO + 0.35N_2 + 0.50CO + 0.50CO_2 + 0.30H_2 + 1.2H_2O$$
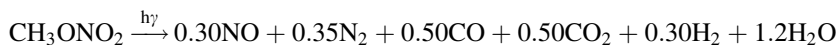
Therefore, the explosive decomposition of methyl nitrate is radical reaction

$$2CH_3ONO_2 \rightarrow CO_2CO + 3H_2O + N_2$$

or

$$2CH_3ONO_2 \rightarrow 2CO_2 + H_2 + 2H_2O + N_2$$
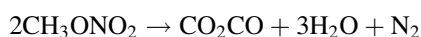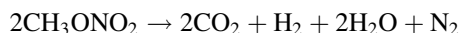
At the initial stage of thermal decomposition of methyl nitrate, as well as other simple nitrate esters, the reactions can be written as [44]:

$$RCH_2ONO_2 \rightleftharpoons RCH_2O^{\ominus} + NO_2$$
$$RCH_2O^{\ominus} + RCH_2ONO_2 \rightarrow RCH_2OH + RC^{\ominus}HONO_2$$
$$RC^{\ominus} + HONO_2 \rightarrow RCHO + NO_2$$
$$RCH_2O^{\ominus} \rightarrow \frac{1}{2}RCHO + \frac{1}{2}RCH_2OH$$
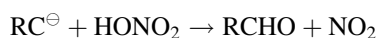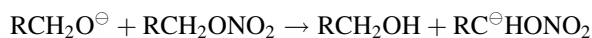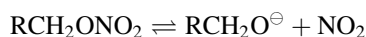
In a tube with diameter of 30–40 mm, the detonation velocity is about 8,000 m/s. In a tube with small diameter, the detonation velocity is approximately 1,500 m/s, while the detonation velocity exceeds 6,000 m/s in large tubes.

5.2.1.3 Preparation of Methyl Nitrate [1, 15, 49]

In early period, methyl nitrate was prepared by nitration reaction between methanol and urea nitrate-contained nitric acid or mixed acid of nitric acid and sulphuric acid (40:60) at 18 °C for 20–40 min [50]. The density of nitric acid is 1.4 g/cm^3 without nitrogen dioxide. After nitration, the products were washed by water to pH 7 and carefully distilled at 40 or 18 °C to obtain methyl nitrate. The yield of the nitration reaction is 45–80 %. The production period of the preparation method is long and the yield is very low.

People [51] prepared methyl nitrate with yield of 85 % through displacement reaction between nitrate salt and methanol. Methyl nitrate also can be prepared in acetic acid [52]. At 5 °C, methanol was nitrated by nitric acid with methyl nitrate yield of 72–81 %. However, high concentration of mixed acids would cause serious heat release in the water-washing step. The other disadvantages include severe hydrolysis and heavy environmental pollution.

Those preparation methods are very complicated and even the maximum yield is not more than 81.5 %. In the preparation process, it requires a critical control of reaction temperature. Otherwise, explosion could happen if temperature is out of control.

Because of low boiling point and high volatility, methyl nitrate cannot be washed by hot water. However, cold water also cannot be used in washing step because of the low viscosity of methyl nitrate. A new preparation method [46, 49] of methyl nitrate was proposed as the following equation.

$$CH_3OH + HNO_3 \xrightarrow{\ CON_2H_4\ } CH_3ONO_2 + H_2O$$
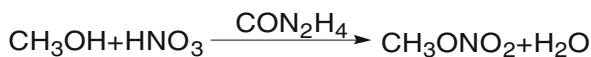
In industry, in order to obtain pure products, the amount of used methanol should be controlled to reduce the impurities that might be dissolved into methyl nitrate, thus that nitric acid could be completely converted to methyl nitrate. The schematic diagram of methyl nitrate production by continuous nitration is shown in Fig. 5.1.

Two normal funnels with a liquid mixture of methanol, water, and urea, referred as methanol mixture, are separately set at two sides of the set-up. In the middle, it is equipped with a distillation head, a temperature controller, a condenser, and a receiver. The procedure of the continuous nitration for methyl nitrate is described as follows. HNO$_3$ and distilled water are slowly added to urea in a reaction vessel at 110 °C. The temperature at the position of the distillation head is in the range of

Fig. 5.1 Schematic diagram of continuous nitration for methyl nitrate

80–85 °C. The methanol mixture and nitric acid are added dropwise with a rate of 80–160 drop/min. Layering would be observed in the receiver. The temperature of the distillation head is decreased to 65 °C and the reaction temperature is decreased to 95 °C. After dropwise addition, the temperature will be kept for another 30 min to ensure the complete installation of products in the vessel. The product at the bottom of the receiver is methyl nitrate.

The acidic crude product would be washed by water to pH 7. Sodium carbonate solution would be then used to continuously wash the product to pH 7.2–7.5. The final crude methyl nitrate product with yield 98.7 % would be stored with the desiccant of magnesium sulfate. The production process of methyl nitrate is shown in Fig. 5.2.

In the process, the main steps include nitration, distillation, washing, drying, rectification, and waste treatment. The crude methyl nitrate is rectified to obtain pure methyl nitrate at the boiling range of 64.5–65 °C. The IR spectrum of pure methyl nitrate is shown in Fig. 5.3.

The bands at 1,625 and 1,282 cm^{-1} can be assigned to the stretching vibration of –ONO$_2$ group of methyl nitrate, as shown in Fig. 5.3, and a series of strong and broad bands are shown at 855 and 760 cm^{-1}.

In summary, by this preparation method, 100 units of methanol can be converted to 234.98 units of methyl nitrates after rectification and collection at 64.5–66 °C. The theoretical yield is 97.5 %.
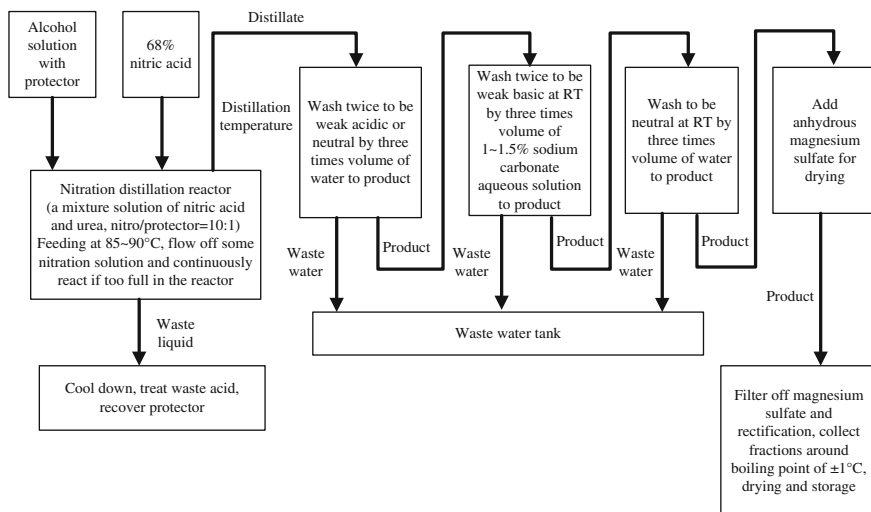
Fig. 5.2 The production process of methyl nitrate
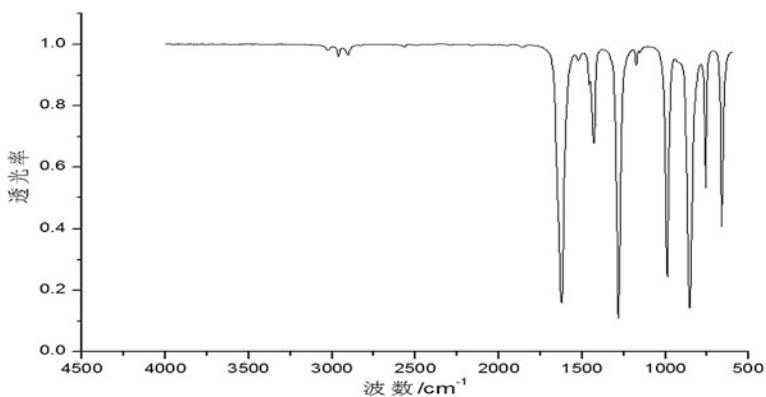
Fig. 5.3 IR spectrum of methyl nitrate

5.2.1.4 Toxicity of Methyl Nitrate

Methyl nitrate is a kind of compound with slight toxicity. However, because of the low viscosity and volatile, methyl nitrates usually poison human respiratory system. After inhalation of methyl nitrate vapor, the feeling of headache is similar to nitroglycerine. However, the symptom for methyl nitrate comes and goes faster than nitroglycerine.

5.2.2 Property and Preparation of Ethyl Nitrate [53]

5.2.2.1 Chemical–Physical Property of Ethyl Nitrate

Ethyl nitrate, with other names of ethanol nitrate ester and nitric acid ethyl ester, is a transparent oily liquid with a slight sweetish odor. It can be dissolved into water and be miscible with alcohols and most other organic reagents. It also can dissolve cellulose nitrate.

Molecular formula: $C_2H_5NO_3$

Chemical structure:

$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-ONO_2$$
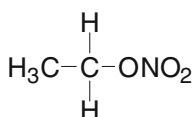
Molecular weight: 91.07

Oxygen balance: −61.5 % (CO_2-based)

Nitrogen content: 15.38 %

Boiling point: 87 °C

Density: 1.12

Combustion heat: 322 kcal/mol

The nitration heat of ethanol is 25.94 kJ/mol, Thomson calculated the combustion heat $-\Delta H$ and detonation heat (water) of ethyl nitrate to obtain the values of 1355.78 kJ/mol and 3568.95 J/g, respectively. The explosion property of ethyl nitrate has been well known. However, in a long period, few attentions have been paid to the compound. It only has been used as a component in the liquid fuel of rockets and in explosive mixture with other oxidizers for blasting.

5.2.2.2 Explosive Property

The expanding value of lead block with water of ethyl nitrate is 345 cm. The detonation velocity of ethyl nitrate in wide tubes is 6,000–7,000 m/s. A steady detonation can be obtained to fill ethyl nitrate into a thick-wall metal tube. The detonation velocities in a steel tube with a diameter of 27 and 60 mm are 5,800 and 6,020 m/s, respectively. In a steel tube with a diameter of 10 mm, the detonation cannot happen. The lead-block value of ethyl nitrate is larger than chrysolepic acid approximately by 20 %. Its shock sensitivity is low. 50 % of ethyl nitrate would be exploded at the height of 500 mm for 2,000 g falling weight.

5.2.2.3 Preparation of Ethyl Nitrate [1, 15, 53]

In the preparation method of ethyl nitrate, cold ethanol will be dissolved into concentrated nitric acid with the density of 1.41 g/cm^3 without nitrogen oxides. The

solution will be distilled to obtain ethyl nitrate [54]. If amine oxide is in the reaction system, ethanol will be oxidized to aldehyde. The nitration could be influenced by quite a bit nitrogen oxide in the acids.

The writer [53] invented the approach of continuous nitration of nitric acid vapor to prepare ethyl nitrate. The solution of alcohol and nitric acid was added dropwise into a reactor, in which a protective agent of carbonyl groups was contained. The products were continuously distilled out of the reaction system during the process of nitration reaction. Thus, the removal of ethyl nitrate makes the concentration of products low, favoring the forward reaction and increasing the yield of nitration. Meanwhile, because the retention time of nitrate esters in the thermal reactor is shortened, the amount of nitrous acid, as well as intermediates, is reduced, improving the safety of the production process. The reaction process can be described by the following equation.

$$CH_3CH_2OH + HNO_3 \rightarrow CH_3CH_2ONO_2 + H_2O$$
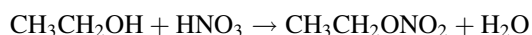
Two normal funnels with an alcohol/protective agent solution and 68 % nitric acid solution, respectively, with the same weight are separately set at two sides of a reactor, in which zeolites are added. In the middle, it is equipped with a distillation head, a temperature controller, a condenser, and a receiver.

The nitrated agent is composed of 75–90 % HNO_3, 5–15 % H_2O, and 5–10 % protective agent. The protective agent consists of urea, cyanoguanidine, and melamine.

The preparation procedure of ethyl nitrate is described below. A certain amount of the protective agent aqueous solution is added into the reactor. A quantity of HNO_3 is slowly added into the solution. The temperature of an oil bath is set at 130 °C and the temperature of the distillation head is controlled in a reasonable range. When the protective agent is dissolved and the solution is boiled at the temperature of set point, the vapor of nitric acid is full of the reaction. Anhydrous ethanol and nitric acid solution are dropwisely added into the reactor with a certain adding rate. Oily drops can be observed in the condenser. The solution in the receiver starts to be layered. Keeping the reaction temperature and the reactants adding rate makes the reaction steadily running.

After addition of reactants, the temperature of the oil bath is kept at 130 °C for another 20 min to ensure that the products are completely distilled out of the reactor. Obvious layers can be seen in the receiver. The product of nitrate ester is in the bottom layer. The crude product would be washed by water to pH 7. Sodium carbonate solution would be then used to continuously wash the product to pH 7.2–7.5. The crude nitrate ester product would be stored with the desiccant of magnesium sulfate. The product could be added into rectification system with zeolites to obtain highly pure nitrate esters.

The above-described process has changed the traditional preparation method to produce ethyl nitrate. The advantages of this method, including carbonyl protection, effective vapor usage in nitration, quick removal of product out of the reactor, and controllable feedstock addition rate of feedstock and reaction rate, reduce the
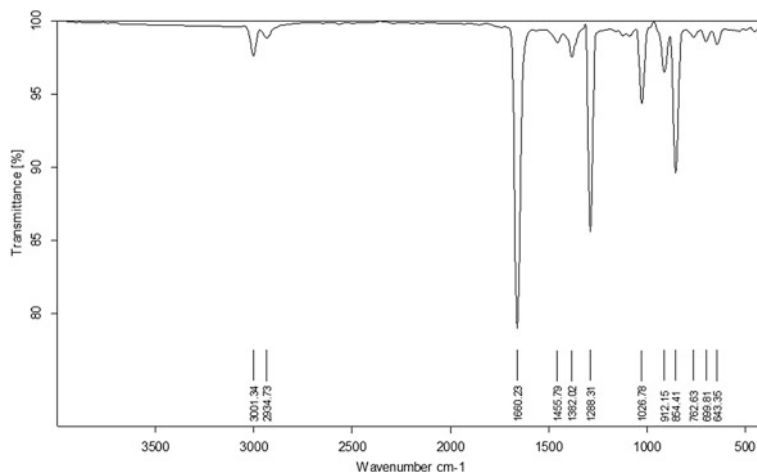
Fig. 5.4 IR spectrum of ethyl nitrate

retention time of nitrate esters in the thermal reactor. Therefore, the production of nitrous acid can be decelerated to significantly improve the safety of the production process.

The crude products will be put into a distillation system to collect the fraction in the boiling range of 88–91 °C. The obtained colorless liquid is pure ethyl nitrate, whose IR spectrum is shown in Fig. 5.4.

The band at 3,000 cm^{-1} can be assigned to C–H stretching vibration with frequency multiplication. The bands at 1,660 and 1,288 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of NO_2, respectively. The bands at 1,455 and 1,382 cm^{-1} are attributed to C–H bending vibrations of methyl and methylene groups, respectively. The band at 1,026 cm^{-1} is the stretching vibration of C–O and the band 864 cm^{-1} is the stretching vibration of N–O. The H-NMR spectrum of the ethyl nitrated is shown in Fig. 5.5.

The δ_H is at 4.506–4.559 (2H, m) and 1.366–1.402 (3H, t), as shown in Fig. 5.5. Based on the IR and H-NMR spectra, the product can be believed as ethyl nitrate with a yield of 94.5 %.

5.2.3 Property and Preparation of n-Propyl Nitrate

N-propyl nitrate is also called as n-propyl alcohol nitric ester.
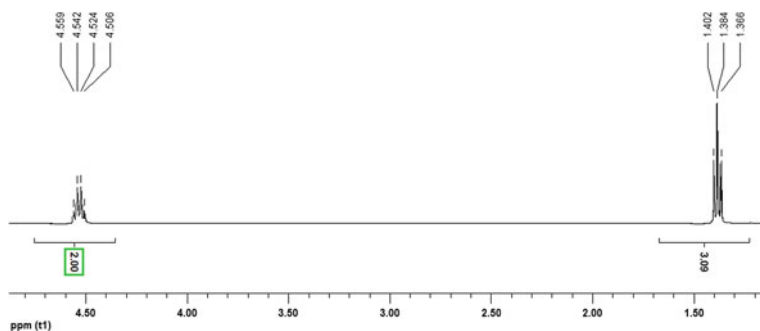
Fig. 5.5 H-NMR spectrum of ethyl nitrate

5.2.3.1 Chemical–Physical Properties of *n*-Propyl Nitrate

Molecular formula: $C_3H_7NO_3$
 Chemical structure:

$$H_3C-H_2C-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-ONO_2$$
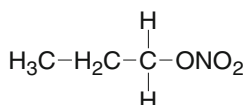
 Molecular weight: 105.09
 Oxygen balance: −99.0 % (CO_2-based)
 Nitrogen content: 13.33 %
 N-propyl nitrate is a flammable liquid with boiling point of 110.5 °C and density of 1.063. Its explosive property is not severe, thus that it is difficult to be detonated. The calculated explosion heat is 549 kcal/kg (water vapor). The lead-block value after rectification of the detonator is only 15 cm. The explosion limit of the mixture with air is 2–100 %. Its flash point is 20 °C and the ignition point in air is 176.7 °C. Its vapor, which is heavier than air, can spread around and be ignited by distant fire. Furthermore, the ignition flame would be returned to the *n*-propyl nitrate source. Being heated, *n*-propyl nitrate would be exploded. A significant detonation could be happened if it mixes with diatomaceous earth with ratio of 71.5/28.50. The lead-block value is 230 cm. *N*-propyl nitrate can be used as a sensibilizer in cloud detonation, a rocket propellant, and a promoter of cetane number for diesel oil.

5.2.3.2 Preparation of *n*-Propyl Nitrate

Hinkamp et al. [55] prepared *n*-propyl nitrate with a yield of 66.5 % by using mixture acids of 20 wt% HNO_3, 68 wt% H_2SO_4, and 12 wt% H_2O. For this preparation method, the yield is low and acid mist could be formed for environmental pollution in the process of waste acid treatment by sulfuric acid method. People [56] improved the *n*-propyl alcohol nitration on the nitrating agent and the

yield. The yield was significantly improved and the pollution of waste acids was reduced.

The writer [15, 57] addressed a method to prepare *n*-propyl nitrate. In a reactor, a mixture of 68 % nitric acid and urea was added to vapor temperature of 98 °C. At the moment, the temperature of the liquid surface was 112 °C and the temperature of the oil bath was 142 °C. The 68 % nitric acid solution and the *n*-propyl alcohol solution with water and 5 % urea were dropwisely added into the reactor. At the beginning of the addition, the temperature of the distillates was 98–106 °C. In the steady state, the vapor temperature was 102–104 °C with the temperatures of liquid surface of 110 °C and the oil bath of 145 °C. The addition was finished in 90 min and the reactor was kept warm for another 15 min. The crude products with yield of 89 % was successively water-washed and alkaline-washed (1.5 % sodium carbonate) to pH 7 and oil-water separation. Anhydrous magnesium sulfate was added to the oil part for 24 h. After filtration, the crude product was then rectified and the final product was obtained from the cut of 109.5–110.5 °C with a yield of 86.3 % and purity of 99.62 %.

5.2.4 Property and Preparation of Isopropyl Nitrate

Isopropyl nitrate, also called as isopropanol nitrate ester, is an isomer of *n*-propyl nitrate and one of the most extensively used monobasic alcohol nitrates.

5.2.4.1 Chemical–Physical Property of Isopropyl Nitrate

Molecular formula: $C_3H_7NO_3$
  Chemical structure:

$$H_3C - \underset{\underset{ONO_2}{|}}{\overset{\overset{H}{|}}{C}} - CH_3$$
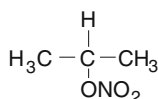
  Molecular weight: 105.09
  Oxygen balance: −99.0 % (CO_2-based)
  Nitrogen content: 13.33 %
  Boiling point: 101–102 °C

5.2.4.2 Preparation of Isopropyl Nitrate

The preparation method of isopropyl nitrate is different from that of *n*-propyl nitrate. Because of the boiling point, the relative density of 1.036, and the secondary hydroxyl groups, the direct nitration is relatively difficult. In the early literatures, it was believed that isopropyl nitrate only can be obtained from

2-iodopropane and silver nitrate [58]. In British patent [55], isopropanol was continuously nitrated in urea. At the temperature of the boiling point of nitric acid, isopropanol and urea were added into nitric acid with concentration of over 40 %. Unstable products were removed by a flowing gas. The theoretical yield of isopropyl nitrate obtained by this method is 80 % [59]. The main methods to prepare isopropyl nitrate include (1) sliver nitrate–alkyl halide reaction, (2) nitration by the mixed acids of nitric acid and sulfuric acid, and (3) inert adsorption nitration [60, 61]. Based on those preparation methods, The writer [15, 62–64] invented the dual inert complementary adsorption nitration. In the method, the concentration of nitric acid is over 50 % and the reaction temperature is 108–110 °C. Commercial production of isopropyl nitrate has been done by this method. A certain amount of urea and ammonium nitrate is used in the method to absorb nitrogen oxides, which will be oxidized to isopropyl nitrate. The isopropyl nitrate would be catalytically hydrolyzed at high temperature. The reaction mechanism can be expressed as the following equation.

$$(CH_3)_2CHOH + HNO_3 \xrightarrow[\text{[100–105 °C]}]{\text{(NH)}_2\text{CO+NH}_4\text{NO3}} (CH_3)_2CHONO_2 + H_2O$$
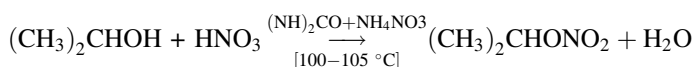
The inert adsorption nitration is suitable for commercial production of isopropyl nitrate because of its features, such as simple procedure, cheap raw materials, low-cost production, and easy treatment of waste acid. The procedure is described below.

70 % nitric acid is poured into a stainless steel reactor, and then urea and ammonium nitrate are added in proportion. The temperature is slowly increased to 70–80 °C under agitation till the urea and ammonium nitrate are completely dissolved. The temperature is then increased to 95–100 °C and isopropanol is dropwisely added by a dropping funnel with the end under the solution. Cooling water and vacuum systems are used to pump out the produced nitrogen oxide gases in time. The addition time of isopropanol is 20–50 min at temperature of 100 °C. After addition, the temperature is kept at 100–105 °C for another 10–20 min till no more refluxed and condensed products. Shut down the system of agitation, vacuum, and condensation, the liquid condensate is separated to two layers and the bottom layer of acid waste is discarded. The crude product is first washed by 3 % Na_2CO_3 aqueous solution and then washed by deionized water till pH 7. The crude product is dried and rectified under normal pressure. The final product with a yield of 97.6 % is collected in the cut range of 101–102 °C. The isopropyl nitrate product is a colorless liquid with relative density of 1.036 and purity of 99.6 % determined by GC.

In order to study the relationship between the reaction condition and yield, the writer [63, 65] investigated the effects of urea amount, ammonium nitrate amount, concentration of nitric acid, the addition time of isopropanol, the feeding system, and feed types on the yield of isopropyl nitrate. The effect of urea amount on the yield of isopropyl nitrate is summarized in Table 5.6, under the reaction condition

Table 5.6 Effect of urea amount on the product yield

Urea/g	4.0	5.0	5.5	6.0	6.5	7.0
Isopropyl nitrate/g	13.7	14.8	16.6	15.0	13.1	11.5
Yield/%	63.7	68.9	77.3	69.7	60.9	53.6

Table 5.7 Effect of nitric acid concentration on the product yield

Nitric acid concentration/%	65.0	70.0	73.0	75.0	77.0	80.0
Isopropyl nitrate/g	13.9	18.6	18.7	15.4	14.1	8.9
Yield/%	66.2	86.3	88.9	71.7	65.6	41.3

Table 5.8 Effect of ammonium nitrate amount on the product yield

Ammonium nitrate/g	9.0	11.0	13.0	15.0	17.0
Isopropyl nitrate/g	12.8	15.0	18.9	16.2	13.7
Yield/%	59.7	69.9	87.9	75.3	63.8

Table 5.9 Effect of isopropanol addition time on the product yield

Addition time/min	35	20	12	7
Isopropyl nitrate/g	14.8	17.8	21.0	18.2
Yield/%	68.7	82.6	97.7	84.5

as, temperature: 100 ± 2 °C; composition: 13 % ammonium nitrate, 12 % nitric acid, 50 mL nitric acid with concentration of 70 %; addition duration: 30 min.

It can be seen that the maximum yield is obtained if the amount of urea used is 5.5 %. Table 5.7 summarizes the effect of the concentration of nitric acid, under the reaction conditions as mentioned above.

In the concentration of nitric acid of 70 %, the yield of isopropyl nitrate is up to 88.9 %. Changes of the yield of isopropyl nitrate with the amount of ammonium nitrate are shown in Table 5.8, under the reaction condition as mentioned above.

The maximum yield of isopropyl nitrate is obtained with the amount of ammonium nitrate of 13 %. The addition time of isopropanol influenced the yield of isopropyl nitrate significantly, as shown in Table 5.9.

The maximum yield of isopropyl nitrate can be obtained in the addition time of 7–15 min. The nitration rate of isopropanol will be accelerated at high temperature. Thus, by shortening the reaction time, the oxidization reaction can be reduced.

The nitration reaction is operated at temperature above the boiling point of isopropanol of 82.5 °C. Thus, if isopropanol is added above the surface of the reaction solution, it will be vaporized before being nitrated. Because the end of the dropping funnel is dip into the nitration solution, isopropanol is quickly nitrated to isopropyl nitrate, which will be vaporized at 100 °C. The unreacted isopropanol

Fig. 5.6 Industrial production device of isopropyl nitrate

will be refluxed and come back to the reactor. The isopropyl nitrate product is condensed and collected to reduce the conversion of oxidation reaction at high temperature. This modified method shows high production efficiency and stable yield. The industrial production device of isopropyl nitrate is shown in Fig. 5.6.

The optimal condition to produce isopropyl nitrate is that the nitration temperature is 106 °C. The holding temperature is 100–105 °C for 5–10 min. The feeding time is about 15 min. The mass ratio of feedstock is isopropanol (99.5 %): nitric acid (70 %): urea (99 %): ammonium nitrate (98 %) = 1:6:0.43:0.96. At this condition, the yield of isopropyl nitrate with the purity of 99.6 % is up to 97.6 %.

5.2.5 Property and Preparation of n-*Butyl Nitrate* [56]

5.2.5.1 Chemical–Physical Property of *n*-Butyl Nitrate

Molecular formula: $C_4H_9NO_3$
   Chemical structure:

$$H_3C-H_2C-H_2C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-ONO_2$$
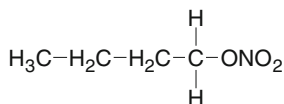
   Molecular weight: 119.12
   Oxygen balance: −127.6 % (CO_2-based)
   Nitrogen content: 10.52 %

5.2.5.2 Preparation of *n*-Butyl Nitrate [66]

The conventional preparation method of *n*-butyl nitrate is to nitrate *n*-butanol by the mixed acid of nitric acid and sulfuric acid. However, the yield is very low by this
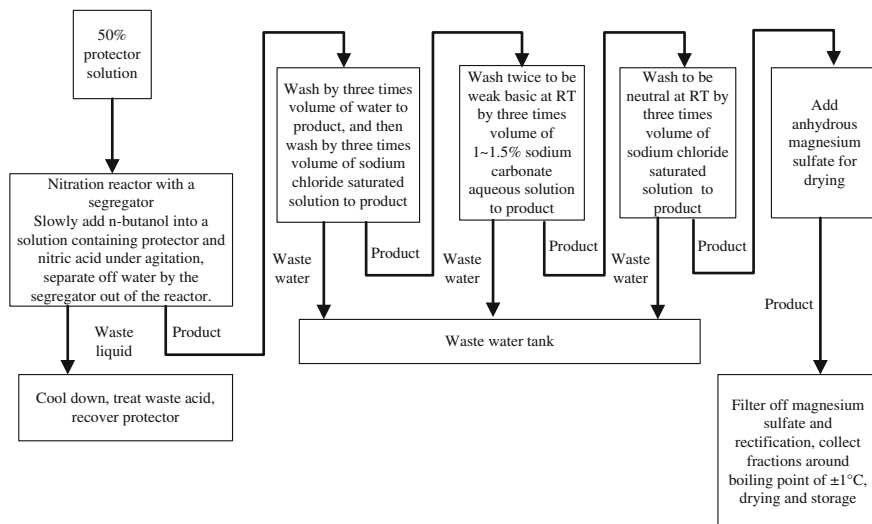
Fig. 5.7   Preparation process of *n*-butyl nitrate

method and there are safety risks in the process of production [12]. The writer prepared *n*-butyl nitrate by direct continuous nitration method by dilute nitric acid in protecting agent. The preparation process flow is shown in Fig. 5.7.

As shown in Fig. 5.7, the differences between the preparation of *n*-butyl nitrate and the other monobasic alcohol nitrates are evident: (1) The nitration process for the other nitrate esters, such as methyl nitrate, is the continuous nitration-distillation method, while for *n*-butyl nitrate, the process is the reflux and water segregator method; (2) In the washing process, *n*-butyl nitrate is washed by saturated sodium chloride solution because its density is close to that of water.

The key device in the preparation of *n*-butyl nitrate is the water segregator, which is seldom used in chemistry. The segregator is particularly designed in application of the preparation of *n*-butyl nitrate based on the requirements and working condition. The production facilities of *n*-butyl nitrate are shown in Fig. 5.8.

The volume of the nitration reactor is about 110 L equipped with an explosion proof motor, a cycloidal reducer, mechanical seals, an anchor agitator, a temperature sensor, a pressure gauge, three feeding holes with different size, a segregator with a glass mirror, 1,000 mm condenser, and a jacket of heat transfer oil. The system also includes a temperature controller, an agitation controller, and a washing vessel. By application of the production unit, the yield of *n*-butyl nitrate is up to 95.7 % with the purity of 98.88 %.

Fig. 5.8 Facilities of producing *n*-butyl nitrate. *Left* nitration reactor, *right* segregator with a glass mirror

5.2.6 Property and Preparation of n-*Amyl Nitrate*

5.2.6.1 Chemical Physical Properties of *n*-Amyl Nitrate

Molecular formula: $C_5H_{11}NO_3$
 Chemical structure:

$$H_3C-H_2C-H_2C-H_2C-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-ONO_2$$
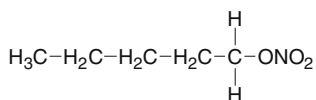
 Molecular weight: 133.15
 Oxygen balance: −150.2 % (CO_2-based)
 Nitrogen content: 10.52 %

5.2.6.2 Preparation of *n*-Amyl Nitrate [56]

The composition of nitration solution is 60 wt% HNO_3, 30 wt% H_2O, and 10 wt% protective agent. The protective agent is composed of 80 wt% urea and 20 wt% ammonium nitrate. The nitration solution in a reactor is heated to 82 °C, and then both *n*-pentanol and 15 % urea aqueous solution are slowly added into the reactor. If the addition rate of *n*-pentanol is too fast, the reaction solution would be overflown. When the temperature reaches 95 °C, water in the reaction system will be segregated. The temperature of the oil bath is set at around 160 °C and the

temperature of distillation head is also controlled in a range. When the vapor temperature is increased to about 100 °C, water reflux in the condenser will be observed. Two liquid layers will be formed in the segregator by further heating the reactor. The supernatant is an ester layer and the subnatant is a water layer. The water layer will be continuously separated out of the segregator and measured. When the vapor temperature in the reactor is raised to 150 °C and 75 % water is separated by the segregator, the reaction will be ceased. It can be seen that the supernatant in the reactor is light yellow, suggesting that esters are in the layer. The subnatant is water. Cool down the temperature under agitation in air. At around 30 °C in the reactor, liquid will be poured out and solid precipitates will be filtered away. There is obvious stratification in the filtrate. The target product of *n*-amyl nitrate is in the supernatant and will be obtained after washing and drying. The procedure of separation of waste acid from *n*-amyl nitrate is to wash the product first by distilled water with five times the volume of *n*-amyl nitrate. The ester layer after water washing will be washed by sodium carbonate–sodium chloride saturated solution with pH 10 to alkalescence. The obtained liquid will be then washed by sodium chloride saturated aqueous solution to pH 7.2–7.5 and magnesium sulfate will be added for drying. The crude *n*-amyl nitrate is obtained with yield of 97.0 %. The pure *n*-amyl nitrate with the yield of 92.4 % can be obtained by rectifying the crude product with zeolite and cutting the fraction between 154.5 and 155.5 °C.

5.2.7 *Property and Preparation of Chlorinated Glycerol Nitrate*

Chlorinated glycerol nitrate is a homologue of nitroglycerine, in which a hydroxide group is substituted by nitrate group and a hydrogen atom at carbon site of methylene is substituted by a chloro group. Chlorinated glycerol nitrate is a nitrate ester with very weak explosion property.

Molecular formula: $C_3H_6NO_4Cl$

Chemical structure (three isomers with different substitution sites):

CH_2ONO_2 CH_2OH CH_2ONO_2

$CHOH$ $CHONO_2$ $CHCl$

CH_2Cl CH_2Cl CH_2OH
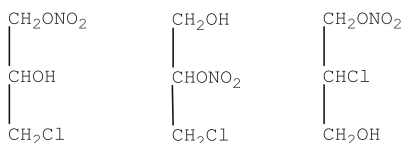
Molecular weight: 155.58

Oxygen balance: −51.42 % (CO_2-based)

Nitrogen content: 9.00 %

Chlorinated glycerol nitrate is one of the liquid explosives with weak shock sensitivity. It exploded only under the action of booster charges.

Table 5.10 Properties of two isomers of glycerol nitrate [3]

Configuration	Density (g/cm^3)	Melting point (°C)	Boiling point (°C)
α	1.53	58.5–59.0	159 (15 mmHg)
β	1.52	54	155 (15 mmHg)

5.2.8 Property and Preparation of Glycerol Nitrate [3]

Glycerol nitrate, also called as mononitroglycerin, has α and β isomers. Their melting point and boiling point are slightly different. The discrimination between two isomers is listed in Table 5.10.

Molecular formula: $C_3H_7NO_5$

Chemical structure:

CH$_2$ONO$_2$

CHOH

CH$_2$OH

α isomer

CH$_2$OH

CHONO$_2$

CH$_2$OH
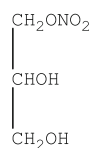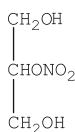
β isomer

Molecular weight: 137.08

Oxygen balance: −52.52 % (CO_2-based)

Nitrogen content: 10.22 %

CH$_2$ONO$_2$

CH$_2$ OH

CH$_2$ONO$_2$

CH$_2$ONO$_2$

CHONO$_2$

CH$_2$OH

CH$_2$ONO$_2$

CH

CH$_2$

O

-H$_2$O

CH$_2$ONO$_2$

CHOH

CH$_2$OH
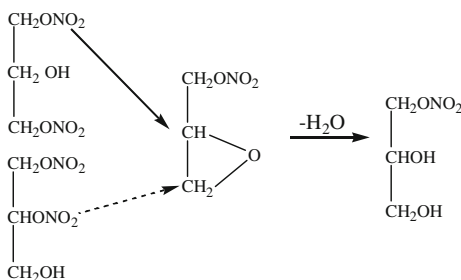
Glycerol nitrate is a very stable compound. It would be decomposed at 100 °C and be exploded at 170 °C in a sealed container.

Glycerol nitrate is a weak explosive with obvious negative oxygen balance. Its explosive heat (water vapor condition) is about 1815.9 J/g. Its shock sensitivity is low, thus that it can be a desensitizer. The instability for detonation is related to its physical status. The lead-block value of glycerol nitrate is only 75 cm^3. The crystal of glycerol nitrate is easy to be detonated with lead-block value of 245 cm^3.

5.2.9 Property and Preparation of Glycidyl Nitrate [3]

Molecular formula: $C_3H_5NO_4$
   Chemical structure:

CH_2ONO_2
|
CH
| >O
CH_2
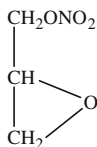
   Molecular weight: 119.07
   Oxygen balance: −60.46 % (CO_2-based)
   Nitrogen content: 11.76 %
   Glycidyl nitrate is decomposed at 174–175 °C under atmosphere pressure and 94 °C under 20 mmHg pressure. Its density at 20 °C is 1.332. Glycidyl nitrate is slightly dissolved into cold water. At 20 °C, 100 mL water can dissolve 5 g glycidyl nitrate. Glycidyl nitrate in water at boiling condition is hydrolyzed to α-glycirine nitrate. The solubility of collodion in glycidyl nitrate is high.
   The explosive heat of glycidyl nitrate is 3447.62 J/g. It will be detonated under shock with a characteristic height of 10–20 cm. Under continuous heat to 195–200 °C, it will explode. The lead-block value with water filling is about 430 cm (falling weight of 2 kg).
   Glycidyl nitrate is formed by hydrolysis of two isomers of glycerine dinitrate. Glycerine dinitrate is hydrolyzed in 30 % KOH solution at room temperature. The oily precipitate is glycidyl nitrate with the yield of 95 %. After stability treatment, the final product can be obtained by water washing to pH 7 and drying with a desiccant.

5.2.10 Property and Preparation of Dichloroglycerol Nitrate [3]

Dichloroglycerol nitrate, without explosive property, is formed by substituting two oxhydryl groups of glycerol nitrate with two chloro groups.
   Molecular formula: $C_3H_5NO_3Cl_2$
   Chemical structure:

CH_2Cl CH_2ONO_2
| |
$CHONO_2$ CHCl
| |
CH_2Cl CH_2Cl

β isomer   α isomer
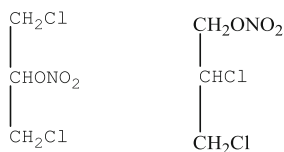
Molecular weight: 174.07

Oxygen balance: −50.55 % (CO_2-based)

Nitrogen content: 8.04 %

Dichloroglycerol nitrate has two isomers, α and β with boiling points of 183 and 174 °C, respectively. The mix of isomers can be added to nitroglycerine to produce dynamite with low freezing point. Many properties of dichloroglycerol nitrate are not compatible with explosives. It is more volatile than chlorinated glycerol dinitrate. It is a poor solvent for collodion. Its explosive power is very small. The explosive heat of dichloroglycerol nitrate is 1464.4 J/g and the lead-block value is 75 cm^3 with booster charges. The compound can be obtained in nitration of dichloroglycerol by anhydrous mixed acids. The theoretical yield is 94.5 %. That is, 100 units of dichloroglycerol can produce 127.5 units of dichloroglycerol nitrate.

5.3 Property and Preparation of Dibasic Alcohol Nitrates

5.3.1 Property and Preparation of Glycol Dinitrate

Glycol dinitrate, referred as to EGDN or GDN, is also called as nitrated glycol. It is a transparent liquid and an important liquid explosive [67].

5.3.1.1 Chemical Physical Properties of Glycol Dinitrate

Molecular formula: $C_2H_4N_2O_6$

Chemical structure:

$$O_2NO-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-ONO_2$$
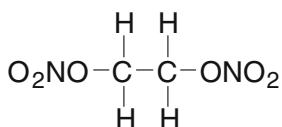
Molecular weight: 152.06

Oxygen balance: 0 % (CO_2-based)

Nitrogen content: 18.42 %

The melting point of glycol dinitrate is −22.3 to −22.80 °C and the boiling point is 197.5 °C. It density is 1.489 g/mL at 2 °C and the latent heat of fusion is 125.52 J/g.

Glycol dinitrate is nonhygroscopic. Its solubility in water is small and increased with temperature elevation. The solubility of glycol dinitrate in 100 mL water is listed in Table 5.11.

Glycol dinitrate can be dissolved into most of organic solvents, slightly dissolved into carbon tetrachloride and gasoline. The solubility of collodion in glycol dinitrate is higher than nitroglycerine and the volatility is 20 times higher than

Table 5.11 Solubility of glycol dinitrate in 100 mL water

Temperature (°C)	Solubility (g)
0	0.57
15	0.62
20	0.68
50	0.92

Table 5.12 Vapor pressure of glycol dinitrate [68, 69]

Temperature (°C)	Vapor pressure (mmHg)
0	0.0044
20	0.046
30	0.125
40	0.289
50	0.735
60	1.302
70	3.986
80	5.976
90	13.972
100	22.062

nitroglycerine. Its volatility is 2.2 mg/cm^2/h. Its vapor pressure is increased with increasing temperatures, as shown in Table 5.12.

The viscosity of glycol dinitrate is 0.08056 poise at 15 °C and 0.02831 poise at 40 °C, about 10 times smaller than nitroglycerine.

The refractive index of glycol dinitrate is slightly increased with temperatures, as shown in Table 5.13.

Glycol dinitrate will be hydrolyzed in the aqueous solution of sodium hydroxide or potassium hydroxide under heating. If glycol dinitrate is added into the ethanol solution of potassium hydroxide, a vigorous reaction would take place to produce potassium nitrite and potassium glycolate.

Glycol dinitrate of 0.008 % can be hydrolyzed by hot water at 60 °C for 120 h. It will be decomposed in the condition of concentrated acids in long time.

5.3.1.2 Chemical Stability

Glycol dinitrate has high thermal stability and chemical stability [44]. Glycol dinitrate will not be decomposed at 75 °C for 260 h, suggesting its stability is better than nitroglycerines. Its volatility is high. In Abel test, the heat resistance of glycol dinitrate is 30 min. It would explode at 195–200 °C. The activation energy of its thermal decomposition is $E = 149.37$ kJ/mol.

Table 5.13 The relationship between the refractive index of glycol dinitrate and temperature [70]

Temperature (°C)	0	15	25	35
n	1.4546	1.4491	1.4454	1.4417

5.3.1.3 Explosive Property

Glycol dinitrate is a strong liquid explosive with zero oxygen balance. The reaction of detonation can be expressed as:

$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \longrightarrow 2CO_2 + 2H_2O + N_2$$

As shown in the reaction, all elements of C, H, and O are involved in the detonation. Thus, its explosive heat is 6610.72 J/g (water vapor) or 7133.72 J/g (liquid water). The heat of formation $-\Delta H_f$ for glycol dinitrate is 283.26 kJ/mol. It is not sensitive to shock and the characteristic height is about 20–25 cm with 2,000 g falling weight. Glycol dinitrate is sensitive to flames [71, 72]. It is flammable in air at normal atmosphere. In a glass tube with diameter of 4 mm, the combustion velocity of glycol dinitrate is linearly proportional to the pressure at 14–15 °C in the pressure range of 300–770 mmHg.

$$U = A + BP$$

Under 230 mmHg, glycol dinitrate cannot be burnt, but it is easy to be detonated. A quite amount of glycol dinitrate would be exploded when burnt.

The lead-block value with water filling of glycol dinitrate is 650 cm. Brisance value is about 110 % NG. The detonation velocity is changed with loading condition. The correlation between the detonation velocity of glycol dinitrate and the loading condition is shown in Table 5.14.

Table 5.14 Correlation between the detonation velocity of glycol dinitrate and the loading condition

Loading condition/ method	Materials of container	Initiation approach	Detonation velocity (m/s)
Loading diameter φ36 mm	Seamless steel tube (wall thickness 2.5 mm)	Directly by 8# detonator	7,780
Loading diameter φ38 mm	Seamless steel tube (wall thickness 2.5 mm)	80 g mandelic acid as booster charge, and directly by 8# detonator	7,960
Loading diameter φ45 mm	Seamless steel tube (wall thickness 2.5 mm)	80 g mandelic acid as booster charge, and directly by 8# detonator	8,100
φ60 mm Porcelain crucible	Open	Directly by 8# detonator	1,830
φ60 mm Porcelain crucible	Cool down to −70 °C	Directly by 8# detonator	7,980

5.3.1.4 Preparation of Glycol Dinitrate

The early preparation method of glycol dinitrate is to nitrate ethylene [73]. The product includes β type nitroethyl alcohol and glycol dinitrate.

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + 2HNO_3 \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2NO_2 \end{array} \xrightarrow{HNO_3} \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2NO_2 \end{array} + \begin{array}{c} CH_2NO_2 \\ | \\ CH_2ONO_2 \end{array}$$
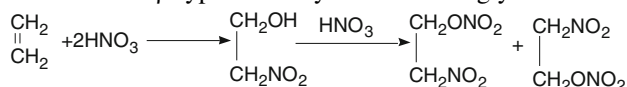
In later method, glycol dinitrate can be directly obtained by dehydration in the process of ethylene nitration.

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + 2HNO_3 \xrightarrow{H_2SO_4} \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO \end{array} \xrightarrow{HNO_3} \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$
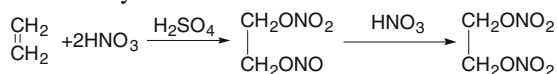
About 50–60 % ethylene is converted by the first equation and the other 40–50 % is converted by the second reaction.

(1) Electrolytic ethylene method

This method [74] can be used to produce glycol dinitrate and diethylene glycol dinitrate. Platinum wire mesh dipped in calcium nitrate-acetone solution is used as an anode. The gaseous ethylene is continuously going through the solution. Back the aluminum cathode, calcium nitrate-nitric acid solution is filled. At anode, the nitrate ions will be converted to free group of NO_3, part of which will be reacted with ethylene to form glycol dinitrate.

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + 2 \cdot NO_3 \longrightarrow \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$
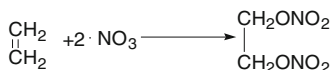
The interreaction among free groups of NO_3 will produce oxygen free groups, which can be further reacted with NO_3 to form diethylene glycol dinitrate.

$$2 \cdot NO_3 \longrightarrow N_2O_5 + [O] \xrightarrow{+H_2O} 2HNO_3 \longrightarrow 2NO_3$$

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + [O] + 2 \cdot NO_3 \longrightarrow \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2 \\ O \\ CH_2 \\ | \\ CH_2ONO_2 \end{array}$$
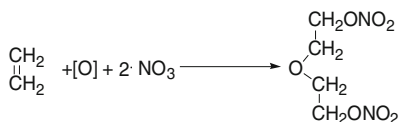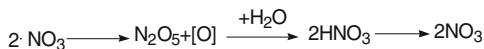
The anode solution will be neutralized by calcium hydroxide and acetone will be removed by distillation. The main products are calcium nitrate and glycol dinitrate. The calcium nitrate can be removed by filtration. The filtrate solution can be washed by water and treated for stability. After drying, the final product of glycol dinitrate can be obtained.

(2) Modern manufacturing technologies of glycol dinitrate [73, 75–78]

It is well known that glycol dinitrate can be produced by nitration of glycol in a mixed acid of nitric acid and sulphuric acid. The typical composition of the mixed acid is 11.5–20 % H_2O, 18–40 HNO_3, and 45–68.5 % H_2SO_4. The appropriate reaction temperature is 5–15 °C. The nitration coefficient is in the range of 12–24. The conversion of glycol is up to 92–96 %. It is an exothermal reaction with ΔH of 355.64 J/mol glycol.

Table 5.15 Specification of glycol in nitration reaction [27]

Parameter	Value
Boiling point (°C)	196–200
Density (g/cm^3)	1.1130–1.1135
Acidity (H$_2$SO$_4$-based %)	<0.1
Saponification value (Na$_2$O %)	<1.0

In industry, because of the accumulation of nitration heat, the reaction heat usually exceeds the value obtained in laboratory scale. The main reaction mechanism of nitration of glycol can be expressed as:

$$C_2H_4(OH)_2 + HNO_3 \xrightarrow{H_2SO_4} C_2H_4(ONO_2)_2 + H_2O + 355.64 J/mol$$
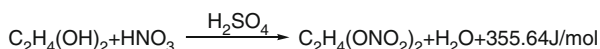
Actually, the nitrate heat of the nitration reaction of glycol in industry is double times higher than that in small scale. The reaction rate is as fast as only 1–1.5 s to finish the nitration reaction when glycol is fully mixed with the mixed acid.

The writer [15] studied the influence of reaction conditions and the production processes [5] of mixed acid injection nitration and air-agitated nitration. Those processes were successfully applied in the industrial manufacture of glycol dinitrate. The specification of glycol to produce glycol dinitrate is shown in Table 5.15.

The nitration processes of glycol and glycerine are not the same because of the difference of property of the raw materials and products. In the nitration process of glycol, heat pretreatment is not necessary and the optimal nitration temperature is 10–15 °C. Too high nitration temperature will cause low yield of products. The process diagram of glycol dinitrate is shown in Fig. 5.9.

Glycol of 100 kg can produce glycol dinitrate of 229.075 kg at 10–12 °C, that is, the theoretical yield is 93.5 %.

5.3.2 Property and Preparation of Diethylene Glycol Dinitrate

5.3.2.1 Chemical Physical Properties

Molecular formula: C$_4$H$_8$N$_2$0$_7$
  Chemical structure:

```
      H H    H H
O2N-O-C-C-O-C-C-O-NO2
      H H    H H
```
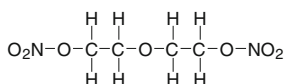
Molecular weight: 196.12
Oxygen balance: −40.8 % (CO$_2$-based)
Nitrogen content: 14.28 %
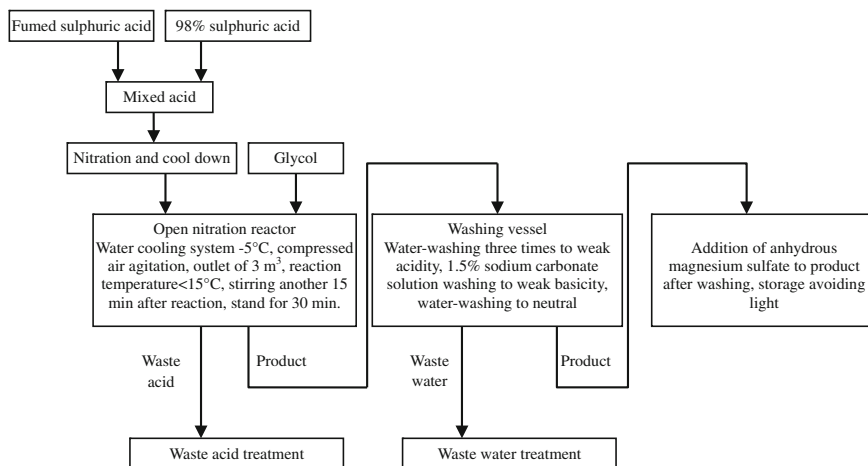
Fig. 5.9 Process diagram of glycol dinitrate production

Table 5.16 A list of eutectic mixture formed by diethylene glycol dinitrate and nitro aromatics

Nitro aromatics	Eutectic mixture			
	Stable		Unstable	
	Fraction of nitro aromatics (%)	Melting point (°C)	Fraction of nitro aromatics (%)	Melting point (°C)
Dinitrobenzene	8.0	−13.2	11.5	−1.4
Trinitrobenzene	17.0	−15.5	20.5	−3.0
Dinitrobenzene naphthalene	19.0	−11.2	25.0	−1.5

Diethylene glycol dinitrate has two crystalline forms, stable form melted at 2 °C and unstable form with melting point of −10.9 °C. It is an oily liquid at 20 °C with density of 1.385 g/cm^3, boiling point of 160 °C, decomposition temperature of 160 °C, and refractive index of 1.4517 (20 °C). Its vapor pressure is 0.0036 mmHg at 20 °C and 0.130 mmHg at 60 °C. Its volatility at 60 °C is 0.19 mg/cm^3 h.

Diethylene glycol dinitrate can be mutually soluble with nitro aromatics to form eutectic mixture, as shown in Table 5.16.

Diethylene glycol dinitrate is soluble in some organic solvents. It is hardly soluble in ethanol, carbon tetrachloride, and carbon disulfide. Its solubility in 100 g water is as small as 0.40 g at 25 °C and 0.46 g at 60 °C.

The viscosity of diethylene glycol dinitrate, about 8.1 centipoises at 20 °C, is lower than glycerine. Its dissolving capacity to collodion is strong and it is an excellent energetic solvent and resource for double-base propellants.

Fig. 5.10 The denitration
rate of several nitrate esters in
a mixed acid
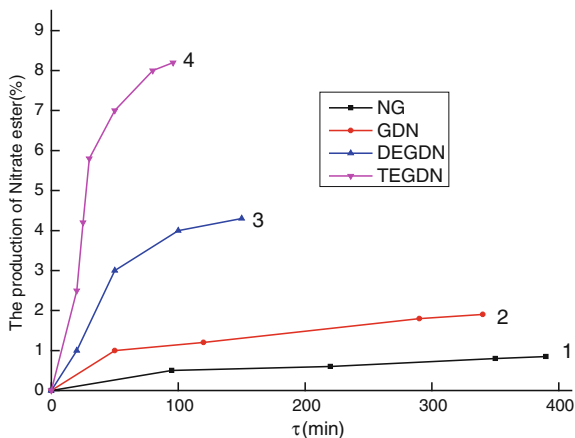
5.3.2.2 Stability and Property of Thermal Decomposition

The chemical stability of diethylene glycol dinitrate is roughly equal to nitroglyc-
erine. Its hydrolysis is very slow even under hot water. For example, only 0.003 %
diethylene glycol dinitrate is hydrolyzed at 60 °C for 120 h. It will be decomposed
by waste acids. The denitration rate of diethylene glycol dinitrate in the mixed acid
with 7.5–10.5 % HNO_3 and 0.5–1.1 % H_2O is shown in Fig. 5.10.

The chemical stability of diethylene glycol dinitrate is related to the denitration
temperature. The stability of diethylene glycol dinitrate with high denitration
temperature is better than that with low denitration temperature. The relationship is
shown in Table 5.17.

Based on the properties of diethylene glycol dinitrate, it can be applied in
propellant with smokelessness, no ablation, and non-flame, and in liquid
explosives.

5.3.2.3 Explosion Property

Diethylene glycol dinitrate will be exploded at 200 °C with explosion heat of
4476.9 J/g. Its shock sensitivity is poorer than TNT. The characteristic height is
160 cm for 2 kg falling weight. The ignition is difficult directly by a flame. It would
not be exploded like nitroglycerine after ignition. In a glass tube with a diameter of
5–6 cm, it would be burnt at 15 °C.

The detonation velocity of diethylene glycol dinitrate is dependent on the con-
ditions of loading. At optimal conditions, the detonation velocity is up to 6,800 m/s.
However, at some conditions, the detonation velocity is only 1,800–2,300 m/s. Its
detonation property is poorer than nitroglycerine with lead-block value of 425 cm^3,
about 70 % of nitroglycerine. The liquid explosive mixture of diethylene glycol
dinitrate, nitroglycerine, and glycol dinitrate has twice explosion strength to TNT.

Table 5.17 The relationship between nitration temperature and the chemical stability of diethylene glycol dinitrate

Nitration temperature (°C)	Composition of residue acid (%)			Noise reduction test (min)
	HNO_3	H_2SO_4	NO_2	
0	0.217	0.0053	0.0015	12
5	0.191	0.0047	0.0012	16
15	0.138	0.0025	0.0009	22
25	0.0069	0.0015	0.0004	30

5.3.2.4 Preparation of Diethylene Glycol Dinitrate [15]

Diethylene glycol dinitrate is prepared by a condensation reaction first between glycol and a saturated solution of epoxyethane at 100 °C to obtain diethylene glycol. Diethylene glycol is then nitrated by a mixed acid of nitric acid and sulfuric acid. After water washing and stability treatment, the product of diethylene glycol dinitrate is obtained. The composition of the mixed acid is shown below.

$$HNO_3 \quad 50\,\%$$
$$H_2SO_4 \quad 45\,\%$$
$$H_2O \quad 5\,\%$$
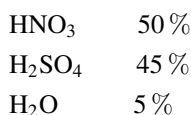
The nitration coefficient is usually in the range of 3–6 and the nitration temperature is 5–25 °C. 100 kg diethylene glycol can produce 168.7 kg of nitrate ester with a theoretical yield of 91.3 %.

The reaction between glycol and epoxyethane to diethylene glycol can be written below:
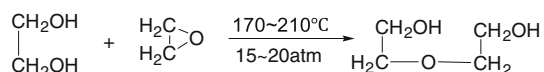
The specification of diethylene glycol for nitration reaction is listed in Table 5.18. The composition of the mixed acid in nitration reaction of diethylene glycol:

$$HNO_3 \quad 65\,\%$$
$$H_2SO_4 \quad 35\,\%$$
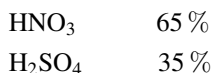
The nitration reaction of diethylene glycol is performed in an open reactor, which contains a compressed air agitator, a jacket of circulating water, a temperature sensor, an explosion-proof quick-opening valve, and a water tank. The unit is equipped with a circulating cooling system of ice-salt solution, a circulating system of thermostatted water, an air compressor, washing vessel, and a hot water vessel. The reactor of nitration is shown in Fig. 5.11.

Table 5.18 Specification of diethylene glycol for nitration reaction

Parameter	Value
Color/appearance	Colorless, odorless, transparent liquid
Density (20 °C)	1.1157–1.1165
H_2O (%)	<0.5
Acidity (%, H_2SO_4-based)	<0.02°
Saponification value (%, Na_2O-based)	<0.05
Chloride	Trace
Reducing substance	0.00
Glycol (%)	<2.00
Distillate (%)	99 % in 241.0–246.5 °C, 1.0 % in 247–249 °C

Fig. 5.11 Facilities and control systems of preparation of diethylene glycol dinitrate. *1* Open nitration reactor, *2* stability treatment vessel, *3* temperature-controlled meter, *4* frequency variator

The nitration temperature in the reaction process is not more than 25 °C. It will take 25 min to finish the nitration reaction. All materials in the reactor after nitration will be cooled down below 15 °C for separation process. The crude product will be water-washed and stability treated. The composition of separated waste acid, which will be treated for denitration, is listed in Table 5.19.

Table 5.19 Composition of the separated waste acid after nitration reaction for diethylene glycol dinitrate

Compound	Fraction (%)
HNO_3	28–29
H_2SO_4	44–46
H_2O	20–24
Diethylene glycol dinitrate	4–5

Table 5.20 Composition of the waste washing water for the separated diethylene glycol dinitrate

Compound	Fraction (%)
HNO_3	3–4
H_2SO_4	5–6.5
Diethylene glycol dinitrate	2–3

The separated diethylene glycol dinitrate will be washed twice by water with 300 L apiece. The composition of acidic washing water is listed in Table 5.20.

After several times of washing by cold water, diethylene glycol dinitrate will be washed by hot water of 60 °C, and then washed and neutralized by 5 % sodium carbonate solution, followed by another water-washing. The final product will be tested for heat resistance at 82 °C at least to last 20 min.

By the method of intermittent nitration, the feedstock is 450 kg each time. The mixed acid is 1,500 kg. 778 kg diethylene glycol dinitrate can be obtained after stability treatment with a yield of 93.5 %.

5.3.3 Property and Preparation of Triethylene Glycol Dinitrate

Triethylene glycol dinitrate, as one of the most wide used nitrate esters, is also called binitro triethylene glycol, or nitrified triethylene glycol.

5.3.3.1 Chemical Physical Properties

Molecular formula: $C_6H_{12}O_8N_2$
  Chemical structure:
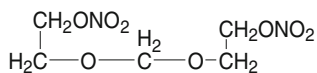
Molecular weight: 240.17
Oxygen balance: −66.6 % (CO_2-based)
Nitrogen content: 11.66 %
Density: 1.335

Melting point (°C): −40

Viscosity (20 °C): 2.5 times to nitroglycerine

Hygroscopicity: 0144 at relative humidity of 65, similar with diethylene dinitrate

Volatility: about 1/5–1/6 value of nitroglycerine.

Triethylene glycol dinitrate is an oily liquid with similar chemical properties with diethylene glycol dinitrate. Its thermal stability is better than nitroglycerine. The time is up to 40 min at 72 °C in the Abel test. 100 g water can dissolve 0.7 g triethylene glycol dinitrate at 20 °C and the solubility is increased with decreasing pH value. Triethylene glycol dinitrate can be dissolved into diethyl ether, acetone, and acetic acid, but cannot be dissolved into alcohols. It has strong plastic solubility to cellulose nitrate, as one of the most strong polybasic alcohol nitrates to dissolve plastics.

5.3.3.2 Explosive Property

The explosion heat of triethylene glycol dinitrate is 3,138 J/g and the explosion heat of constant volume is 2629.2 J/g or 613.37 kJ/mol. Its specific volume is 1,214 mL/g (liquid water). The explosion temperature is 2,100 K. Its lead-block value is 320 mL. The coefficient of explosion heat is 26.07 J/g. The heat coefficient is 44.18 J/g. The coefficient of specific volume is 12.13 mL/g. The explosion point is 245 °C. Triethylene glycol dinitrate is insensitive to shock. Its shock sensitivity is similar with dinitrobenzene. The height is 100 cm for 2 kg falling weight.

5.3.3.3 Preparation of Triethylene Glycol Dinitrate [15]

Triethylene glycol dinitrate has the same production process as nitroglycerine and diethylene glycol dinitrate, including mechanism, method, unit, and procedure.

The main reaction is expressed as the following equation:

$$C_6H_{12}O_2(OH)_2 + 2HNO_3 \rightleftharpoons C_6H_{12}O_2(ONO_2)_2 + 2H_2O$$

$$\begin{array}{cccc} 150 & 126 & 240.17 & 36 \\ 100 & 160 & & \end{array}$$
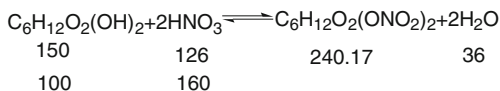
The theoretical yield is 160 %, but the real yield is only 89.2 % of the theoretical yield with the maximum of up to 91.55 %. The main conditions are shown below.

The composition of the mixed acid: 70 % HNO_3 and 30 % H_2SO_4

Nitration coefficient: 2.5.

In container-type nitrator, the nitration of 500 kg triethylene glycol will be finished in 30 min.

The solubility of triethylene glycol dinitrate in waste acids is quite high, up to 8–9 %. Thus, the waste acids are easy to be decomposed and it is more dangerous to treat those waste acids. Water must be added into the separated waste acids to

prevent triethylene glycol dinitrate from separation. The diluted waste acids need to be treated immediately.

It is slow to separate triethylene glycol dinitrate from the waste acids. For example, more than 30 min is needed by the gravimetric method. Thus, it would raise the risk of operation.

The separated acidic triethylene glycol dinitrate is successively washed by water twice, Na_2CO_3 aqueous solution, and then water to alkalescence. The obtained product should be tested in the Abel test. Based on literatures, the duration time is not less than 20 min at 82 °C and 40 min at 72 °C.

The parameters of triethylene glycol for preparing triethylene glycol dinitrate are listed in Table 5.21.

The separated oily material is successively washed by water twice, Na_2CO_3 aqueous solution, and then water. After washing and neutralization, the duration time of the product of triethylene glycol dinitrate should not less than 20 min at 82 °C.

500 kg triethylene glycol can produce 714.11 kg triethylene glycol dinitrate.

5.3.4 Property and Preparation of Glycerine Dinitrate [3, 15]

Glycerine dinitrate, also called dinitro glycerine, is a viscous light yellow liquid with lower explosive property than nitroglycerine. Glycerine dinitrate has two isomers.

Table 5.21 Specifications of triethylene glycol

Parameters	Value
Color/appearance	Slightly odorous transparent yellow liquid
Density (20 °C)	1.1217
Refractive index (20 °C)	1.4552
H_2O (%)	<0.1
Acidity (H_2SO_4-based)	<0.005
Saponification value (Na_2O-based)	<0.630
Chloride	Trace
Reducing substance	0.00
Glycol (%)	0.00
Distillate in 278.8–310 °C (%)	<95.2
Residues	<0.001

5.3.4.1 Chemical Physical Properties

Molecular formula: $C_3H_6N_2O_7$
   Chemical structure:

```
CH2ONO2                        CH2ONO2
|                              |
|                              |
CHOH                           CHONO2
|                              |
|                              |
CH2ONO2                        CH2OH
```

   α isomer   β isomer
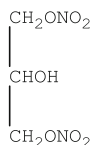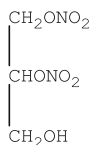
   Molecular weight: 182.06
   Oxygen balance: −17.58 % (CO_2-based)
   Nitrogen content: 15.38 %
   The commercial isomers of glycerine dinitrate have a density of 1.47 (15 °C) and
are frozen at 40 °C. At the pressure of 15 mmHg, the distillate collected at 146 °C
will not be decomposed. Glycerine dinitrate can be dissolved into most of organic
reagents, but carbon tetrachloride and gasoline. It can dissolve collodion easily. The
solubility in water is 8.6 % at 20 °C [24].
   The heat resistance of glycerine dinitrate is better than nitroglycerine. In the Abel
test, the decomposition phenomenon only can be observed at set temperature for
16 days. At 150 °C, brown nitrogen oxide can be released. Its explosive decom-
position temperature is above 170 °C.

5.3.4.2 Explosive Property of Glycerine Dinitrate

The explosive decomposition of glycerine dinitrate takes place based on the fol-
lowing equation.

$$C_3H_5(OH)(ONO_2)_2 \rightarrow 2CO_2 + CO + 2H_2O + N_2 + H_2 + 5024.98\,J/g$$
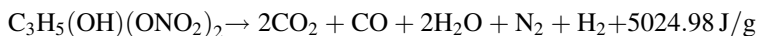
   The shock sensitivity of glycerine dinitrate is less than nitroglycerine with the
characteristic height of about 7–10 cm for 2 kg falling weight. The characteristic
height is 90–100 cm for hydrate crystals of α-isomer and 30–40 cm for liquid
β-isomer.
   The lead-block value with water filling of glycerine dinitrate is 500 cm^3, equals
to 82 % power of nitroglycerine. The detonation velocity of the blasting gelatin
with 92 % glycerine dinitrate is 3,320 m/s, while the corresponding value for
nitroglycerine is 7,400 m/s. The detonation velocity of dynamite explosive with
75 % diatomaceous earth produced by glycerine dinitrate is 4,300 m/s.

5.3.4.3 Preparation of Glycerine Dinitrate

In industry, there are four methods to prepare glycerine dinitrate. The first method is to nitrate glycerol by a mixed acid, in which the fraction of sulfuric acid is lower than that in the common mixed acid. The product is a mixture of glycerine dinitrate and nitroglycerine with any ratios. The typical composition of a mixed acid is shown in Table 5.22.

In the oily product, the ratio of dinitro nitrate and trinitro nitrate is about 70:30. The product is diluted by water for the waste acids. After separation, the precipitate includes more nitrate ester, which contains about 90 % glycerine dinitrate.

In the second method, dilute mixed acid, for example 9 % water mixed acid, is used in the nitration to prepare glycerine dinitrate. After dilution by water, glycerine dinitrate is separated. This is a simple but uneconomical method. The third method was developed by DuPont based on ammonium method [10]. Ammonium is used to neutralize the dilute nitric acid solution to form recoverable ammonium nitrate solution. For glycerine dinitrate without any trinitro esters, one unit of glycerine is dissolved into 3.3 units of nitric acid with the density of 1.5 at 15 °C. The solution will be diluted by one unit of water and neutralized by calcium carbonate. The oily product will be separated out. The small amount of product in water solution will be extracted by ethers.

Glycerine dinitrate can also be prepared through denitration process of nitroglycerine by sulfuric acid. Nitroglycerine is simply dissolved into concentrated sulfuric acid at room temperature for the denitration reaction. The product solution will be dissolved into water and extracted by diethyl ether to obtain glycerine dinitrate.

The writer [15] summarized those methods and developed a new process to prepare glycerine dinitrate. At 15–20 °C, one unit of glycerine is dissolved into 3–4 units of 68 % nitric acid under agitation. After addition, the solution is agitated for another 30 min and put aside for 2–6 h. The solution is diluted by water based on the ratio of 1:1 with acid amount and neutralized by calcium carbonate. A concentrated calcium carbonate solution (1.51 g/mL) is formed. The supernatant oil layer is the product of glycerine dinitrate. Separate out the oil layer and be washed by a concentrated sodium or ammonium carbonate-sodium chloride solution. The function of sodium chloride is to reduce the solubility of glycerine dinitrate. For example, at 20 °C, 100 units of water can dissolve 8 units of glycerine dinitrate, while 100 units of 30 % sodium chloride solution can only dissolve 2 units of glycerine dinitrate. Thus, the loss of product can be neglected even by washing at 40–50 °C. The product of glycerine dinitrate is then washed by sodium chloride

Table 5.22 The composition of a mixed acid with low fraction of sulfuric acid

Compound	Fraction
HNO_3	60
H_2SO_4	30
H_2O	10
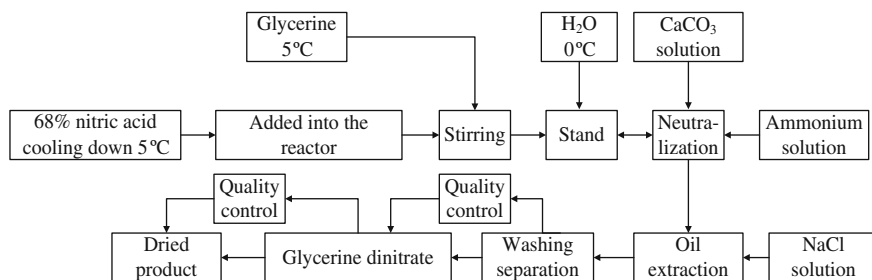
Fig. 5.12 The production process of glycerine dinitrate

Table 5.23 Consumption of raw materials for 100 kg glycerine dinitrate

Raw materials	Consumption (kg)
Glycerine	70.4
Nitric acid	240
Ice	80
Calcium carbonate	120
Ammonium sulfate	165
Ammonium	1.5
H_2O	3,500
NaCl	5

Table 5.24 The fraction of nitroglycerine in glycerine dinitrate

Nitric acid ratio	Products (kg)			Fraction (%)	
	Overall esters	Glycerine dinitrate	Nitoglycerine	Glycerine dinitrate	Nitoglycerine
100:250	115.8	108.2	7.6	93.44	6.56
100:350	151.7	143.5	8.2	94.59	5.41
100:450	179.5	150.4	29.1	88.35	11.65
100:500	184.4	146.9	37.5	79.66	20.34

solution to be neutral. Figure 5.12 shows the production process and the consumption of raw materials for producing 100 kg glycerine dinitrate is listed in Table 5.23.

The side products in the reaction include 200 kg ammonium nitrate and 165 kg calcium sulfate.

The cost of production of glycerine dinitrate by this method is slightly lower than the method of nitroglycerine as a raw material (Table 5.24).

5.3.5 Other Dibasic Alcohol Nitrates

5.3.5.1 Property and Preparation of Methylene Glycol Dinitrate [79, 80]

Molecular formula: $CH_2N_2O_6$
  Chemical structure:

$$H_2C\begin{matrix} \diagup ONO_2 \\ \diagdown ONO_2 \end{matrix}$$
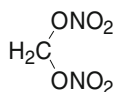
  Molecular weight: 138.04
  Oxygen balance: 34.8 % (CO_2-based)
  Nitrogen content: 20.29 %
  Methylene glycol dinitrate, or called nitrified methylene glycol, is oily liquid with boiling point of 75–77 °C under 20 mmHg. It is a liquid explosive with collodion-dissoluble and strong explosion strength. It is easy to be hydrolyzed. In early years, methylene glycol was considered as a useless substance because its stability is poor but the explosion property is strong.

  The simple procedure to prepare methylene glycol is described below. Formaldehyde-sulfuric acid solution is dropwisely added into a mixed acid of nitric acid and sulfuric acid slowly at 2–5 °C. An oily product will be formed and separated out. The product will be washed by water and treated for stability. The yield of the final product is 35 %.

5.3.5.2 Property and Preparation of 1,3-Propanediol Dinitrate

Molecular formula: $C_3H_6N_2O_6$
  Chemical structure:

$$O_2NO-CH_2-CH_2-CH_2-ONO_2$$

  Molecular weight: 166.09
  Oxygen balance: −28.9 % (CO_2-based)
  Nitrogen content: 16.87 %
  1,3-propanediol dinitrate is an oily liquid with a boiling point of 180 °C under 20 mmHg. It has a density of 1.393 at 20 °C, and a higher volatility and a lower viscosity than nitroglycerine. The mutually soluble regents with 1,3-propanediol dinitrate are the same as nitroglycerine. It can dissolve collodion very well. It would not be decomposed at 75 °C for 600 h.

  1,3-propanediol dinitrate is a strong liquid explosive with explosion heat of 4763.5 J/g (water vapor). The explosion point is 225 °C and the shock sensitivity is low. The characteristic height is 100 cm with 2 kg falling weight. Its lead-block value with water filling is 540 cm, equal to 90 % of nitroglycerine. The 93 %

blasting gelatin prepared by 1,3-propanediol dinitrate has a lead-block value of 470 cm, equal to 80 % of nitroglycerine blasting gelatin.

The nitration temperature of 1,3-propanediol should be controlled in the range of 0–10 °C. Under the appropriate condition, the conversion of 1,3-propanediol to 1,3-propanediol dinitrate is up to 96 %. The writer achieved 210.3 kg 1,3-propanediol dinitrate by 100 kg raw material of 1,3-propanediol.

5.3.5.3 Property and Preparation of 1,2-Propanediol Dinitrate [81]

1,2-propanediol dinitrate, also called methyl glycol dinitrate, is an important dibasic nitrate ester. It has been widely used in liquid propellants, liquid explosives, and explosive mixtures with urea perchlorate or hydrazine.

Molecular formula: $C_3H_6N_2O_6$
Chemical structure:

$$CH_3-CHONO_2$$
$$\qquad\quad |$$
$$\qquad\quad CH_2ONO_2$$
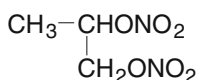
Molecular weight: 166.09
Oxygen balance: −28.9 % (CO_2-based)
Nitrogen content: 16.87 %

1,2-propanediol dinitrate is an oily liquid with a boiling point of 92 °C (10 mmHg), a melting point of −20 °C, and a density of 1.368 (20 °C). It has strong volatility. The explosion heat is 4,644 J/g (water vapor) and the lead-block value with water filling is 540 cm.

In previous reports [4], the composition of the mixed acid for the nitration of 1,2-propanediol at 20 °C is 40 % HNO_3 and 60 % H_2SO_4. 100 units of 1,2-propanediol can be nitrated to produce 187 units of 1,2-propanediol dinitrate, that is, the theoretical yield is 86 %.

The mixed acid with composition of 47.5 % HNO_3, 45.5 % H_2SO_4, and 7 % H_2O was also used to nitrate 1,2-propanediol at 10 °C. If HNO_3 was excessive by 10 %, the theoretical yield of 1,2-propanediol dinitrate is 91–93 %.

5.3.5.4 Property and Preparation of 1,3-Butanediol Dinitrate

Molecular formula: $C_4H_8O_6N_2$
Chemical structure:

$$CH_3-CH-CH_2-CH_2-O-NO_2$$
$$\qquad\quad |$$
$$\qquad\quad ONO_2$$
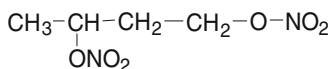
Molecular weight: 180.12
Oxygen balance: −53.2 % (CO_2-based)
Nitrogen content: 15.55 %

1,3-butanediol dinitrate is an oily volatile liquid with excellent chemical stability. It has a freezing point of −20 °C, a density of 1.32, and a lead-block value of 460 cm. Its explosion strength is about 75 % of nitroglycerine. It is a good solvent for collodion.

The conversion of 1,3-butanediol to 1,3-butanediol dinitrate is high. 100 kg 1,3-butanediol can be nitrated to produce 187 kg 1,3-butanediol dinitrate with yield of 93.7 %. In the writer's study, 100 kg raw material of 1,3-butanediol was directly nitrated. 2–5 % ammonium nitrate was added in the process. The nitration temperature is 17 °C. The product was successively treated by separation, water-washing, and stability. 197 kg final product of 1,3-butanediol dinitrate was obtained with a yield of 96.71 %.

5.3.5.5 Property and Preparation of Dimethylol Nitroethane Dinitrate [82]

Molecular formula: $C_4H_7O_9N_4$
  Chemical structure:

$$O_2N-\underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2ONO_2$$
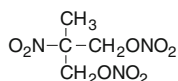
  Molecular weight: 255.10
  Oxygen balance: 15.68 % (CO_2-based)
  Nitrogen content: 21.96 %

Dimethylol nitroethane dinitrate (2-nitro-2-methylpropanediol-1,3-dinitrate) is a solid with a melting point of 38 °C, low volatility, and easy solubility of cellulose nitrate.

Its explosion strength is slightly weaker than nitroglycerine and slightly stronger than cyclotrimethylene trinitramine. The explosion heat is about 5,230 J/g. Its shock sensitivity is significantly lower than nitroglycerine and slightly higher than tetryl, equals to cyclotrimethylene trinitramine.

5.3.5.6 Property and Preparation of Dimethylol Nitropropane Dinitrate

Molecular formula: $C_5H_9O_8N_3$
  Chemical structure:

$$O_2N-\underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-CH_2ONO_2$$
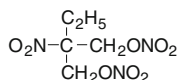
  Molecular weight: 239.13
  Oxygen balance: 36.8 % (CO_2-based)
  Nitrogen content: 17.57 %

Dimethylol nitropropane dinitrate (2-ethyl-2-nitropropyleneglycol-1,3-dinitrate) is a liquid, which cannot dissolve cellulose nitrate. Dimethylol nitropropane dinitrate is a liquid explosive with weak explosion property, slightly higher than chrysolepic acid. Its lead-block value is larger than chrysolepic acid by 25 % and the shock sensitivity is weaker than chrysolepic acid.

5.3.5.7 Property and Preparation of Nitromethoxy Methanol Nitrate

Nitromethoxy methanol nitrate, also called methyl ether nitro nitrate, is a colorless oily liquid with slightly higher explosion property than glycol dinitrate. It is a liquid explosive with a wide application potential.

(1) Properties of nitromethoxy methanol nitrate

Molecular formula: $C_2H_4O_6N_2$

Chemical structure:

CH_2ONO_2
|
O
|
CH_2NO_2
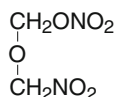
Molecular weight: 151.96

Oxygen balance: 0 % (CO_2-based)

Nitrogen content: 18.43 %

Boiling point: 48 °C (15 mmHg)

Density: 1.50 (20 °C)

Ignition point: 150 °C (220 °C for glycol dinitrate)

Its shock sensitivity is stronger than glycol dinitrate. It has been found that 10 % explosion risk for glycol dinitrate needs shock energy of 0.91 kg m/cm^2, while for nitromethoxy methanol nitrate only 0.11 kg m/cm^2 is needed. Nitromethoxy methanol nitrate is able to dissolve collodion and more volatile than glycol nitrate. The chemical stability and explosion property of nitromethoxy methanol nitrate and its cellulose nitrate solution are weak.

The lead-block value of nitromethoxy methanol nitrate is 420 cm^3. In the same conditions, the value of glycol dinitrate is 450 cm^3. Nitromethoxy methanol nitrate has similar explosion property and low chemical stability. Its shock sensitivity is high and the lead-block value is 440 cm^3.

(2) Preparation method [83]

Nitromethoxy methanol nitrate can be prepared by nitration reaction of bis-chloromethyl ether. Bis-chloromethyl ether can be obtained by the following reaction between 40 % formaldehyde solution and hydrogen chloride gas:

$$2CH_2O + 2HCl \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ O \\ | \\ CH_2Cl \end{array} + H_2O$$

$$\begin{array}{c} CH_2Cl \\ | \\ O \\ | \\ CH_2Cl \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \begin{array}{c} CH_2ONO_2 \\ | \\ O \\ | \\ CH_2NO_2 \end{array}$$
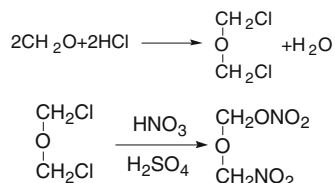
In the reaction, chlorine ether of $ClCH_2OCH_2OCH_2Cl$ is formed. The chlorine ether will be converted to another nitrate ester, $O_2NOCH_2–O–CH_2OCH_2NO_2$, with boiling point of 88 °C (9 mmHg) in the later nitration reaction. Nitromethoxy methanol nitrate is more volatile than glycol nitrate, but less than other nitro nitrate esters.

5.3.5.8 Property and Preparation of Chloroglycerine Dinitrate [3]

Chloroglycerine dinitrate is a liquid explosive with explosion strength only less than nitroglycerine. Such an explosive property attracted people's attention in early year. In 1904, chloroglycerine dinitrate was used to mix with nitroglycerine to produce cold-tolerant dynamite. The commercial product of chloroglycerine dinitrate is a mixture of two isomers, mainly α-isomer. Chloroglycerine dinitrate can move as a liquid even at −20 °C.

(1) Property of chloroglycerine dinitrate

Molecular formula: $C_3H_5N_2O_6Cl$
Chemical structure:

$$\begin{array}{c} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2Cl \end{array} \qquad\qquad \begin{array}{c} CH_2ONO_2 \\ | \\ CHCl \\ | \\ CH_2ONO_2 \end{array}$$

α-isomer   β-isomer
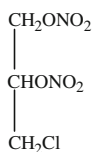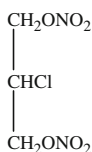
Molecular weight: 200.57
Oxygen balance: −19.94 % (CO_2-based)
Nitrogen content: 13.96 %

The melting points of α-isomer and β-isomer are 5 and 16.5 °C, respectively. The density of chloroglycerine dinitrate is 1.541 (15 °C) and the explosion heat is 4769.76 J/g. It is slightly decomposed at 117.5 °C (10 mmHg). The commercial product of chloroglycerine dinitrate would be boiled and quickly decomposed at 190 °C. Its volatility is slightly higher than nitroglycerine. The weight loss of chloroglycerine dinitrate in an open container of 50 mm diameter at 75 °C for 24 h is 3.1 %, while it is 0.35 % for nitroglycerine. Chloroglycerine dinitrate is

nonhygroscopic with a small solubility in water (2.3 g in 1 L water at 15 °C). It is easily soluble in most of organic solvents but carbon disulfide and gasoline. Chloroglycerine dinitrate can mix with nitroglycerine by any ratios. The formed mixture has a low freezing point. The mixture of 75 % nitroglycerine and 25 % chloroglycerine dinitrate is usually used in nonfreezing solution. At room temperature, collodion is difficult to be dissolved into chloroglycerine dinitrate. However, at 40 °C, it can be dissolved quickly. After cooled down, chloroglycerine dinitrate can be separated out from the "gelatin." The mixture of chloroglycerine dinitrate and nitroglycerine can dissolve cellulose nitrate easily. The viscosity of chloroglycerine dinitrate is low, about 1.55 times to the value of water. Its chemical stability is higher than nitroglycerine with the duration time of 30 min at 72 °C in Abel test. It would not be decomposed at 75 °C for 10–12 days and a trace would be decomposed in a tube at 170 °C to release nitrogen oxide. At 180 °C, it would be completely decomposed without an explosion. At 190 °C, a weak explosion would happen based on the following reaction:

$$C_3H_5Cl(ONO_2)_2 \rightarrow CO_2 + 2CO + 2H_2O + HCl + N_2 + 4,184\,J/g$$
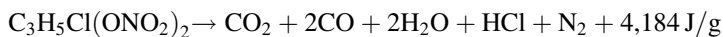
If there is enough oxygen, the following reaction would have happened:

$$C_3H_5Cl(ONO_2)_2 \rightarrow 2CO_2 + CO + H_2O + H_2 + HCl + N_2 + 4,393\,J/g$$

Chloroglycerine dinitrate is difficult to be ignited and further exploded. It can be calmly burnt even staying in fire in an open container. Its shock sensitivity is lower than nitroglycerine and glycerine dinitrate [17]. The characteristic height is about 10–20 cm for 2 kg falling weight.

The lead-block value with water filling of chloroglycerine dinitrate detonated by #8 detonator is 475 cm, while the value is 380 cm by using #1 detonator and 440 cm by using blasting gelatin (42 % chloroglycerine dinitrate). Its explosion strength is about 80 % of nitroglycerine. As a component of explosives, chloroglycerine dinitrate in explosion process would produce hydrogen chloride gas, which will cause pollution to environment. Thus, it is not suitable for the explosion work in the under pit operation.

(2) Preparation of chloroglycerine dinitrate [3]

The equipment and method to prepare chloroglycerine dinitrate are similar with that of nitroglycerine. Chloroglycerine is nitrated by the mixed acid of nitric acid and sulfuric acid to prepare chloroglycerine dinitrate. The reaction heat is less than that process of preparing nitroglycerine. The viscosity of chloroglycerine dinitrate is lower than nitroglycerine. The time needed in preparation process is shorter than that for nitroglycerine. The nitration coefficient is generally larger than 4.5. The composition of the mixed acid is listed in Table 5.25.

172.5 kg chloroglycerine dinitrate with two isomers can be obtained by nitrating 100 kg chloroglycerine at 8–12 °C after water washing and stability treatment. The yield is 93.35 %.

Table 5.25 Fraction of the mixed acid in chloroglycerine nitration

Acid	Fraction (%)
HNO_3	40
H_2SO_4	60

Table 5.26 The composition of the waste acid after nitration of 100 kg chloroglycerine

Compounds	Fraction (%)
HNO_3	116.9
H_2SO_4	75.0
H_2O	7.9
NO	0.2

Based on the nitration coefficient of 4.75, the result of component analysis of the waste acid after nitration is shown in Table 5.26.

5.3.5.9 Property and Preparation of Formoxyl Glycerine Dinitrate [3]

Formoxyl glycerine dinitrate is a liquid explosive with strong explosion strength.

(1) Properties of formoxyl glycerine dinitrate

Molecular formula: $C_4H_6N_2O_8$
Chemical structure:

```
CH2ONO2
|
CHONO2
|
CH2OCHO
```
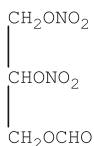
Molecular weight: 210.01
Oxygen balance: -22.86 % (CO_2-based)
Nitrogen content: 13.34 %
Explosion heat: 4,284 J/g

(2) Preparation of formoxyl glycerine dinitrate

The preparation procedure of formoxyl glycerine dinitrate is described below
Thermally treat 2 mol glycerine and 1 mol anhydrous oxalic acid to 140–150 °C. After 20 h, formoxyl glycerine will be formed and part of glycerine will be not reacted. It is a formoxyl glycerine-glycerine solution. The main reaction is shown below:
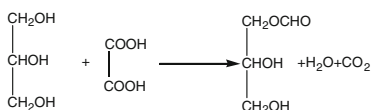
The solution will be then nitrated by a mixed acid of nitric acid and sulfuric acid to form a mixture of 70 % nitroglycerine and 30 % formoxyl glycerine dinitrate.

$$
\begin{array}{c}
CH_2OCHO \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\quad + HNO_2 \xrightarrow{\ H_2SO_4\ }
\begin{array}{c}
CH_2OCHO \\
| \\
CHONO_2 \\
| \\
CH_2ONO_2
\end{array}
\ + H_2O
$$
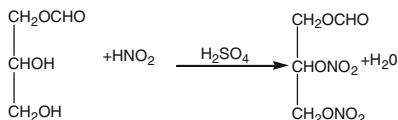
The mixture can be used as an additive for nitroglycerine to produce dynamite explosives with low freezing point. Its explosion strength is about 90 % of nitroglycerine.

5.3.5.10 Property and Preparation of Acetyl Glycerine Dinitrate [3]

(1) Properties of acetyl glycerine dinitrate
Acetyl glycerine dinitrate is a liquid explosive with a low freezing point and 92 % explosion strength of nitroglycerine.
Molecular formula: $C_5H_8N_2O_8$
Chemical structure (two isomers):

$$
\begin{array}{c}
CH_2ONO_2 \\
| \\
CHOCOCH_3 \\
| \\
CH_2ONO_2
\end{array}
\qquad
\begin{array}{c}
CH_2ONO_2 \\
| \\
CHONO_2 \\
| \\
CH_2OCOCH_3
\end{array}
$$
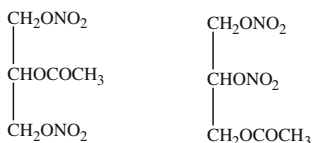
Molecular weight: 169.99
Oxygen balance: -56.47 % (CO_2-based)
Nitrogen content: 16.47 %
The commercial acetyl glycerine dinitrate with both isomers is not frozen at $-20\ ^\circ C$. It has a boiling point of 147 °C under 15 mmHg, a density of 1.42 at 15 °C, and an explosion heat of 2761.4 J/g. The commercial acetyl glycerine dinitrate is more volatile than nitroglycerine, but lower than chloroglycerine dinitrate. It can be mutually soluble with water and dissolve cellulose nitrate. Its stability is weaker than nitroglycerine. It will be obviously decomposed at 75 °C for 24 h with a release of nitrogen oxide. It starts to be decomposed at 160 °C and is vigorously decomposed at 170–180 °C.

Acetyl glycerine dinitrate is insensitive to shock. The lead-block value is 200 cm^3 detonated by #8 detonator. The lead-block value of 92 % blasting gelatin made by acetyl glycerine dinitrate is 145 cm^3.
(2) Preparation of acetyl glycerine dinitrate
The preparation equipment is the same as that to prepare nitroglycerine. Acetyl glycerine (glycerine acetate) is nitrated by anhydrous mixed acid at 10–15 °C. The crude product is washed and stability-treated to obtain the final product. 100 units of acetyl glycerine (by mass) can be converted to 159 units of acetyl glycerine dinitrate with yield of 95 %.

(3) Application of acetyl glycerine dinitrate

Acetyl glycerine dinitrate is usually mixed with nitroglycerine with a ratio of 80:20 to be a liquid explosive mixture. The explosion strength of this liquid explosive mixture is about 90 % of nitroglycerine.

5.4 Property and Preparation of Trinitrate Esters

5.4.1 Property and Preparation of Nitroglycerine [1, 84–87]

Nitroglycerine with code of NG, also called glycerine trinitrate or propanetriol trinitrate, is the most widely used liquid explosive with strong explosion strength.

5.4.1.1 Properties of Nitroglycerine

Molecular formula: $C_3H_7N_3O_9$
   Chemical structure:

$$CH_2\!\!-\!\!ONO_2$$
$$|$$
$$CH\!\!-\!\!ONO_2$$
$$|$$
$$CH_2\!\!-\!\!ONO_2$$
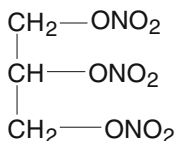
   Molecular weight: 229.10
   Oxygen balance: 3.5 % (CO_2-based)
   Nitrogen content: 18.34 %
   Nitroglycerine is a colorless transparent oily liquid. The industrial products are usually light yellow or light brown, based on the purity of raw materials and production conditions. A sweetish odor can be smelled when heated at 50 °C. It tastes bittersweet and hot.

 (1)   Physical properties of nitroglycerine [67, 75]

   Nitroglycerine has two modifications with different freezing points and crystalline forms. For the crystalline structure, the molten phase at low temperature is not stable. It can be spontaneously converted to the stable phase with high melting point. The freezing points of nitroglycerine obtained in different references are summarized in Table 5.27.
   Crystal line speed of stable nitroglycerine phase formed at different temperature is listed in Table 5.28.
   Nitroglycerine is slightly soluble in water. The solubility of nitroglycerine in water is shown in Table 5.29.
   The solubility of nitroglycerine in sodium carbonate aqueous solution (1–10 %) is smaller than that in water. In 1,000 mL 8 % sodium carbonate aqueous solution,

Table 5.27 A summary of freezing points of different phases of nitroglycerine (°C)

Phases	Ref. [3]	Ref. [3]	Ref. [3]	Ref. [3]
Unstable	–	2.1–2.2	1.9	1.9
Stable	12.4	13.2	13.0	13.0

Table 5.28 Crystal line speed of stable nitroglycerine phase

Temperature (°C)	Speed (mm/min)
+5	0.145
0	1.183
−5	0.267
−17	0.125

Table 5.29 The solubility of nitroglycerine in 1,000 mL water

Solution temperature (°C)	Nitroglycerine mass (g)
15	1.6
20	1.8
50	2.5

Table 5.30 The solubility of nitroglycerine in ethanol [3]

Ethanol	Temperature (°C)	Solubility (g/100 ml ethanol)
Anhydrous	0	~30
Anhydrous	20	~43
96 %	20	31.6
50 %	20	1.8
25 %	20	0.7

the maximum solubility of nitroglycerine is 1.0 g. Nitroglycerine itself is a good solvent. It can be dissolved into most of organic solvents and mutually dissolved into methanol and acetic ether in any ratios at room temperature. It is also mutually dissolved into nitrate esters, azide nitrate esters, and dichloroethylene in any ratios. However, only 20 units of nitroglycerine can be dissolved into 100 units of trichloroethylene at room temperature. Nitroglycerine is very hard to be dissolved into tetrachloroethylene and pentachloroethane.

The solubility of nitroglycerine is related to the temperature of solvents and water contents. In anhydrous ethanol, the solubility is increased with temperature. At 50 °C, nitroglycerine can be mutually dissolved into 96 % or anhydrous ethanol. Table 5.30 shows the solubility of nitroglycerine in ethanol.

Nitroglycerine is slightly dissolved into polybasic alcohols. It is slightly soluble in propanol, isopropanol, and amyl alcohol solvents at room temperature, but it is mutually soluble in those solvents at 90–100 °C. 100 g glycol can dissolve 20 and 12 g nitroglycerine at 200 and 80 °C, respectively. The solubility of nitroglycerine is very low in glycerine. It is easily soluble in 65 % acetic acid, hardly soluble in

carbon disulfide, and slightly soluble in gasoline, crude oil, kerosene, liquid paraffin, lubricant oil, and paraffinum liquidum. The solubility is increased with increasing the solution temperature. It can be mutually soluble in plant oils. The solubility of nitroglycerine in solvents is summarized in Table 5.31.

Nitroglycerine is slightly soluble in the aqueous solutions of ammonium, sodium hydroxide, or potassium hydroxide. It is easily soluble in concentrated sulfuric acid and mutually soluble in anhydrous nitric acid. The solubility of nitroglycerine in the mixed acid with H_2SO_4:H_2O of 5.8 and H_2SO_4:HNO_3 of 10.4 is listed in Table 5.32.

The solubility of nitroglycerine in a mixed acid with a similar composition of the mixture M_3 is shown in Table 5.33. The part of nitroglycerine in the waste acid is easily hydrolyzed. In general, nitroglycerine in not soluble in concentrated hydrochloric acid. At elevated temperatures, it would be gradually decomposed and hydrolyzed to dark yellow nitrosyl chloride.

The freezing point of nitroglycerine can be significantly lowered by adding glycerine dinitrate or other dinitrate esters, such as glycol dinitrate. It is a necessary step to prepare various liquid explosives and liquid or gel mining explosives. Nitroglycerine is compatible with nitro compounds and is able to effectively improve the energy. A liquid explosive with high energy and low sensitivity can be obtained by adding nitroglycerine to nitro glycol, chlorohydrins dinitrate, and diglycerine tetranitrate, and then mixing with pentaerythrite tetranitrate and RDX.

Table 5.31   A summary of the solubility of nitroglycerine in fatty hydrocarbon

Solvents	Temperature (°C)	Solubility (g/100 g solvent)
Crude oil	20	~1.5
	80	~6.0
Gasoline	20	~2
	80	~6
Refining oil	20	~4
	80	~9
Olive oil	20	20
	100	25
Castor oil	20	26
	100	30

Table 5.32   The solubility of nitroglycerine in the mixed acid of nitric acid and sulphuric acid

Code of the mixed acid	Fraction %			Solubility of nitroglycerine (%)
	HNO_3	H_2SO_4	H_2O	
M_1	24	50	26	13.5
M_2	38	20	42	1.6
M_3	13	75	12	2.5

Table 5.33 Solubility of nitroglycerine in the mixed acid of nitric acid and sulphuric acid (%)

Compound	I	II	III	IV	V	VI
HNO_3	10	10	10	15	15	15
H_2SO_4	70	75	80	80	75	75
H_2O	20	15	10	5	10	15
Solubility (g/100 g mixed acid)	6.00	3.55	3.33	4.37	2.60	2.36

Table 5.34 Composition of the eutectic formed from nitroglycerine and aromatic compounds

Compounds	Stable form		Unstable form	
	Fraction (%)	M.P. (°C)	Fraction (%)	M.P. (°C)
Nitrobenzene	45.5	−15.2	57.5	−22.9
Meta-dinitrobenzene	82.5	5.0	88.0	−5.4
2,4-dinitrotoluene	72.7	6.1	89.0	−4.1
2,4,6-trinitrotoluene	82.9	6.3	90.0	−4.0
Tetryl	90.0	9.8	94.0	−0.6
RDX	99.5	12.3	99.7	1.2
Nitroglycol	~20	~40	~40	~−40
Pentaerythrite tetranitrate	98.5	12.3	98.9	1.3
Alkyl phenyl urea	90.0	9.6	93.0	−0.8
Phthalide	76.5	0.8	8.10	−8.2
Methyl centralite	96.5	10.6	98.0	0.8
Diphenylamine	93.0	9.8	96.0	−0.4
HMX	99.4	11.8	99.8	6.2
CL-20	98.6	13.6	99.3	5.4

The composition of the prepared eutectic with a low melting point is shown in Table 5.34.

Nitroglycerine is able to dissolve cellulose nitrate with low nitrogen content. The consistency of the obtained solution is related to the viscosity and percentage of cellulose nitrate in nitroglycerine. The mechanical property of propellant is mainly related to the content of cellulose nitrate.

The stability of nitroglycerine is related to the trace impurity in the nitration process and the reaction temperature [x, 33], especially the impurities of trace metals and alkali metals in the processes of nitration and water-washing. Nitroglycerine obtained at relatively high temperature, before stability treatment in the common approach of washing by water and sodium carbonate solution, contains little residue acids. The relationship between nitration temperature and stability is shown in Table 5.35.

Nitroglycerine will be boiling at 180 °C and decomposed to release nitrogen oxide and water vapor. There are diluted nitric acid and a small amount of nitroglycerine in distillate. The boiling point of nitroglycerine is 180 °C at 50 mmHg

Table 5.35 The relationship between nitration temperature and stability of nitroglycerine

Nitration temperature (°C)	Content of residue acid		Heat resistance in Abel test (min)
	HNO_3 (%)	H_2SO_4 (%)	
15	0.0132	0.0024	15
25	0.0057	0.0017	24
40	0.0052	0.0008	30

Table 5.36 The vapor pressure of nitroglycerine at different temperatures

Temperature (°C)	Vapor pressure (mmHg)
20	0.00025
30	0.00038
35	0.0020
40	0.0024
45	0.0072
50	0.0081
60	0.0188
70	0.043
80	0.095
93	0.29

Table 5.37 The evaporation heat ΔH of nitroglycerine at different temperature

Temperature (K)	ΔH (kJ/mol)
100	86.36
140	85.27
180	84.14

and 125 °C at 2 mmHg. The relationship between the vapor pressure of nitroglycerine and temperature is shown in Table 5.36.

The evaporation heat ΔH of nitroglycerine is nearly not influenced by temperature, as shown in Table 5.37.

The vapor pressure of the binary solution of nitroglycerine and glycol dinitrate was calculated, as shown in Table 5.38.

Nitroglycerine is volatile. The amount of volatilization of 20 g nitroglycerine, which was put in an open glass tube with a diameter of 70 mm at different temperature for 24 h, is shown in Table 5.39.

The weight loss of nitroglycerine based on volatilization is not only related to temperature, but related to the contact area. The weight loss of nitroglycerine at 60 °C is 0.11 mg/cm^2/h.

The specific gravity of nitroglycerine is slightly decreased with increasing temperature, as shown in Table 5.40.

Table 5.38 The vapor pressure of the binary solution of nitroglycerine and glycol dinitrate

Fraction of glycol dinitrate (%)	Total vapor pressure (mmHg)			
	10 °C	30 °C	40 °C	50 °C
10	0.0027	0.0186	0.0433	0.1002
20	0.0051	0.0345	0.1159	0.1841
40	0.0093	0.0624	0.1475	0.3314
60	0.0137	0.0874	0.2417	0.6316

Table 5.39 Volatilization of nitroglycerine at different temperatures

Temperature (°C)	Volatilization amount (g)	Percentage of volatilization (%)
50	0.04	0.2
75	0.32	1.6
100	2.00	10.0

Table 5.40 The relationship between the specific gravity of nitroglycerine and temperature

Temperature (°C)	Specific gravity (g/cm^3)
4	1.614
15	1.600
25	1.590

The volume shrinkage of nitroglycerine upon freezing is 8.3 %. The specific gravity of the stable form at 100 °C is 1.735 g/cm^3. Its refractive index n_D^{20} is 1.4732.

The dielectric constant of nitroglycerine ε_{20} is 19.25. Its dipole moment μ is shown in Table 5.41.

The infrared spectrum of nitroglycerine is shown in Fig. 5.13.

NO_2 (asymmetric stretching vibration): 1675, 1654, 1645 cm^{-1}

NO (symmetric stretching vibration): 1293, 1276 cm^{-1}

Those frequencies are formed, most likely, because of the optical isomers.

(2) Chemical properties

Nitroglycerine is easily reduced to glycerine and ammonium by reducers, such as tin and hydrochloric acid, zinc and acetic acid, alkali metal sulfides, and hydrogen sulfide. As the other esters, nitroglycerine can be hydrolyzed. In the aqueous solution or alcohol solution of sodium or potassium hydroxide, nitroglycerine is not only hydrolyzed but also converted by oxidation-reduction reaction to organic acids, salt nitrates, and salt nitrites. It will be reduced to glycerine by the substances that are easily oxidized in the process of hydrolysis. If there are thiophenols, nitroglycerine will be hydrolyzed by potassium hydroxide to glycerine with diphenyl sulfide. Nitroglycerine reacting with strong reducible acid will be quickly decomposed to glycerine and nitrogen oxide.

Table 5.41 Dipole moment of nitroglycerine

Solution	Dipole moment (Debye)
Pure nitroglycerine	3.82
Nitroglycerine in hexane	2.56
Nitroglycerine in carbon tetrachloride	2.88
Nitroglycerine in benzene	3.16

Fig. 5.13 Infrared spectrum of nitroglycerine
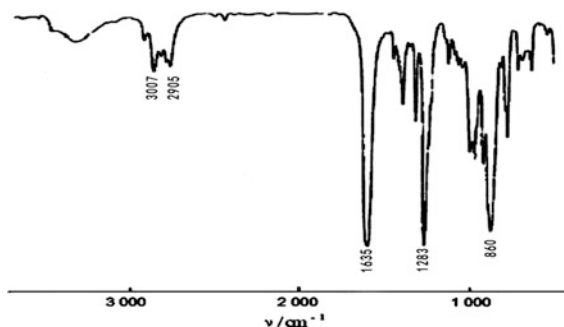
(3) Thermal properties

(1) Specific heat and crystallization heat of nitroglycerine

The specific heat of nitroglycerine is 1.49 J/g. The specific heat of its crystal (stable form) is 0.315 cal/g. The specific heat of liquid nitroglycerine is 1.318 J/g. The crystallization heat (freezing) of nitroglycerine is listed in Table 5.42.

(2) Combustion heat and formation heat of nitroglycerine

The combustion heat ΔH of nitroglycerine in constant volume is 1541.39 kJ, equal to 6791 J/g. The formation heat $-\Delta H_f$ is 356.9 kJ (1564.82 J/g). The nitration heat of glycerine to nitroglycerine in industry is 502.08–711.28 J/g.

(4) Stability of nitroglycerine

Nitroglycerine will be decomposed in 3–4 days at 75 °C to produce acidic substances. On the sixth day, nitric acid should be observed. If the volatile products were removed quickly in the decomposition process, nitroglycerine would be decomposed very slowly.

In an open system, it is no risk for the decomposition of a small amount of nitroglycerine. In a closed space, NO_x produced in the decomposition process will play a part of catalysis. Meanwhile, the gas products will increase reaction pressure gradually and catalytically accelerate the reaction. The chain reaction will impel nitroglycerine to be decomposed more quickly and, eventually, cause an explosion.

The mixture of 0.3 g nitroglycerine and 5 % nitric acid in a closed glass tube at 42 °C for 6 h will explode. The plot of the decomposition temperature of nitroglycerine catalyzed by nitric acid versus time is shown in Fig. 5.14.

The decomposition of nitroglycerine is mainly caused by the dilute acid formed through NO_2 and water. The dilute acid will catalytically decompose nitroglycerine.

Table 5.42 Crystallization heat of nitroglycerine with different phases

Phase	Crystallization heat (J/g)
Stable form	138.91
Unstable form	21.76
Conversion from unstable form to stable form	117.20
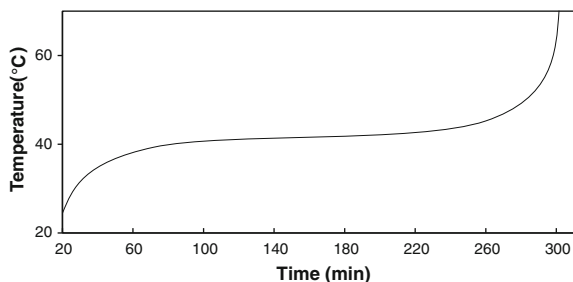
Fig. 5.14 The catalytic decomposition of nitroglycerine by 5 % nitric acid at 42 °C [3]

The other products, such as N_2, NO, CO, and CO_2, will not influence the decomposition rate of nitroglycerine. Nitroglycerine will be decomposed in 30 h if the content of water in feedstock is 0.01 % and in 2 h if the content of water is up to 1.5 %.

The result of thermogravimetric analysis of nitroglycerine at 90–135 °C demonstrates that the volatile products of decomposition can be removed by CO_2. The pH value of nitroglycerine will be increased with heating time. The pH values of water-extracted materials of nitroglycerine at 110 °C in different heating time are listed in Table 5.43.

The relationship of pH of nitroglycerine and time is shown in Fig. 5.15.

The mechanism of nitroglycerine decomposition at 135 °C is obviously different from that at low temperatures. The color of samples will be changed to be red because they adsorb the decomposition products. At heating temperature of 145 °C, the decomposition will become vigorous with a release of gases of nitrogen oxides. At heating temperature of 165 °C, nitroglycerine will be more vigorously decomposed to nitric acid, which will be distilled off with nitroglycerine. The residue contains glycerine, nitrate esters, dinitrate esters, and trace liquid impurities, which are difficult to be determined. At heating temperature of 180–185 °C, nitroglycerine will become very sticky. The explosion behavior of nitroglycerine will be terminated at 215–218 °C. Those observations indicate that nitroglycerine is not as safe and insensitive as people used to believe.

Nitroglycerine will be exploded at extreme high temperature. If nitroglycerine is dripped on a preheated metal plate of 215–250 °C, a detonation will be happened and the metal plate will be severely deformed. When the metal plate is preheated to over 420 °C, the nitroglycerine drops on the surface of the plate will form a sphere-like

Table 5.43 pH values of nitroglycerine in water at 110 °C

Nitroglycerine mass (g)	pH value at 110 °C in different heating time			
	1 h	2 h	3 h	4 h
5	5.88	5.40	4.90	4.31
10	11.82	10.90	9.36	7.63

Fig. 5.15 Plot of pH of nitroglycerine at 110 °C versus time [3]
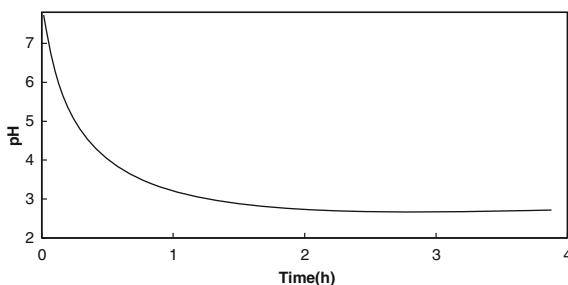
Fig. 5.16 The decomposition behavior of nitroglycerine on a hot metal plate [3]
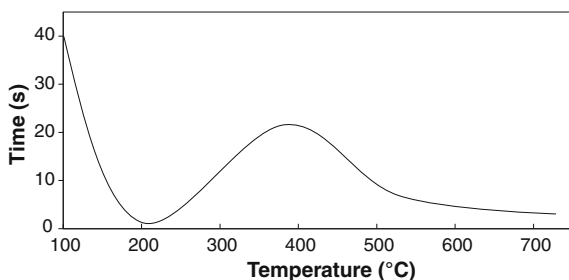
ball and be burnt moderately. The explosion behavior of nitroglycerine on a hot metal plate is shown in Fig. 5.16.

The decomposition curve of nitroglycerine on a hot metal plate can be seen in Fig. 5.16. The activation energy E of the thermal decomposition of nitroglycerine can be calculated. The activation energy E is 156.48 kJ/mol in the temperature range of 215–250 °C and 20.82 kJ/mol at 470 °C.

The activation energies of nitroglycerine decomposition at low temperatures of 150–190 °C, 125–150 °C, and 20–125 °C are 209.2, 188.28, and 178.24 kJ/mol, respectively.

Nitroglycerine could be gradually and slowly decomposed under ultraviolet irradiation for 1–2 min. The decomposition behavior will be terminated after 2–3 days. In the experiment of the irradiation of light ray, which was obtained by incandescent lights going through a 3,200–4,100 Å filter, if 3 g nitroglycerine was irradiated at 15 °C for 60 min and 6 h, pH was measured as 6.86 and 6.12, respectively. If nitroglycerine is heated to 100 °C and then irradiated by ultraviolet

rays with 900 J, it will be exploded immediately. Nitroglycerine is very sensitive to γ-rays and gases of N_2, nitrogen oxides, H_2, CO, and CO_2 will be released under irradiation.

5.4.1.2 Explosion Property

Generally, the explosive decomposition of nitroglycerine is done by the following equation:

$$C_3H_5(ONO_2)_3 \rightarrow 3CO_2 + \frac{5}{2}H_2O + \frac{3}{2}N_2 + \frac{1}{4}O_2$$
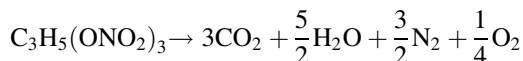
The explosion heat of nitroglycerine under normal conditions is 6,213 J/g and the specific volume V_0 is 715.7 mL/g. The explosion strength f_0 at 4,250 °C is 9,292 m.

The sensitivity of nitroglycerine is related to the condition of stability treatment. Based on the experiments performed in Liu Jieping's group, it was found that nitroglycerine, which was treated for stability by normal filtrated water after nitration, was exploded at the condition of vibration of 200 Hz. However, if it was treated by deionized water, nitroglycerine was not exploded even under vibration of 800 Hz.

Nitroglycerine is sensitive to shock. Solid nitroglycerine after adsorption has an enhanced impacted force. Liquid nitroglycerine or its shock wave has a minimum impact force. The relationship between the shock sensitivity of nitroglycerine and its phase is shown in Table 5.44.

The shock sensitivity of the mixture of liquid and crystallite nitroglycerine is higher than single phase of nitroglycerine because of the friction between sensitive liquid and crystallites. The probability of nitroglycerine explosion after gun shooting is 100 %. The lead-block value of nitroglycerine is related to the detonating strength. The lead-block values of nitroglycerine detonated by different detonators are listed in Table 5.45.

Table 5.44 The relationship between the shock sensitivity of nitroglycerine and its phase

Phase	Impacted force (kg m/cm^2)	Explosion ratio (%)
Liquid	0.08	10
	0.11	50
	0.40	100
Stable crystallite	0.51	10
	0.65	50
	0.82	100
Unstable crystallite	0.63	10
	0.78	50
	0.93	100

Table 5.45 The lead block values of nitroglycerine detonated by different detonators

Detonator type	Lead-block value (cm)
1	190
2	225
6	460
8	590

Table 5.46 Lead block values of nitroglycerine detonation

Type	Pure (cm^2)	Sand-filling (cm^2)	Water filling (cm^2)
Stable crystallite	–	380	540
Unstable crystallite	–	390	525
Liquid	–	390	530

Fig. 5.17 Picture of lead block after nitroglycerine detonation

The detonating strength of nitroglycerine is different from that of glycol dinitrate and methyl nitrate. The other nitrate esters can be detonated by a relatively weak method and formed a complete explosion. The detonation of nitroglycerine is related to the loading constitution. The current loading constitution demonstrates that nitroglycerine will be steadily detonated in a steel vessel with a diameter of 5 mm and initiated by #1 detonator. The lead-block values of nitroglycerine detonation are listed in Table 5.46 and the result of the lead-block is shown in Fig. 5.17.

The sensitivity of nitroglycerine after treatment of deionized water is weak. It will not be exploded even being rubbed on the coarse surface of a magnetic mortar [85].

The detonation velocity of liquid nitroglycerine is closely related to the loading diameter and constitution. In the range of 1,000–8,000 m/s, the detonation velocity of nitroglycerine is increased with an increase of loading diameter. If the loading diameter is less than 5 mm, the maximum detonation velocity is only 920 m/s. The

Table 5.47 The relationship between the detonation velocity of nitroglycerine and the condition of loading and initiation

Loading medium	Loading diameter (mm)	Detonation condition	Detonation velocity (m/s)
Lead tube	30	Directly detonated by #8 detonator	1,560
Aluminum tube	3.0	Directly detonated by #8 detonator	915
Aluminum tube	9.0	Directly detonated by #8 detonator	1,130
30CrMnSi tube	30	Directly detonated by #8 detonator	3,780
Glass tube with wall thickness of 3.0 mm	22	Directly detonated by #8 detonator	1,165
Plexiglass tube	28	Detonated by #8 detonator, 15 g Tetryl as transmitted detonation pellets	7,800
30CrMnSi tube with wall thickness of 1.0 mm	37.5	Detonated by #8 detonator, 2 g ful-minating mercury for transmitted detonation	8,520
Plexiglass tube	25	Detonated by #8 detonator, 50 g Tetryl as transmitted detonation pellets	7,410
30CrMnSi tube	22	Detonated by #8 detonator, 75 g Tetryl as transmitted detonation pellets	7,760
#12 antirust aluminum tube	40	Detonated by #8 detonator, 20 g Tetryl as transmitted detonation pellets	8,560
#12 antirust aluminum tube	35	Detonated by #8 detonator, 20 g Tetryl as transmitted detonation pellets	7,830
#12 antirust aluminum tube	30	Detonated by #8 detonator, 20 g Tetryl as transmitted detonation pellets	6,970
#12 antirust aluminum tube	25	Detonated by #8 detonator, 20 g Tetryl as transmitted detonation pellets	6,100
#12 antirust aluminum tube	20	Detonated by #8 detonator, 20 g Tetryl as transmitted detonation pellets	5,870

relationship between loading condition and the detonation velocity is shown in Table 5.47.

The nitroglycerine emulsion exhibits a certain detonation velocity. The detonation velocity of nitroglycerine emulsions with water is listed in Table 5.48.

The emulsions with a ratio of water to nitroglycerine over 2:1 cannot be exploded. The detonation reaction of nitroglycerine with low detonation velocity is done by the following equation.

Table 5.48 The detonation velocity of nitroglycerine emulsions

H$_2$O: nitroglycerine	Detonation condition	Detonation velocity (m/s)
0.75:1	Detonated by #8 detonator, 15 g Tetryl as transmitted detonation pellets	6,370
1:1	Detonated by #8 detonator, 15 g Tetryl as transmitted detonation pellets	5,520
1.5:1	Detonated by #8 detonator, 15 g Tetryl as transmitted detonation pellets	5,150
2:1	Detonated by #8 detonator, 15 g Tetryl as transmitted detonation pellets	4,300

$$C_3H_5(ONO_2)_3 \rightarrow 2CO + CO_2 + 2\frac{1}{2}H_2 + 1\frac{1}{2}N_2O + 1\frac{3}{4}O_2 + 87.86\,\text{KJ}$$
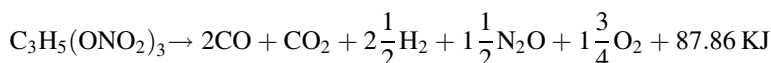
The detonation of nitroglycerine in a closed vessel and detonated by transmitted detonation pellets can be described by the following reaction equation.

$$C_3H_5(ONO_2)_3 \rightarrow 3CO + 2\frac{1}{2}H_2O + 1\frac{1}{2}N_2 + \frac{1}{4}O_2 + 1334.7\,\text{KJ}$$
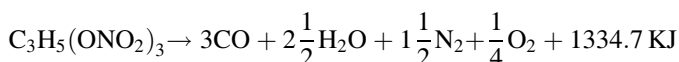
The final materials are carbon dioxide and water vapor. Thus, the detonation velocity must be very high.

Many people concern the power and sensitiveness of nitroglycerine [84]. In fact, although nitroglycerine is flammable, it is difficult to be ignited. For example, if nitroglycerine is put into a glass tube with a diameter of 20 mm and ignited by a gas burner or hot wire, it will be steadily burnt and partly decomposed rather than quickly spread and exploded. However, if it is ignited at the position where it has been pre-heated or pre-burnt, nitroglycerine will be across the precombustion stage and exploded directly.

The critical pressure of nitroglycerine at the moment of flame extinction, is changed in the range of 234–375 mmHg, depending on the experimental conditions. The linear velocity of combustion is 0.075 cm/s. At the temperature of 98 °C and critical pressure of 320 mmHg, its combustion velocity is 0.13 cm/s. Under the pressure of 400 mmHg, nitroglycerine can burn steadily with a rate changing with the pressure. The relationship between combustion velocity and pressure is shown in Fig. 5.18.

The following equation can be used to describe the stable combustion of nitroglycerine.

$$v = 0.0067 + 0.216P^{0.831}$$

By an extrapolation method, the combustion velocity of nitroglycerine can be obtained as 0.23 cm/s at the normal atmosphere. If nitroglycerine adsorbs cellulose nitrate, it will be more flammable than pure nitroglycerine.

Fig. 5.18 Relationship between combustion velocity of nitroglycerine and pressure
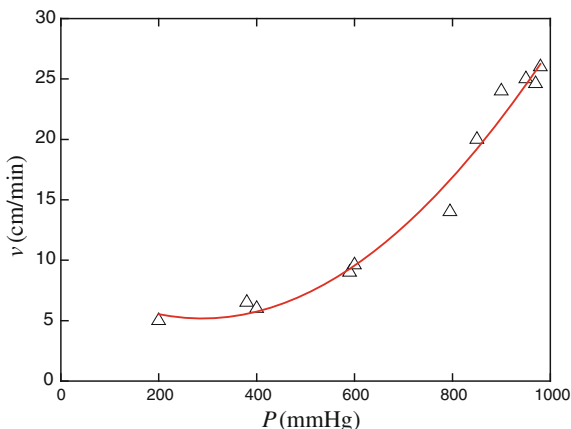
5.4.1.3 The Preparation of Nitroglycerine

The early preparation method of nitroglycerine included direct esterification by glycerinum and nitric acid.

CH$_2$OH   CH$_2$ONO$_2$

CHOH + 3HNO$_3$ ⟶ CHONO$_2$ + 3H$_2$O

CH$_2$OH   CH$_2$ONO$_2$
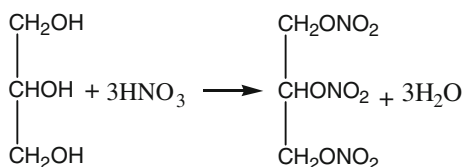
It was later discovered that the reaction designed had low reaction rate but also that the glycerinum and intermediate products of the reaction have some side effects in the oxidation environment for a long time, resulting in unsafety of the production process. The preparation process of nitroglycerine with nitro-sulfuric acid as nitrating agent and sulfuric acid as dehydrating agent is used in the modern method of nitrification.

It is well known that glycerinum dinitrate can be produced by nitration of glycerinum in a mixed acid of nitric acid and sulfuric acid. The typical composition of the mixed acid is 1.0 % H$_2$O, 47–50 % HNO$_3$, and 49–52 % H$_2$SO$_4$. The appropriate reaction temperature is 5–15 °C. The nitration coefficient is in the range of 5–11. The conversion of glycerinum is up to 95–97.6 %. It is an exothermal reaction with ΔH of 439.5 J/mol glycerinum.

In industry, because of the accumulation of nitration heat, the reaction heat usually exceeds the value obtained at laboratory scale. The main reaction mechanism of nitration of glycerinum can be expressed as:

$$C_3H_5(OH)_3 + 3HNO_3 \xrightarrow{\quad H_2SO_4 \quad} C_3H_5(ONO_2)_3 + 3H_2O + 439.5 \text{ mol}$$

Actually, the nitrate heat of the nitration reaction of glycerinum in industry is two times higher than that at small scale. The reaction rate is as fast as only 1–1.5 s to finish the nitration reaction when glycerinum is fully mixed with the mixed acid.

The writer [13] studied the influence of reaction conditions and the production processes of mixed acid injection nitration and air-agitated nitration [5, 13, 86, 87]. These processes were successfully applied in the industrial manufacture of NG.

A. The control process conditions of the preparation of nitroglycerine in indirect nitrification

   (a) Nitrification and separation
       The composition of mixed acid

HNO_3	48−52 %
H_2SO_4	49−52 %
H_2O	0.2−0.5 %
SO_3	≯2.0 %
ash	<0.5 %

The nitration coefficient is in the range of 4.9–5.3. Temperature during nitrification.
The onset temperature is below 5 °C.
The reaction temperature is in the range of 15–18 °C.
The final temperature is lower than 22 °C.
The temperature during nitration is below the range of 25–28 °C
The temperature of glycerinum is 30–35 °C.
The temperature for refrigerating chilled solution is −5 to −15 °C.
The speed of drop is 10–13 kg/min.
The speed of air string is 2–3 min/ET.
The composition of waste acid is

HNO_3	≮8 %
H_2SO_4	≮67 %
H_2O	≯18 %
N_2O_4	≯0.3 %
NG	≯2.2 %

Ratio of waste acid is 1.70–1.71.

   (b) Washing process
The temperature during cold water washing process is 20–25 °C, the time is 6 min.
The temperature during warm water washing process is 30–35 °C, the time is 6 min.
The stability temperature during washing process is 40–45 °C, the time is 6 min.

B. The control process condition during the preparation of nitroglycerine in injection nitrification

   (a) The composition of mixed acid is

HNO_3	48−50 %
H_2SO_4	50−52 %
H_2O	<0.2 %
N_2O_4	<0.6 %
SO_3	≯2.0 %
ash	<0.1 %

(b) The control condition of process.
   The nitration coefficient is 12–15.
   The temperature during nitrification is 45–48 °C.
   The vacuum degree is 280–350 mmHg (in nitrification).
   The temperature of mixed acid is 0 ± 1 °C.
   The press of mixed acid in reactor is 2.6–3.2 kg/cm^2.
   The nitrogen content of mixed acid is 29.5 ± 0.5 %.
   The speed of nitration is 3–4 kg/min.
   The nitrogen content of waste acid is 14.0 ± 0.3 %.

(c) Condition of separation
   The temperature during separation is 16 ± 1 °C.
   The speed of centrifuge is <2,900 r/min.

(d) Washing condition
   In the cold water washing process the ratio of glycerinum and water is
   1:1.2–1.5.
   In the warm water washing process the ratio of glycerinum and water is
   1:0.7–1.2 (the temperature is 40 ± 5 °C).
   For stability of treatment the ratio of glycerinum and water is 1:0.7–1.2
   (the temperature is 40–45 °C, the concentration of sodium carbonate is
   0.80 ± 0.1 %).
   The press of string in washing process is 2 ± 0.2 kg/cm^2

Comparing with the different preparation processes of indirect nitrification and
injection nitration, the different processes of nitrification have different productivities
of nitroglycerine. The capacity of indirect nitrification is lower, producing 300–400 kg
per hour; while the capacity of indirect nitrification is beyond 600 kg per hour.

5.4.1.4 The Application of Nitroglycerine

Nitroglycerine was first used in mining by Alfred Nobel, a Swedish engineer. In
1862, Nobel built a factory to produce "blasting oil". Nitroglycerine was also tried
to be used in charging as a high explosive in many countries. For example, Russia
made an attempt to do this kind of work in 1854. Nobel also used nitroglycerine
(blasting oil) substituting for black powder (smoke powder).

   Nitroglycerine can be a high explosive as soon as separated from water–alcohol
solutions. Based on previous studies, nitroglycerine can be absorbed by diatoma-
ceous earth to prepare a slug Guhr dynamite. It was invented by Nobel in 1867 and
composed of 75 units of nitroglycerine and 25 units of diatomaceous earth. In order
to lower its shock sensitivity, nitroglycerine can be mixed with a solid adsorbent of
magnesium carbonate. Since 1867, nitroglycerine has been used in the gold mines
at Upper-Uspleaskii in Trans-Baykal of Siberia.

   In 1875, Nobel dissolved cellulose nitrate into nitroglycerine to produce so called
blasting gelatin [7]. This sort of dynamite based on the blasting gelatin mixing with

oxygen carriers, such as ammonium nitrate or sodium nitrate, has been produced since then. In 1888, Nobel invented "nitroglycerine" smokeless powder. Nitroglycerine also has been widely used as a component of ammonium nitrate explosives.

The wide applications of nitroglycerine in medicine, clinic, aviation, aerospace, and military have been studied in many references [9, 10, 88–91] and will be discussed in this book.

5.4.1.5 The Toxicity of Nitroglycerin

Nitroglycerine is a toxic chemical causing the dilation of blood vessels and the reduction of blood pressure. Nitroglycerine can cause poisoning through percutaneous or mucosal penetration after inhalation. The cardinal symptom of nitroglycerine poisoning is severe headache with a feeling of grinding. For alcoholics, they could be accustomed to nitroglycerine quickly in a couple of days after contacting with nitroglycerine. However, the adaptability will be lost as soon as they are separated from nitroglycerine. It will take time to resume the adaptability when in contact with nitroglycerine again. Workers in double-base propellant production used to fabricate and sieve dynamite (nitroglycerine) with bare hands without any harm. Nitroglycerine does not cause chronic poisoning. Thus, the chemical should not be considered as an industrial toxicant. Some people might have an allergy to nitroglycerine. The symptoms of accidental poisoning include headache, vomit, cyanosis, visual disturbance, and limb itching and edema. The approach of detoxification is to intramuscularly inject caffeine, sodium benzoate, and orally take amphetamine sulfate.

5.4.2 Property and Preparation of Nitro Isobutyl Glycerine Trinitrate

Nitro isobutyl glycerine trinitrate with code of NB is also called trimethylol nitromethane trinitrate and nitro isobutanetriol trinitrate.

5.4.2.1 Property of Nitro Isobutyl Glycerine Trinitrate

Nitro isobutyl glycerine trinitrate is a light yellow sticky oily liquid. The industrial products are dark yellow because of the impurities in feedstock. Some products show abnormal brown or light green because of different production process.

Molecular formula: $C_4H_6N_4O_{11}$

Chemical structure:

$$O_2N-\underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_2ONO_2}{|}}{C}}-CH_2ONO_2$$
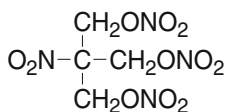
Fig. 5.19 The volatilization loss of nitro isobutyl glycerine trinitrate with time at different temperature [5]
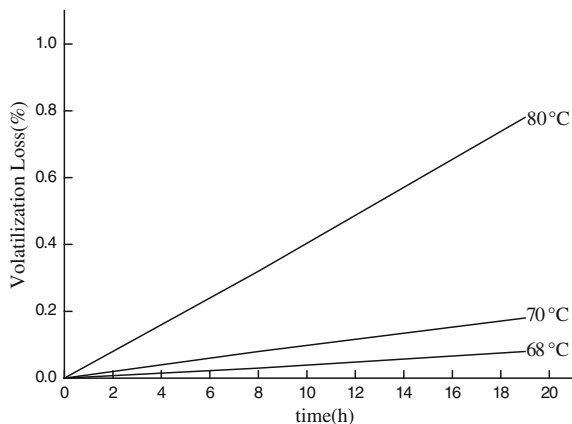
Molecular weight: 286.11

Oxygen balance: 0

Nitrogen content: 19.58 %

Density: 1.6171 g/cm^3 (20 °C)

Viscosity: 308.55 centipoises (20 °C)

Freezing point: −39 °C

Refractive index: $n_d^{25} = 1.4896$

Formation heat: 702.08 J/g (constant volume) or 200.83 kJ/mol (constant volume) or 226.35 kJ/mol (constant pressure)

Combustion heat: 2217.52 kJ/mol (constant volume) or 7765.5 J/g (constant volume)

Vapor pressure and volatility: Less than nitroglycerine. Nitro isobutyl glycerine trinitrate is little volatile at room temperature without odor. It is slightly volatile at 30 °C with odor of tar and acridity. The volatility is increased at elevated temperature. It is obviously volatile at 50 °C. Its volatility at 25 °C is 0.127 × 10 mg/cm/day. The relationship of the volatility of nitro isobutyl glycerine trinitrate and temperature is shown in Fig. 5.19 and its vapor pressures are listed in Table 5.49.

The relationship between the surface tension of nitro isobutyl glycerine trinitrate and temperature is shown in Table 5.50.

Table 5.49 Vapor pressure of nitro isobutyl glycerine trinitrate [5]

Temperature (°C)	40	50	60	70	80
Vapor pressure (mmHg)	2.74×10^{-4}	5.00×10^{-4}	14.8×10^{-4}	33.6×10^{-4}	79.3×10^{-4}

Table 5.50 Relationship between the surface tension of nitro isobutyl glycerine trinitrate and temperature [5]

Temperature (°C)	20	30	40	50	60
Surface tension (dyne/cm)	56.62	55.87	55.13	54.38	53.64

Fig. 5.20 Relationship between of the surface tension of nitro isobutyl glycerine trinitrate and temperature [5]
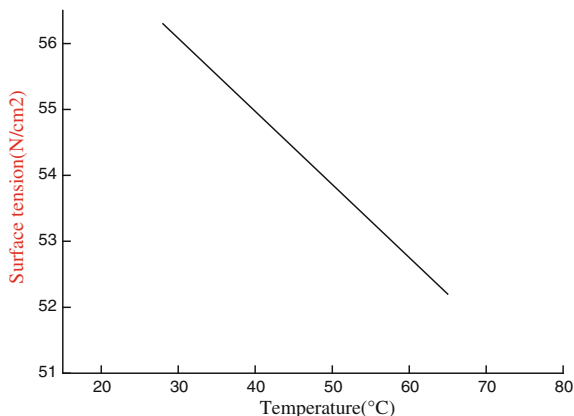
Figure 5.20 shows the linear relationship between the surface tension of nitro isobutyl glycerine trinitrate and temperature in the range of 20–60 °C.

The freezing point of nitro isobutyl glycerine trinitrate is −35 °C and its viscosity is very large at 0 °C. At the temperature near the freezing point, it is like molten glass and can be drawn into a wire. Under the freezing point, it becomes hard wax with similar mechanical property of liquid phase.

The solubility of nitro isobutyl glycerine trinitrate in water is less than that of nitroglycerine. Its solubility at 20 °C is 0.081 % and it is mutually soluble to diethyl ether, acetone, benzene, acetic ether, tetrachlormethane, dichlormethane, nitro-benzene, and nitrotoluene. Nitro isobutyl glycerine trinitrate can dissolve nitro aromatics. The property can be used to produce double-base propellants or multi-base propellants. It is, to some extent, soluble to low nitrogenous cellulose nitrate (nitrogen content: 11.8–12.2 %) for the production of double-base propellants.

Nitro isobutyl glycerine trinitrate is soluble to concentrated sulfuric acid and dissociated to produce nitric acid. It is sensitive to react with bases as saponification reaction, especially for hydroxides of alkali metals and alkali-earth metals. Nitro isobutyl glycerine trinitrate can be destroyed by NaOH. In water or dilute acids, it is difficult to be hydrolyzed. However, in dilute base solution, it can be hydrolyzed to a yellow solution with a hydrolyzation constant of 1.81×10^{-3}.

Nitro isobutyl glycerine trinitrate is less thermally stable than nitroglycerine. It would be slowly decomposed during storage. The decomposition will be acceler-ated by acids, bases, water, and other impurities, or under heat treatment because of the self-catalyzed reaction of nitrogen oxide released in the decomposition process. The molecular structure of asymmetric nitro groups ($\overset{O}{\underset{\delta-}{\overset{\parallel}{N}}}\overset{|}{\underset{|}{C}}-$), which influence the thermal stability of ester groups ($-\overset{|}{\underset{|}{C}}-O-N\overset{O}{\underset{O}{\diagdown}}$), is the main reason of the poor thermal stability. The curve of thermal decomposition of nitro isobutyl glycerine trinitrate is shown in Fig. 5.21.
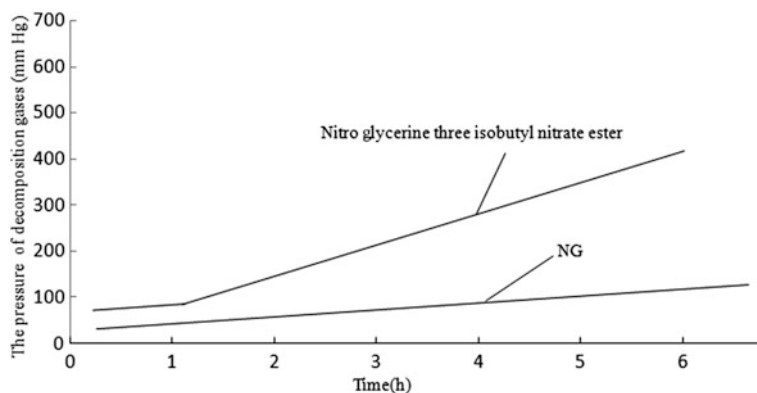
Fig. 5.21 Thermal decomposition of nitro isobutyl glycerine trinitrate [5]

It can be seen that the decomposition amount of nitro isobutyl glycerine trinitrate is four times larger than that of nitroglycerine after 5–6 h in the same decomposition conditions.

5.4.2.2 Explosion Property

The explosive decomposition of nitro isobutyl glycerine trinitrate to all gaseous products can be expressed as the following reaction equation:

$$C(CH_2ONO_2)_3NO_2 \rightarrow 4CO_2 + 3H_2O + 2N_2$$
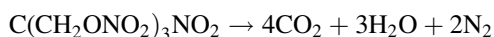
It is a process of zero oxygen balance.
Explosion heat: 6,924 J/g (water vapor) and 7,389 J/g (liquid water)
Detonation temperature: 4,870 °C (4,627 °C and 4,800 K in some references)
Specific volume: 705 ml/g
Detonation velocity: 7,860 m/s
Explosive grading: Brisance compression height of nitro isobutyl glycerine trinitrate is listed in Table 5.51.
Strength: 184 (TNT 100) calculated by the Caste equation.
Heat coefficient hi: 77.09 J/g.

Table 5.51 Brisance compression height of nitro isobutyl glycerine trinitrate

Compression height of copper cylinder (mm)	Relative pressure (kg/cm^2)
12.07	2,493
11.97	2,552
12.64	2,156
12.55	2,210

Detonation heat coefficient 54.39: 77.086 J/g.

Specific coefficient (I): 7.049 ml/g.

Sensitivity: falling height of explosion limit is 15 cm for 2 kg falling weight, 100 % explosion is 25 cm; 6 % explosion in friction test (nitroglycerine: 16 %); ignition point of 5 s delay time is 255 °C.

5.4.2.3 Preparation of Nitro Isobutyl Glycerine Trinitrate [5, 15]

It is different to prepare nitro isobutyl glycerine trinitrate from other nitrate esters. Two steps must be adopted in sulfuric acid predissolution method before nitration because the viscosity of isobutyl glycerine is high. Nitro isobutyl glycerine sulfate is first prepared and then nitrated to the nitrate ester by a mixed acid, as shown in the following mechanism.

$$
\begin{array}{c}
CH_2OH \\
O_2N{-}C{-}CH_2OH \\
CH_2OH
\end{array}
\; +3H_2SO_4 \; \rightleftharpoons \;
\begin{array}{c}
CH_2OHSO_3 \\
O_2N{-}C{-}CH_2OHSO_3 \\
CH_2OHSO_3
\end{array}
\; +3H_2O
$$

$$
\begin{array}{c}
CH_2OHSO_3 \\
O_2N{-}C{-}CH_2OHSO_3 \\
CH_2OHSO_3
\end{array}
\; +3HNO_3 \; \overset{H_2SO_4}{\rightleftharpoons} \;
\begin{array}{c}
CH_2ONO_2 \\
O_2N{-}C{-}CH_2ONO_2 \\
CH_2ONO_2
\end{array}
\; +3H_2SO_3 \; +3H_2O
$$
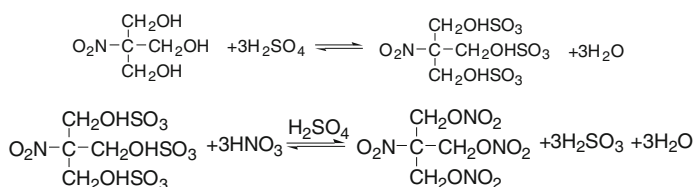
Those two steps are reversible reactions. Thus, the parameters in the reactions, such as concentrations of acids, amounts of acids, esterification temperature, would significantly influence the yield and purity of nitro isobutyl glycerine trinitrate.

The specification of raw materials for preparation of nitro isobutyl glycerine trinitrate is shown in Tables 5.52 and 5.53.

The preparation process of nitro isobutyl glycerine trinitrate is shown in Fig. 5.22.

In the preparation process, the appropriate concentration and amount of concentrated sulfuric acid is important to ensure the formation of the sulfate ester in the first step and to constrain the formation of an ester mixture of nitrate and sulfate in

Table 5.52 Specification of nitro isobutyl glycerine

Item	Value
Appearance	White or light yellow crystal, no visible impurities
Purity (%)	>96
Melting point (°C)	>130
Moisture (%)	<1.0
Ash (%)	<0.5

Testing conditions: (1) measurement by Caste brisance meter; (2) material of the sample container: galvanized steel, wall thickness: 1 mm, loading amount: 40 g, initiation: #8 tetryl detonator; and (3) copper cylinder: 10 × 15 mm, without precompaction

Table 5.53 Specification of Na_2SO_3

Item	Value	
	First class	Second class
Na_2SO_3 (%)	≥96	≥93
Iron (%)	≤0.02	≤0.02
Water insoluble (%)	≤0.03	≤0.03
Free alkali (%, Na_2SO_3-based)	≤0.6	≤1.0
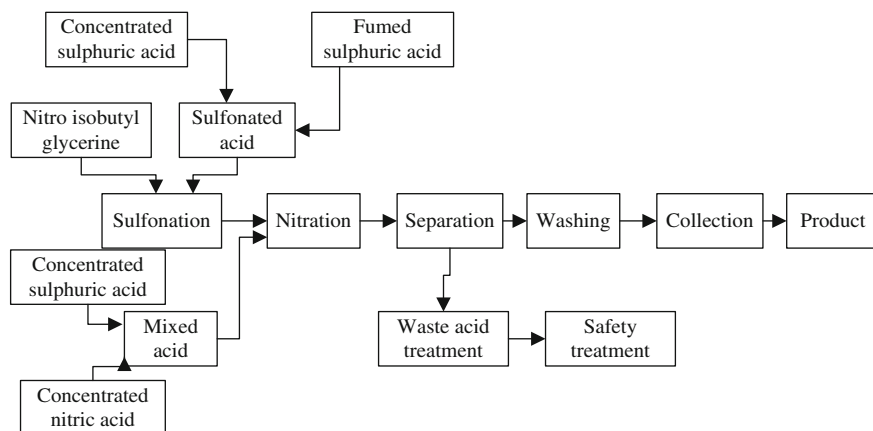
Fig. 5.22 Preparation process of nitro isobutyl glycerine trinitrate

the second step. The concentration and amount of nitric acid is determined by the need of NO_2 in later esterification and the conversion of the sulfate ester to nitrate ester. Meanwhile, the side reactions, such as oxidation and resinification, should be avoided. The yield and quality of the product, as well as the safety issue, are related to reaction temperature. In the sulfonation process of nitro isobutyl glycerine, the reaction rate is too slow at low temperature. However, if the temperature is too high, dehydration condensation would happen. Thus, the sulfonation temperature is usually at 45–50 °C. The nitration temperature in a reaction vessel under agitation is usually at 44 ± 1 °C. The nitration time is about 10–15 min.

Stability treatment of nitro isobutyl glycerine trinitrate is difficult because of its sensitivity to bases. The mixture solution of Na_2CO_3 and Na_2SO_3 can be used as a washing solution. A good washing effect can be obtained with relatively few products of saponification. The saponification and semi-solid impurities are related to pH value of the solution after washing. At pH < 7, nitro isobutyl glycerine trinitrate would not be saponified and the washing solution is ivory-white or light yellow. At pH > 9, the saponification is serious and the washing solution is yellow and turbid with flocculent materials on the surface. Therefore, the critical point to constraint saponification is to control [OH] concentration. Both Na_2CO_3 and

Na_2SO_3 belong to salts of a strong acid and a weak base, which can control and buffer the concentration of [OH] through hydrolysis reaction:

$$Na_2CO_3 + 2H_2O = 2Na^+ + 2OH^- + H_2CO_3$$
$$Na_2SO_3 + 2H_2O = 2Na^+ + 2OH^- + H_2SO_3$$
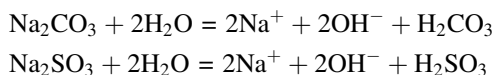
Because of $Na_2CO_3 > Na_2SO_3$, and H_2SO_3 obtained in Na_2SO_3 hydrolysis can be further ionized:

$$H_2SO_3 = 2H^+ + SO_3^{2-}$$

The ionization constant of H_2SO_3 is larger than that of H_2CO_3, and its ionization rate is considerably higher than that of H_2CO_3. H^+ should neutralize OH^- in the solution to form water and reduce the basicity of the solution, and further slow down the saponification.

The preparation conditions of nitro isobutyl glycerine trinitrate are summarized below.

(1) Sulfonation: H_2SO_4 concentration of 100 ± 0.5 %, $NO_2C(CH_2OH)_3$: H_2SO_4 = 1:2.75, temperature of 45 ± 5–55 ± 5 °C.

(2) Composition of nitration mixed acid: 80 ± 1.5 % HNO_3, 20 ± 1.5 % H_2SO_4, 2 % H_2O, and <0.4 % N_2O.

(3) Ratio of feedstock: sulfate ester: mixed acid = 3.75:2.75 (by weight)

Nitration temperature: 40 ± 1–46 ± 1 °C, stop feeding temperature: 45–49 °C, feeding temperature: 51 °C.

(4) Separation temperature: 35 ± 6 °C, retention time in gravity separation method of 35 ± 5 min.

(5) Washing and stability treatment: feed ratio in prewashing step (by volume) of oil/water = 1:8 (20 ± 5 °C), agitation pressure of 0.1–0.2 kg/cm, feed ratio in water-washing step (by volume) of oil/water = 1:8 (20 ± 5 °C), concentration of alkali-washing solution: 2 % Na_2CO_3 and 6 % Na_2SO_3, feed ratio (by volume) of oil/alkali-washing solution = l:2.8–3.8, pH in tower #1 of 9–10 and in tower #2 of 11–12.

The theoretical yield based on the reaction equation is 189 %, but the actual yield is 163.5 %, about 86.5 % of the theoretical yield. The specification of nitro isobutyl glycerine trinitrate is summarized in Table 5.54.

Table 5.54 Specification of nitro isobutyl glycerine trinitrate

Parameter	Value
Appearance	Colorless or light yellow transparent oily liquid
Abel test at 72 °C	>25 min
Basicity (Na_2CO_3-based)	<0.01 %
Acidity	None
Moisture	N.A.

5.4.2.4 Application of Nitro Isobutyl Glycerine Trinitrate

Nitro isobutyl glycerine trinitrate is applied in gelatin explosives, which have better properties than blasting gelatin of nitroglycerine. The explosives have a property of freezing resistance, suitable for application at low temperature. Except for sensitivity, the other properties are better than ammonium nitrate explosives, whatever for liquid explosives and powder explosives. Nitro isobutyl glycerine trinitrate also have wide application potentials in high plastic-type explosives, plastic-type explosives, dynamite, gelatin explosives (mixture explosives, powder explosives, gun propellants, and rocket propellants).

By comparison with nitroglycerine, nitro isobutyl glycerine trinitrate has the following advantages. The freezing point is lower, improving the low-temperature properties and freezing resistance of propellants and explosives. The sensitivity is weaker, in favor of the safety in production and application. It has lower vapor pressure and volatility, less irritating operators. However, there are some disadvantages, including poorer stability, smaller specific volume than nitroglycerine by 1.5 %, higher detonation temperature than nitroglycerine by 190 °C, and 8–9 times higher viscosity than nitroglycerine. Those disadvantages make nitro isobutyl glycerine trinitrate often fail in Abel test and be not suitable for propellant powder.

5.4.2.5 Toxicity

Nitro isobutyl glycerine trinitrate is a toxic substance with less toxicity than nitroglycerine. Its toxicity lies in the irritation to human body. Contacting with liquid nitro isobutyl glycerine trinitrate, people will have poisoning symptoms of swollen erythema and headache. However, the symptoms are weaker than that of nitroglycerine. The prevention and treatment are the same as nitroglycerine.

5.4.3 Property and Preparation of Pentaerythritol Trinitrate

Pentaerythritol trinitrate with the code of ITMETN, also called 1,1,1-trimethylol ethane trinitrate, trimethylol methane trinitrate, dimethylol-2-propanol-1-trinitrate, methyl isobutanetriol trinitrate, methyl isobutyl glycerine trinitrate, or methyl tert-butanetriol trinitrate, is a very important nitrate ester.

5.4.3.1 Chemical Physical Property of Pentaerythritol Trinitrate

Pentaerythritol trinitrate is a light yellow sticky liquid with an odor of burning alcohols.

Molecular formula: $C_5H_9N_3O_9$
Chemical structure:
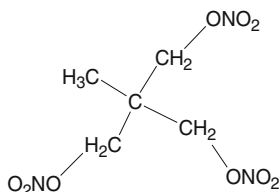
Molecular weight: 255.14
Oxygen balance: −34.49 %
Nitrogen content: 16.47 %

Pentaerythritol trinitrate has a specific weight of 1.4685 at 20 °C, a freezing point of −60 °C, a refractive index of 1.4760 at 17.5 °C, a 71 times larger viscosity than of nitroglycerine, and a weaker volatility of 1.21 mg/dm/h than nitroglycerine, about 1/3 of nitroglycerine at 60 °C. Its hygroscopicity is 0.07 and 0.14 % in the relative humidity of 65 and 90 %, respectively. Its solubility in water is related to temperature: 0.516 g/L at 19 °C and 0.685 g/L at 36 °C. It is soluble to diethyl ether, acetone, ethylene chloride, and other organic solvents. It is also soluble to concentrated nitric acid and sulfuric acid. It can dissolve cellulose nitrate. Its plasticizing capacity is weaker than nitroglycerine. The solubility of pentaerythritol trinitrate to 65 % acetic acid is 11.4 and to 96 % ethanol is 4 %.

5.4.3.2 Explosion Property

The explosion heat (constant volume) of pentaerythritol trinitrate is 5271.8 J/g with liquid water. The specific volume is 967 ml/g and explosion temperature is 3,500 K. The lead-block value is 480 mL. The heat coefficient is 2824.2 J/g and the detonation coefficient is 49.91 J/g. The coefficient of specific coefficient is 9.661 L/kg. The detonation velocity of pentaerythritol trinitrate in an open vessel with a diameter of 30 mm is listed in Table 5.55.

The detonation point of pentaerythritol trinitrate is 20 °C. Its shock sensitivity is much weaker than nitroglycerine, the characteristic height of which is 4 cm for 2 kg falling weight, but the height is 20–40 cm, or up to 47 cm in some references, for pentaerythritol trinitrate. An ester mixture of pentaerythritol trinitrate, triglycol nitrate, triaceticanhydride, and stabilizer can stand in a jolting truck without explosion. It is a good property for production and application.

The thermal stability of pentaerythritol trinitrate is better than nitroglycerine. The duration time in Abel test at 72 °C is 40–45 min.

Table 5.55 Detonation velocity of pentaerythritol trinitrate with different densities

Loading density (g/cm^3)	1.39	1.48	1.50
Detonation velocity (m/s)	6,750	7,040	7,060

5.4.3.3 Preparation of Pentaerythritol Trinitrate

Pentaerythritol trinitrate is prepared by a condensation reaction between formaldehyde and propionic aldehyde to pentaerythritol, which is further nitrated by a mixed acid of nitric acid and sulfuric acid. The preparation condition is nitration coefficient of 5–6, nitration temperature of 20–25 °C, and nitration time of 25–30 min. The nitration yield at 10 °C with a mixed acid of 45 % nitric acid and 55 % sulfuric acid is 197–198 %, about 93 % of the theoretical yield. If 20 % fuming sulfuric acid is used, the yield can be increased to 97–98 % of the theoretical yield. The parameters of stability treatment with water-washing coefficient of 5 are listed in Table 5.56.

In summary, the product can be obtained by sulfonation first and nitration later by a mixed acid with a yield of no less than 90 % theoretical yield.

5.4.3.4 Application of Pentaerythritol Trinitrate

Pentaerythritol trinitrate is used in explosives and propellants, partly or wholly replacing nitroglycerine. Americans believe that there is 2.0 % pentaerythritol trinitrate in modified double-base propellants with cellulose nitrate and an adhesive of polyglycol.

5.4.3.5 Toxicity

The toxicity of pentaerythritol trinitrate to human body is similar with nitroglycerine, but slightly lighter. Its treatment is also similar with nitroglycerine.

5.4.4 Property and Preparation 1,2,4-Butanetriol Trinitrate

1,2,4-butanetriol trinitrate with code of BTTN, also called butanetriol trinitrate or butanetriol nitrate, is used in double-base propellants.

Table 5.56 Parameters of stability treatment of pentaerythritol trinitrate in water-washing process

Washing solution	Temperature (°C)	Agitation time (min)	Washing times
Water	15	5	1
Water	50	5	1
5 % Na_2CO_3	70	15	2
Water	50	5	1
Water	30	5	1
Water	15	5	1

5.4.4.1 Chemical Physical Property of 1,2,4-Butanetriol Trinitrate

1,2,4-butanetriol trinitrate is a yellow transparent liquid.

Molecular formula: $C_4H_6N_3O_9$

Chemical structure:

Two isomers: 1,2,4-butanetriol trinitrate and 1,2,3-butanetriol trinitrate

$$CH_2\!-\!CH\!-\!CH_2\!-\!CH_2 \qquad CH_2\!-\!CH\!-\!CH\!-\!CH_3$$
$$\;\;ONO_2\;\;ONO_2\qquad\quad ONO_2 \qquad ONO_2\;ONO_2\;ONO_2$$
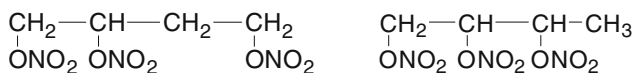
Molecular weight: 241

Oxygen balance: $-13.3\ \%$

Nitrogen content: 19.91 %

Specific weight: 1.52

Viscosity: 2.2 times to nitroglycerine

Freezing point: $-2.7\ ^\circ C$

Vapor pressure and volatility: about 1/2 of nitroglycerine

Hygroscopicity: 0.04 % in the relative humidity of 65 %

Solubility: 0.08 g/100 g water at 20 °C, 0.15 g/100 g water at 60 °C

It is mutually soluble to diethyl ether, alcohols, ketones, and other organic solvents. The plasticizing capacity to cellulose nitrate is similar with nitroglycerine.

The explosion heat of butanetriol trinitrate is 6,025 J/g (constant volume, vapor water) and 5,941 J/g (constant volume, liquid water). The specific volume is 840 ml/g (liquid water). The detonation point with delay period of 5 s is 230 °C. The characteristic height is 58 cm for 2 kg falling weight. The chemical stability of butanetriol trinitrate is excellent.

5.4.4.2 Preparation of 1,2,4-Butanetriol Trinitrate

The route to prepare 1,2,4-butanetriol trinitrate is to adopt the process of acetylene synthesis, as shown in the following equations:

$$CH\!\equiv\!CH + 2H_2O \xrightarrow{\;Cu_2C_2\;} HOH_2C\!-\!C\!\equiv\!C\!-\!CH_2OH$$

$$H_3COH_2C\!-\!C\!\equiv\!C\!-\!CH_2OH \xrightarrow[H_2SO_4+HgSO_4]{+H_2O} HOCH_2\!-\!\overset{\overset{O}{\|}}{C}\!-\!CH_2\!-\!CH_2OH$$

$$HOCH_2\!-\!\overset{\overset{O}{\|}}{C}\!-\!CH_2\!-\!CH_2OH \xrightarrow{\;H_2\;} HOCH_2\!-\!CH_2O\!-\!CH_2\!-\!CH_2OH$$

$$HOCH_2\!-\!CH_2O\!-\!CH_2\!-\!CH_2OH + 3HNO_3 \longrightarrow O_2NO\!-\!H_2C\!-\!\underset{\underset{ONO_2}{|}}{CH}\!-\!CH_2\!-\!CH_2ONO_2 + 3H_2O$$
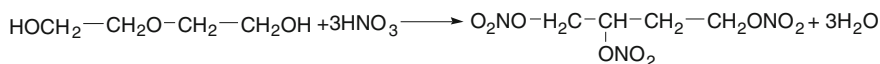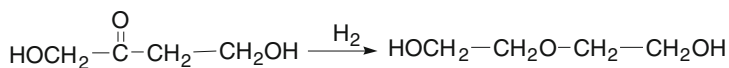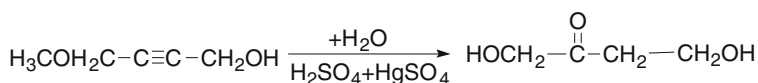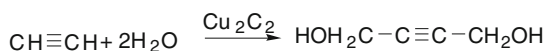
1,2,4-butanetriol is further nitrated by a mixed acid of nitric acid and sulfuric acid to obtain the final nitrate ester.

5.4.4.3 Toxicity

The toxicity of 1,2,4-butanetriol trinitrate is weaker than nitroglycerine.

5.4.4.4 Application of 1,2,4-Butanetriol Trinitrate

There is about 28.04 % 1,2,4-butanetriol trinitrate in double-based propellants modified by diisocyanate cross-linking reaction to improve their mechanical properties. In the propellant of a copolymer of acrylic epoxyethane boryl methyl ester and acroleic acid, there are about 16.3 % triglycol nitrate and 10.8 % 1,2,4-butanetriol trinitrate. Because there are many similar properties between 1,2,4-butanetriol trinitrate and nitroglycerine, it can replace nitroglycerine in explosives and propellants. A mixture of nitroglycerine and 1,2,4-butanetriol trinitrate is used as an adhesive in the well-known highly energetic solid propellant of NEPE, that effectively improves the sensitivity, energy, and mechanical properties of the propellant.

5.5 Property and Preparation of Other Nitrate Esters [1, 3]

5.5.1 Property and Preparation D-Sorbitol Hexanitrate

Sorbitol hexanitrate, or nitro sorbitol, is one of the isomers of nitro mannitol. It is a crystalline chemical at normal condition and molten at 55 °C. It used to be an additive of nitroglycerine in the United States to prepare dynamites with a low freezing point.

Sorbitol is dissolved to five times volume of concentrated nitric acid ($d = 1.52$ at 0 °C). The product can be precipitated by 10 times volume of 20 % fumed sulfuric acid (5 °C). In the product, there is a small amount of impurity of pentanitrate. At 0–10 °C of nitration and precipitation temperature, an oily mixture of sorbitol hexanitrate and sorbitol pentanitrate will be obtained. The explosion property of nitro sorbitol is similar with that of nitro mannitol.

In industry, sorbitol is prepared by catalytic reduction of D-glucose. Thus, its nitrated product has a wide application. For example, it can be used to synthesize 1,4,3,6-dihexanol 2,5-dinitrate for anapetia treatment. It is also use to prepare 1,4,3,6-didehydration dinitrate ester by D-mannitol, D-glucitol, and L-iditol, respectively, as shown below.

Isodimannitol dinitrate: melting point of 64.5–65.5 °C
Isodisorbitol dinitrate: melting point of 50.5–51.5 °C
Isoiditol dinitrate: melting point of 68–69 °C

5.5.2 *Property and Preparation of Polyethenol Nitrate [3]*

Polyethenol nitrate (nitro polyethenol) is a synthetic polymer to replace cellulose nitrate. It was first studied in 1929. Polyethenol was dissolved into concentrated sulfuric acid at 0 °C. The solution was then slowly added to a mixed acid of nitric acid and sulfuric acid and gradually heated to 40–50 °C. Polyethenol nitrate was precipitated out. The plastic precipitate was then filtered and washed to become fragile products with a nitrogen content of 10 %. In the nitration of polyethenol in 10–20 °C, polyethenol is easy to be oxidized. Thus, the oxidation should be prevented by some methods.

Hydroxyl groups of polyethenol cannot be completely esterified whatever in the mixed acid of nitric acid–sulfuric acid or nitric acid–acetic acid because of the cohydrolysis. It is nitrated by a mixture of nitric acid–acetic acid or a nitric acid–carbon tetrachloride solution. The high nitrated product can be softened at 40–50 °C. The lead-block value of polyethenol nitrate with a nitrogen content of 13–15 % is 153–342 cm.

The nitrogen content of polyethenol nitrate is generally in a range of 13.5–14.5 %, while the theoretical maximum nitrogen content is 15.75 %. The detonation velocity of polyethenol nitrate is similar with cellulose nitrate, which has the same nitrogen content as polyethenol nitrate. The detonation velocity of polyethenol nitrate with a nitrogen content of 13.4 % in a paper cylinder with a diameter of 30 mm is shown below.

Loading density of 0.3 g/cm 2,030 m/s
Loading density of 0.6 g/cm 3,450–3,520 m/s
Loading density of 1.0 g/cm 4,920–5,020 m/s
Loading density of 1.4 g/cm 6,090 m/s
Loading density of 1.5 g/cm 6,560 m/s

Polyethenol nitrate is flammable and infusible. It has not been used in industry because of its poor chemical stability. Different from cellulose nitrate, which can be existed as a solution and be a highly mechanical film after evaporation of the solution, polyethenol nitrate cannot be formed as a solution. It might be because of the shortage of oriented molecular chains.

5.5.3 *Property and Preparation of Diglycerine Tetranitrate*

5.5.3.1 Property of Diglycerine Tetranitrate

Diglycerine tetranitrate, shortly called nitro diglycerine, can be prepared by nitration of diglycerine.

Molecular formula: $C_6H_{10}N_4O_{13}$
Chemical structure:

```
CH2ONO2  CH2ONO2
   |        |
HC-O————CH
   |        |
CH2ONO2  CH2ONO2
```
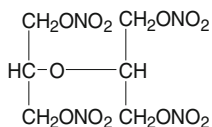
Molecular weight: 346.14
Oxygen balance: 18.49 % (CO_2-based)
Nitrogen content: 16.18 %

Nitro diglycerine is a stickier liquid explosive than nitroglycerine. It is insoluble to water and nonhygroscopic. It can be soluble to most of organic solvents and partly dissolve collodion. Its chemical stability is similar with nitroglycerine. Its remarkable advantage is that it would not freeze at a temperature under -35 °C.

Nitro diglycerine is one of the strongest known explosives. The explosion heat of the explosive mixture consisting of 75 % nitroglycerine and 25 % nitro diglycerine is equal to that of pure nitroglycerine. Its shock sensitivity is very weak with a characteristic height of 8–10 cm for 2 kg falling weight. The explosive decomposition reaction of nitro diglycerine can be written as

$$C_6H_{10}N_4O_{13} \rightarrow 2CO_2 + 4CO + 5H_2O + 2N_2 + 5{,}564.7\,J/g$$
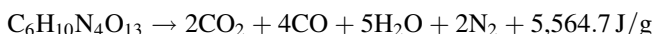
5.5.3.2 Preparation of Diglycerine Tetranitrate

Glycerine can be polymerized with a small amount of sulfuric acid at 130–160 °C. If a small amount of sodium carbonate or sodium sulfite of about 0.5 % is added into glycerine, diglycerine ether of 2,2′,3,3-tetrahydroxyl ether (sym bis(2,3-dihydroxypropyl)ether) is produced with water, as expressed in the following equation.

$$C_3H_5(OH)_3 \rightarrow CH_2OH-CHOH-CH_2-O-CH_2-CHOH-CH_2OH + H_2O$$
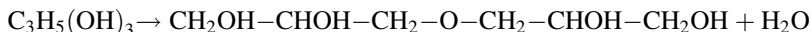
The fraction of triglycerine and polyglycerine is about 4–6 % and unpolymerized glycerine is about 30–40 %. The main product in the mixture is diglycerine with a density of 1.33, a 11 times larger viscosity than glycerine, and a boiling point of 247–249 °C at 8 mmHg.

The nitration of diglycerine to nitro diglycerine is similar with the method of glycerine nitration, but has a little difference because of the difference properties of raw materials. The major reaction is:

$$CH_2OH-CHOH-CH_2-O-CH_2-CHOH-CH_2OH$$
$$\rightarrow CH_2ONO_2-CHONO_2-CH_2-O-CH_2-CHONO_2-CH_2ONO_2 + H_2O$$
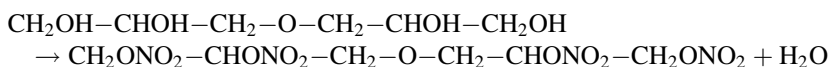
The amount of mixed acid in the nitration of diglycerine is slightly less than that for glycerine. Because of its high viscosity, diglycerine needs to be heated to 50–60 °C before adding into a nitration reactor. In nitration reaction, upper-dropwise addition method is adopted. Meanwhile, an inert gas goes into the nitration solution of mixed acid for bubbling to control the reaction smoothly.

The separation of nitro diglycerine is much slower than nitroglycerine because of its high viscosity. Impure diglycerine would produce an emulsion. The separated nitro diglycerine will be washed by a salt solution, which can prevent nitration solution from emulsification. The water formed in the washing process is more difficult to be removed than nitroglycerine.

100 kg diglycerine can produce 181.7 kg nitro diglycerine with a yield of 87.6 %.

Nitro diglycerine is mainly used to produce dynamites with a low freezing point or other liquid explosive mixtures, which property is better than chloroglycerine dinitrate because it is insoluble to water and there is no hydrogen chloride in explosive products. It is easy to prepare the mixture of diglycerine and glycerine, having a cost advantage of raw materials. The disadvantage is that diglycerine's viscosity is too high. It causes the difficulty of removing diglycerine in products. Furthermore, emulsification would be happened in the process of water-washing.

A new explosive mixture can be obtained by mixing nitro diglycerine with glycol dinitrate, other nitrate esters, and combustibles and applied in civil engineering explosion and mining explosion.

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Chapter 6
Azido Liquid Explosives

Organic azides are a kind of novel energetic materials with azido group (–N$_3$) [1], which are mainly applied in energetic adhesives and energetic plasticizer. Since 1864 numerous studies have been done on the structures, properties, synthesis, and applications [2]. The solvents, molecular bonders, adhesives, plasticizers, oxidants, and other additives with organic azido groups have their own unique properties, and play a distinct role in propellants and high explosive energetic materials. The azido groups improve the energy levels and endue excellent performance of high energetic materials [3]. Alkyl azide, triazo-alcohol, triazo-nitrate, triazo-nitrate esters, and triazo-ethers or ketones are classic azides. Small molecular alkane with two or more azide groups, and triazo-nitrate esters or triazo-ketones with multiple azide groups have the most potential applications. This kind of organic azido compounds have azido groups and nitrate esters. They are a new plasticizer applied in high explosives and propellants [4].

6.1 Properties and Application of Azido Liquid Compounds

6.1.1 Properties of Azido Compounds

(1) Chemical properties

Azido compounds are derivatives of hydrazoic acid (HN$_3$). The molecular feature is that all azido compounds have azido groups. According to the classic electronegativity proposed by Linus Pauling [5], the electronegativity of azido group is 2.95 and 3.18 [6], which is very close to the electronegativity 3.0 of chlorine. Following the rapid development of modern physical methods in characterization of crystal structures, molecular orbit theory divides azido compounds into two groups [7]. The first group is the inorganic azides with symmetric azido groups and ionic bonds in some degree. The second is the organic azido compounds with covalent bonds.

Azido compounds are chemically active. After being illuminated or heated, they decompose to azenes, which are very reactive. Most of azido compounds are explosive, which should be used with caution. The reactions of halogenerated hydrocarbons, aryl chlorides, or diazonium salts with sodium azide, or the reactions of acrylhydrazines with nitrous acid, produce corresponding azido compounds. Azido compounds are reagents for organic synthesis. Lead azide is the most important composition of propellants in industry.

The terminal carbon of organic azido compounds is nucleophilic. Most azido compounds are unstable and release N_2 gas. Curtius rearrangement has the intermediate acyl azide in the reaction. Some azido compounds are 1,3-dipoles, which are used in cycloaddition.

The reaction of azido compounds and acid produces hydragoic acid. The reactions of hydragoic acid and other ions generate explosive chemical compounds with high risk. The reaction of azido chemicals with base is a saponification reaction. This reaction decomposes the chemicals but it is not dangerous.

(2) Stabilities of azido compounds

The thermal decompositions of azido compounds are of two types—ionic and covalent bonds. Most of organic azido compounds are covalent azido compounds. The electromagnetivity of $-N_3$ group strengthens the C–N bond. So the bond lengths of two N–N bonds in $-MN_3$ groups are different. The bond lengths of triazido triazinane trione are $—_N\overset{1.26}{—}_N\overset{1.18}{—}_N$. The decomposition of chemicals is as in the below equation.

$$R-N_3 \rightleftharpoons RN + N_2$$
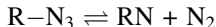
In ionic inorganic azido compounds [8], the lengths of N–N bonds are the same (the polarization of azido group is not in consideration). N–N bonds are not broken in the decomposition, which follows below equations.

$$MN_3 \rightleftharpoons M + N_3 \qquad (I)$$
$$N_3^- \rightleftharpoons N_3^+ + e \qquad (II)$$
$$2N_3^- \rightarrow 3N_2 \qquad (III)$$
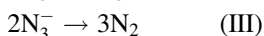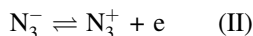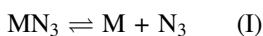
Most azido compounds explode in their decomposition. But thermochemistry, photochemistry, and discharge methods can slow down the decomposition reaction. The products of explosive decomposition are the corresponding simple substances. Decomposition heat of one compound equals its standard formation heat.

Some decomposition reactions generate nitrides.

$$3LiN_3 \rightarrow Li_3N + 4N_2\uparrow$$
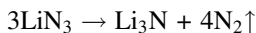
If the decomposition of hydrogen azide is below 1,000 °C and under low pressure, the products are collected on the surface cooled by liquid helium. The decomposition reaction is below:

$$6HN_3 \rightarrow 7N_2 + H_2 + (NH)_4$$
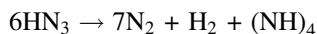
Alkali metal azides do not explode. They decompose slowly.

$$2NaN_3 \rightarrow 2Na + 3N_2 \uparrow$$
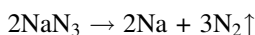
The decomposition of heavy metal azides is from the excitation of azide ion, which produces an azido group. The decomposition of ground state azido group into ground state N and N_2 is forbidden by the selected rules; while the decomposition of ground state azido group into excited state N and N_2 is allowed by the selected rules, but it needs 259 kJ/mol energy. This decomposition reaction is not obvious at room temperature. The interaction of two azide groups is allowed by the selected rules, and it is an exothermic process. The interaction of azide groups is one important step of ionic azido solid compounds.

Silver azide, lead azide, etc., heavy metal azides are highly explosive. Lead azide is very sensitive for impact, so it is used as a detonator. Generally, other azides are nonexplosive. Sodium azide is most widely used. It is water decomposable, and the hydrolysis product is diazoimide (HN_3). Aryl azides are colorful and relatively stable solids. They explode when being impacted, and decompose when being melted and release HN_3. Sodium azide easily combines with lead or copper to produce metal azides, which are highly explosive.

Azido compounds can inhibit the activity of cytochrome oxidase and other enzymes, and cause phosphorylation and respiratory abnormality of cells. The main acute toxicity of hydrazoic acid and its salts extremely lowers angiotasis by directly impacting vascular smooth muscle. The effect is similar but stronger than nitrites. The only difference is that azido alkane does not produce methemoglobin. Azido compounds can stimulate breathing and enhance cardiac force. Large-dose azido compounds elevate the blood pressure and cause convulsions, followed by suppression and shock. In organic azido compounds, azidoethane and azidopentane are effective antivascular tone agents. But several aryl azido compounds do not have this effect.

6.1.2 Application of Azido Compound Liquids

6.1.2.1 Application of Azido Compounds in Cycloaddition Reaction

Organic azido compounds react with alkene, ketone, X≡Y triple bonds, X=Y double bonds, and alkyne to generate cycloaddition products—five-membered nitrogen-containing heterocyclic compounds. Under heating or catalysts, organic

azido compounds react with alkene to produce five-membered triazole cycles. Under the catalysis of Lewis acids, organic azido compounds have cycloaddition with ketone, and react with X≡Y triple bond compounds (nitriles) to form tetrazoles. Organic azido compounds react with X=Y double bond cumulenes with hetero atoms (e.g., isocyanate, isothiocyanate, or carbodiimide) to produce oxazoles with nitrogen heteroatoms.

Huisgen cycloaddition of organic azido compounds and alkyne is 1,3-dipolar cycloaddition of azido compounds and terminal or central alkyne to produce 1,4- or 1,5-substitution triazoles. Their reaction process is below.

1,4-substitution triazole   1,5-substitution triazole
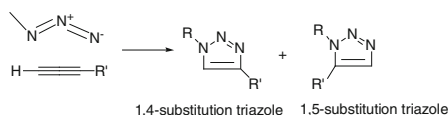
Huisgen's study in 1960s makes Huisgen cycloaddition completely understood and a kind of important novel reactions [9]. In early twenty-first century, Sharpless and Meldal improved Huigen's reaction independently through using Cu(I) catalyst to stereoselect 1,4-substitution triazoles. (1) This reaction is finished quantitatively, and the yield is close to 100 %. (2) This reaction is highly tolerated for function groups, and not sensitive for chemical structures of molecular ligans. Other function groups do not need be protected. (3) The reaction can be conducted in all solvents. (4) The reaction can be operated at room temperature, which helps keep the activity of biomolecules. (5) This reaction occurs not only in homogeneous phases, but also on the intersurfaces, for example, the intersurfaces of liquid–solid, liquid–liquid, or solid–solid. These features make the reaction play an important role in connection of ligands and synthesis blocks, surface modification of macromolecules and nanomaterials, coupling of biomolecules, new drug development, etc.

6.1.2.2 Application of Azido Compounds in Synthesis of Triazoles and Amine-Group Compounds

Triazoles are a kind of nitrogen containing heterocyclic compounds with stable chemical properties. Compared to amides, triazoles do not hydrolyze. Unlike benzene or heteroaromatic compounds, triazoles are seldom oxidized or reduced. The application of triazoles varies from antiseptics, herbicides, and microbial inhibitors of agriculture to light stabilizers, fluorescent brighteners, preservatives, and fire retardants of industry. Triazoles are used in drug delivery and nano devices of functional macromolecules area, and applied in oligonucleotide preparation, cell culture, anti-inflammatory and antiretroviral therapy, HIV protease inhibitors, and messenger ribonucleic acid (m RNA) hairpin loop specific ligands of medical and biology technology. Triazoles with metabolic inertia and donor–acceptor of multiple hydrogen bonds are mock objects of peptide bonds. The molecules synthesized

guidedly using triazoles are used to evaluate the biological effects of other compounds in the database. Cycloaddition of azido compounds and alkyne or active alkene produces triazoles. Available azido compounds include hydragoic acid, metal azides, organic azido compounds. Alkene only reacts with organic azido compounds. In the cycloaddition of azido compounds and alkyne, the types of azido compounds and alkyne impact triazoles. Aromatic and aliphatic azides react with active alkyne to generate 1,2,3-triazoles. Sulfonyl azides react with active alkyne, which produces N-sulpyl triazoles. After rearrangements, the mixtures of triazoles, its isomers with open loops, and α-diazoimides are produced finally [10]. Being catalyzed by Cu(I), the cycloaddition selectively generates 4-substituted 1-(N-sulfonyl-)-1,2,3-triazoles. Adamo et al. [11] discovered another special method to synthesize triazoles. This method is the cycloaddition of α,β-unsaturated aminoketones and diethylaluminum azide. After reduction of azides, amine-group compounds are obtained. Thoils, complex hydrides, and borane with Lindlar catalyst can reduce azide into amine-group compounds. Li/2-tertbutyl biphenyl reduces azido group into primary amine at room temperature. Under catalysis of $FeCl_3$, N,N-dimethylhydrazine is a mild reductant of azides. Trimethyl chlorosilane can reduce aliphatic, romatic, and benzoyl azides into amine with severe reaction conditions. Catalyst samarium diodide (SmI_2) helps the reactions conducted in a moderate condition. Huang et al. [12] reduced alkyl, aryl, acyl, and sulfonyl azides into amines using samarium diodide as catalyst with mild reaction conditions. The yields of amines were very high. Under catalysis of Cu(II), zinc borohydride and sodium borohydride can reduce azido group into amine. Iron salt Fe(II) and stannaimine Sn(II) [13] (acryl substituted tin (II) thiolate) are very good reductants. Acyl azides are not stable. In inert hot solvents, they like to rearrange and release nitrogen gas. The parsed intermediate isocyanates hydrolyze to primary amine. This is the famous Curtius rearrangement (below equation).

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-N-N\equiv N \xrightarrow[\substack{\text{Curtius} \\ \text{Rearrangement}}]{\Delta} R-NCO \xrightarrow[-CO_2]{\text{hydrolysis}} R-NH_2$$
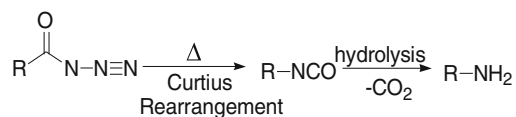
6.1.2.3 Application of Azido Compounds in Azene Chemistry

Azene is a kind of reactive intermediates in organic synthesis, which is produced through the decomposition azido compounds under illumination or heat. Azene is the nitrogen analogs of carbene; it is high electrophilic. Azene is widely applied in cycloaddition, rearrangement, ring expansion, ring contraction, and insertion reactions.

Cycloadditions of azido compounds and various functional groups are a classic synthesis of triazoles with nitrogen containing rings. Their intramolecular cycloadditions derive a lot of organic compounds. Lukina et al. [14] synthesized

hexahydro-1,2,3-triazole-1,5-a-pyrazine using the intramolecular cycloaddition of azido group and alkenyl group. The cyclization reaction formed the C–N bond and released nitrogen gas at the same time. The product pyrazine can be used to synthesize piperazine and its derivatives. After treatments by alkylating and acylating agents, the final objective/target products are obtained.

Benzyl azide decomposed into various reactive intermediates, of which singlet phenyl azene is the key one. Under illumination or being heated, azide agents and ring compounds have ring expansion or contraction reactions. The ring expansion or contraction reaction produces nitrogen-containing ring compounds or nitriles. Under illumination, phenyl azide [15] produces 2-diethylamino-3-hydro-azepine in diethylamide through the ring expansion, derivatives of 2-phenylamine in aniline/trimethylamine, and derivatives of 2-amine in liquid ammonia. After ring expansion, mesitylphosphatriafulven with three-membered ring reacts 1H-2-iminophosphetes with four-membered ring [16]. Under illumination, the six-membered ring of azido pyrazine becomes five-membered.

Under illumination or being heated, organic azides decompose into singlet and triplet azenes. Singlet azenes can have insertion reaction with saturated hydrocarbons. The triplet azenes take the hydrogen atoms of alkane and produce free radicals. Both react with C=C groups. Above reactions can immobilize the functional molecules on the surface of substrates and get wide applied functional materials. The available azido compounds for above reactions include alkyl/aryl, acyl, phosphoryl, sulfonyl and silicyl azides, and ethyl azidoformate. The available base materials have glass, silicon wafers, metals, nanoparticles, macromolecule spheres, and inert polymaterials (membranes, fibers, and nonwovens). Under illumination of ultraviolet or being heated, polymers, natural polymers, enzymes, biological cells, luminescence groups, and labeled molecules are immobilized, adhered, grafted, and coupled onto the substrates. Cross-linking, rheology modification, introducing long chain branching, and functionalization of polymers are achievable in melting processes.

Yan and Ren [17] used spin-coating method and C–H insertion reaction of multiple fluoro-substitute phenyl azide to get the covalent attachment of ultrathin polypropylene membranes on silicon wafers. It supplied the possibility to conduct biochemical reactions on silicon wafer surface and the surface modification of biomedical measuring microdevices, and to improve biocompatibility, increase adhesion, enhance robustness of silicon wafers. Zhu et al. [18] utilized azene insertion reaction to bind chitosan molecules on the surface of polyactide (PLA) membrane, and replicated them using heparin to prepare a new biomaterials, which impedes the conglutination of platelets and strengthen the adhesion of cells. Hicke et al. [19] activated the hyperfiltration membrane of polyacrylonitrile and its copolymers using acyl azides and immobilized amyloglucosidase (AG) on the superfiltration membrane. This membrane makes the hydrolysis of starch or malt sugar and separation of products simultaneously. Weng et al. [20] obtained self-assembled single molecular layers on titania membrane by introducing 3-amino propyl phosphoric acid, then immobilized azido gelatin on titania membrane. The titania membrane with azido gelatin has very good biocompatibility, and potential application in biomedical area. Mehdinia et al. [21] prepared

self-assembled single molecular layer modified Au electrodes using azido hexanethoil, and connected DNA using azido groups to obtain DNA immobilized Au electrodes (DNA/SAM/Au). These electrodes are used as fast-response probes to measure the taxol in blood serum. Boaen and Hillmyer [22] had detailed review in the functionalization area of polymers. Thermo Scientific Company also released series of azido crosslinkers.

6.1.2.4 Application of Azido Compounds in Other Cycloadditions

A lot of researcher tired to improve and simplify the cycloaddition of azido compounds. Appukkuttan et al. [23] activated benzyl chloride/NaN_3 using microwaves and used one-step method to synthesize triazoles through the reaction of activated benzyl chloride/NaN_3 and terminal alkyne. The yield reaches 86–93 %. Another valuable improvement was done by Orguira using element Cu(0) as the catalyst and amine as the co-catalyst [24]. The yield is more than 95 %. Later Yamamoto prepared 1,4,5-trisubstitution triazoles using bimetal catalysts and central alkyne [25]. In 2005, Zhang et al. [26] discovered that Cp*RuCl(PPh$_3$)$_2$ catalyzed cycloaddition with 1,5-substitution triazoles. In addition, tetrahexyl ammonium chloride (THAC) can also catalyze the cycloaddition of aryl azido compounds [27]. The yield from the reaction of azido benzene and methyl propiolate is more 90 %.

1,3-dipolar cycloaddition of azido compounds and alkyne catalyzed by Cu is the well-established point-and-click reaction because of its reliability, specificity, and biocompatibility. The nitrogen-containing rings with triazole products can mime the atom displacement and electrical properties of pipetide bonds. Under reaction conditions, the common functional groups of biological molecules are stable. While the reactivity of azides and alkyne is very high, they do not react with biological functional groups. The biological orthogonal effect makes the reaction particularly suitable for the derivatives synthesis of natural products in biology and medicine, target guided synthesis, and active group proteomic profiling. Benefiting from fast, effective, and predictable single step of multiple-step reactions, the integration of combination of point-and-click reaction with combinatorial chemistry, high-throughput screening, and database building of compounds will accelerate the discovery and development of new drugs.

Once established point-and-click reaction, the relative papers emerge explosively. This practical and intelligent reaction is fruitful in three relative areas: (1) polymers and materials science; (2) biological coupling; (3) drug development. The application of the reaction is the center of attention in synthesis and modification of macromolecules, self-assembly single layer of metals and nanomaterials, synthesis of supermolecules, molecule–electro devices, sensor probes, nonlinear optical materials, surface modification of column packing materials of HPLC, immobilization of enzymes, coupling, labeling and testing of biological molecules (e.g., oligopeptides, polynuleotide, oligosaccharides, lipids, proteins, cell tissue organs, etc.), and new drug development.

Krasia and Steinke [28] first reported the polymer synthesis using diazide and dialkyne under catalysis of cucurbituril.

Sharpless [29] reached that the molecular weight of in situ polymerization of diazide and dialkyne is less than 12,500. This work started a new method of preparing resin structures using point-and-click reactions. Various cross-linked resins from different types of diazides and dialkyles are applied in the connection of metals (e.g., copper substrate), which generates a new technology and process different from that of epoxy. Vora et al. [30] synthesized alkyne-functionalized polycaprolactone and polylactide. Under catalysis by copper bromide, the point-and-click reaction of azido group functionalized compounds with alkyne-functionalized polycaprolactone and polylactide produces miktoarm star polymers. Catalyzed by copper, Azido group functionalized polyving alcohol(PVA-N_3) and photoactive proper pyrene produce photoactive pyrene functionalized PVA after poin-and-click reaction. After alkyne functionalized the thiol group of cysteine in SA, copper-catalyzed point-and-click reaction effectively couples bovine serum albumin (BSA) onto the polystyrene.

Goldmann et al. [31] introduced azido groups using thiol-alkene method through 1-azido-undecan-11-thiol first, then the point-and-click reaction of alkyle functionalized poly-2-hydroxyethanyl acrylate and azido groups to achieve the hydrophilic modification of polydivinylbenzene microspheres.

6.1.2.5 Application of Azido Liquid Compounds in Energetic Materials and Gas Generators

A lot of work has been done for the synthesis of azido nitroamino compounds, their properties and applications [32]. Reed and Dolah first started the study of this kind of compounds. Rosher, Morton, and Eimslic synthesized series of azido nitroamino compounds, and applied them as the composition of propellants. They notably rise the combustion/burning rate and specific impulse without influencing the pressure index. Their energy approximately equals that of HMX. Their detonation sensitivity is relatively low. They are widely applied in smoke-free propellants with low sensitivity to replace HMX.

Azido group has very high positive formation heat ($\Delta H = 3,556$ kJ/mol). As the one composition of propellants, azido materials lower down the average molecular weight, and increase the specific impulse. At the same time, introduction of azido groups increases the nitrogen content, and lowers the relative nitrogen content. Both are good for reducing the smoke or being smoke free in the combustion/burning of propellants. The study of azido compounds gains more and more attention [33].

Azido nitroamino compounds and azido compounds have been synthesized large quantitatively. They are used in energetic plasticizers and energetic oxidants [34] according their properties.

The synthesis of methyl azido nitroamino compounds (1) is based on the preparation of primary nitramine, then introducing a chloride atom using chloromethylation, followed by azidization, the schematics are below.

$$R-\overset{\overset{\displaystyle H}{|}}{N}-NO_2 \xrightarrow[\text{HCl}]{\text{HCHO}} R-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2Cl \xrightarrow[\text{DMF}]{\text{NaN}_3} R-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2N_3$$
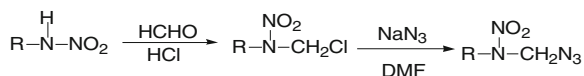
Take the synthesis reaction of 3-nitro-1,5-diazido-3-nitrogen-pentane (2) as an example. Diethanolamine is the raw materials. The reactions of nitrification and azidization are below.

$$HN(CH_2CH_2OH)_2 \xrightarrow[\text{(2)HNO}_3(CH_3CO)_2O]{\text{(1)HNO}_3} \underset{CH_2CH_2ONO_2}{O_2N-N-CH_2CH_2ONO_2} \xrightarrow[\text{DMSO 80°C reflux}]{\text{NaN}_3} \underset{CH_2CH_2N_3}{O_2N-N-CH_2CH_2N_3}$$
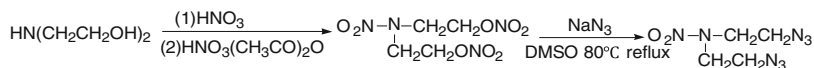
Metallic organic azido compounds are novel energetic materials, which is used in the firelighter/ignition agent of solid and liquid propellants. Take azido diethyl aluminum as an example, its reaction is below.

$$NaN_3 + (CH_3CH_2)_2AICI \xrightarrow{\text{solvent}} (CH_3CH_2)_2AIN_3$$

The rapid decomposition of azido compounds results the shotpoint and initiation. Because of the rapidity of gas production, azido compounds are used in the airbags of cars.

6.2 Properties and Preparation of Azidoalkane [35]

6.2.1 Properties and Preparation of Azidomethane

Azidomethane is a colorless and transparent oily liquid with aromatic odor. Its specific density is a little larger than that of nitromethane.

6.2.1.1 Properties of Azidomethane

The molecular formula of azidomethane: CH_3N_3
The chemical structure of azidomethane:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-N_3$$
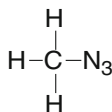
The molecular weight: 57.04
The nitrogen content: 73.65 %

6.2.1.2 Preparation of Azidomethane

Certain amount of sodium azide was dissolved into water. Later, bromomethane
and methanol were added, then the mixture was heated to 65–90 °C and reluxed for
2–3 h. In the reaction, colorless oily production was gradually produced in
refluxing. After reaction, DI water was used to wash the organic layer several times.
Later dichloromethane was used to wash and separate the organic and aqueous
layers. Dichloromethane was evaporated, and the colorless oily liquid product was
collected at 40–41 °C under reduced pressure. The yield of adizomethane is 87.6 %.

6.2.2 Azidoethane

The molecular formula of azidoethane: $CH_3CH_2N_3$
    The chemical structure of azidoethane:

$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-N_3$$
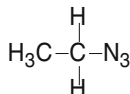
The molecular weight: 71.07
The nitrogen content: 59.11 %

6.2.3 Diazidoethane

The molecular formula of diazidoethane: $C_2H_4N_6$
    The chemical structure of diazidoethane:

$$N_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-N_3$$
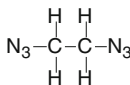
The molecular weight: 112.07
The nitrogen content: 74.97 %

6.2.4 Azidopropane

The molecular formula of azidopropane: $C_3H_7N_3$
   The chemical structure of azidopropane:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-N_3$$
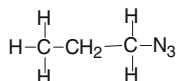
   The molecular weight: 85.09
   The nitrogen content: 49.37 %

6.2.5 Properties and Preparation of 1,3-Diazidopropane (DANG)

1,3-diazidopropane is a colorless and transparent oily liquid. Its chemical code is DANG. DANG is an excellent energetic plasticizer and modifier.

6.2.5.1 Properties of 1,3-Diazidopropane

The molecular formula of diazidopropane: $C_3H_6N_6$
   The chemical structure of diazidopropane:

$$N_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-N_3$$
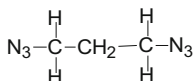
   The molecular weight: 126.12
   The nitrogen content: 66.62 %
   The density: 1.1042 g/cm^3
   The boiling point: 150–151 °C (1 atm), 48–50 °C (2 mmHg), 50–60 °C (6 mmHg)
   The refractive index: 1.4788–1.4789
   pH: 7.00
   Nonvolatile at room temperature
   (1) Reactions with oxidants
   To study the decomposition of 1,3-diazidopropane under strong oxidants, the reactions of 1,3-diazidopropane with concentrated sulfuric acid, concentrated nitric

acid, 40 % sodium hydroxide, and sodium hypochloride are designed and compared with isopropyl nitrate. The results are in Table 6.1.

There is not any reaction for mixtures of 1,3-diazidopropane and isopropyl nitrate with any ratio. Experiments indicated that as a liquid explosive, the mixture of 1,3-diazidopropane and isopropyl nitrate increases both the oxygen consumption and gas products.

(2) Reactions with reductants

The reactions of 1,3-diazidopropane and strong reductants are also designed. Triethyl aluminum was chosen as the strong reductant. One reaction is that 1,3-diazidopropane and triethyl aluminum are mixed in inert gas; the second is in air. The results are in Table 6.2.

The data from above table indicate that the liquid explosive with bodying triethyl aluminum as the main fuel, a catalyst and a sensitizer have both maximum oxygen consumption and gas products. The chemical stability is also good. The explosive with 1,3-diazidopropane as the main fuel, triethyl aluminum as catalyst and sensitizer is also a kind of good-performance liquid explosives.

6.2.5.2 Explosive Properties of 1,3-Diazidopropane

The peak temperature of 1,3-diazidopropane thermal decomposition is 179.32 °C.

The specific volume of 1,3-diazidopropane is 47249.6 mL/g.

The combustion heat of 1,3-diazidopropane is 19319.9 J/g.

The electric spark sensitivity of 1,3-diazidopropane is misfiring.

Friction sensitivity: average fire rate (%) = 0

Impact sensitivity: misfiring

5 s flashpoint: 192 °C

Combustion/burning experiment of 1,3-diazidopropane

200 g 1,3-diazidopropane is placed in a 500-mL thick wall glass container. A pipe of 6 mm double-base propellant is plugged in the center. Ignite the double-base propellant from the top, and 1,3-diazidopropane starts burning, until the glass container explodes.

Table 6.1 The reaction of 1,3-diazidopropane and oxidants

Compositions	Medium	Phenomem
1,3-diazidopropane + conc. H_2SO_4	N_2 (high purity)	Become red, release heat, decomposition
1,3-diazidopropane + conc. H_2SO_4	Air	Decomposition, smoke, explosion
1,3-diazidopropane + conc. HNO_3	N_2 (high purity)	Decomposition explosion
1,3-diazidopropane + conc. HNO_3	Air	Decomposition explosion
1,3-diazidopropane + 40 % NaOH	Air	Red precipitation after 5 h
1,3-diazidopropane + NaClO	Air	Red precipitation

Table 6.2 The reaction of 1,3-diazidopropane and reductants

Compositions	Medium	Phenomem
1,3-diazidopropane +Al(CH$_2$CH$_3$)$_3$	N$_2$ (high purity)	Safe, stable, no reaction
1,3-diazidopropane + Al(CH$_2$CH$_3$)$_3$	Air	Explosion after addition of 1, 3-diazidopropane drop by drop
1,3-diazidopropane + Zn powder	Air	No reaction
1,3-diazidopropane + Zn powder	Air	No reaction

Detonation of 1,3-diazidopropane

To study the detonation of 1,3-diazidopropane, a special experiment is designed. 1,800 g 1,3-diazidopropane is placed in 800 mm aluminum shell, and a booster ignites from the center. The measured super pressures are in Table 6.3.

The above experiments indicate that 1,3-diazidopropane did not burn completely, and there are liquid in the bottom of shells. This is probably because that 1,3-diazidopropane has negative oxygen balance. And there is no explosion without extra oxygen. 1,3-diazidopropane is more stable than nitrates.

Drop test or falling down test

To assess the safety of 1,3-diazidopropane, a drop test is designed. 500 g of 1,3-diazidopropane is placed into a metal container and then the container is sealed. In the packing, one still has 20 % empty room left, and the second is 0. All these containers drop down from 50 m height and the ground is concrete. To see whether there is explosion in the falling down, each packing way is tested 10 times. All test results are in Table 6.4.

All results show that there is no explosion decomposition in all the falling down from 50 m height.

Metal shell experiments

200 g of 1,3-diazidopropane is packed in a 500-mL metal container with a 6 mm double-base propellant plug. After ignited from the top of double-base propellant, 1,3-diazidopropane burns and explodes later. The metal container is broken into two parts.

Table 6.3 The reaction of 1,3-diazidopropane and reductants

Experiment	Super pressure (MPa)							
	3 m				5 m			
	1	2	3	4	1	2	3	4
1,3-diazidopropane	0.265	0.277	0.278	0.293	0.093	0.098	0.088	0.101

Note There is black smoke in the aluminum shell of 1,3-diazidopropane

Table 6.4 Testing results of falling down from 50 m height

Experiment	1	2	3	4	5	6	7	8	9	10	Other phenomena
1,3-diazidopropane (20 %)	×	×	×	×	×	×	×	×	×	×	Temperature increased up 20 °C
1,3-diazidopropane (0)	×	×	×	×	×	×	×	×	×	×	Temperature increased up 20 °C

6.2.5.3 Preparation of 1,3-Diazidopropane [1, 3]

(1) Synthesis mechanism

There are a lot of preparation methods for aliphatic diazides. The most common and convenient method is the displacement reaction of dihalogenerated hydrocarbons and sodium azide. The reaction is displayer in below general expression.

$$X(CH_2)_nX + 2NaN_3 \rightarrow N_3(CH_2)_nN_3 + 2NaX \quad n = 2, 3, 4, 5, 6\ldots$$
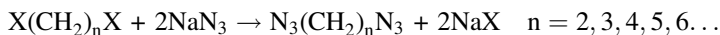
The alphatic dihalogenerated hydrocarbons of linear chains are primary halogenerated hydrocarbons. N_3^- is a kind of strong nucleophile. So, it is predictable that the above reaction has SN2 reaction mechanism.

(2) Preparation

Certain amount of sodium azide is dissolved in water, and then 95 % ethanol with bromoalkane is added. Later, the mixture is heated to 70–90 °C and reluxs until the colorless oily liquid is produced. After reaction, the product is washed using water, and extracted using diethyl ether. The extraction liquid is dried by $MgSO_4$. Diethyl ether is evaporated at normal pressure, and the colorless oily liquid product 1,3-diazidopropane is evaporated under reduced pressure and collected. The yield is 93.6 %. The processes of 1,3-diazidopropane preparations are in Fig. 6.1.

To study the relationship of 1,3-diazidopropane yield and reaction time, and temperature, experiments are designed in Tables. 6.5 and 6.6.

The analysis of 1,3-diazidopropane is in Table 6.7. Figures 6.2 and 6.3 shows the structures of 1,3-diazidopropane.

1,3-diazidopropane is a colorless and transparent liquid with molecular weight 126.12. Its density is 1.1042 g/cm^3. The boiling point is 150–151 °C at ambient pressure, and 50–60 °C under 6 mmHg pressure. Liquid water content is 12 ppm. 1,3-diazidopropane is not volatile at room temperature. After 12 h of moisture absorption, the weight increasing is −52.69 %. The saturated vapor pressures of 1,3-diazidopropane under different temperatures are in Table 6.8.

Thermal decomposition study of 1,3-diazidopropane (Fig. 6.4)

The peak temperature of 1,3-diazidopropane thermal decomposition temperature is at 179.32 °C.
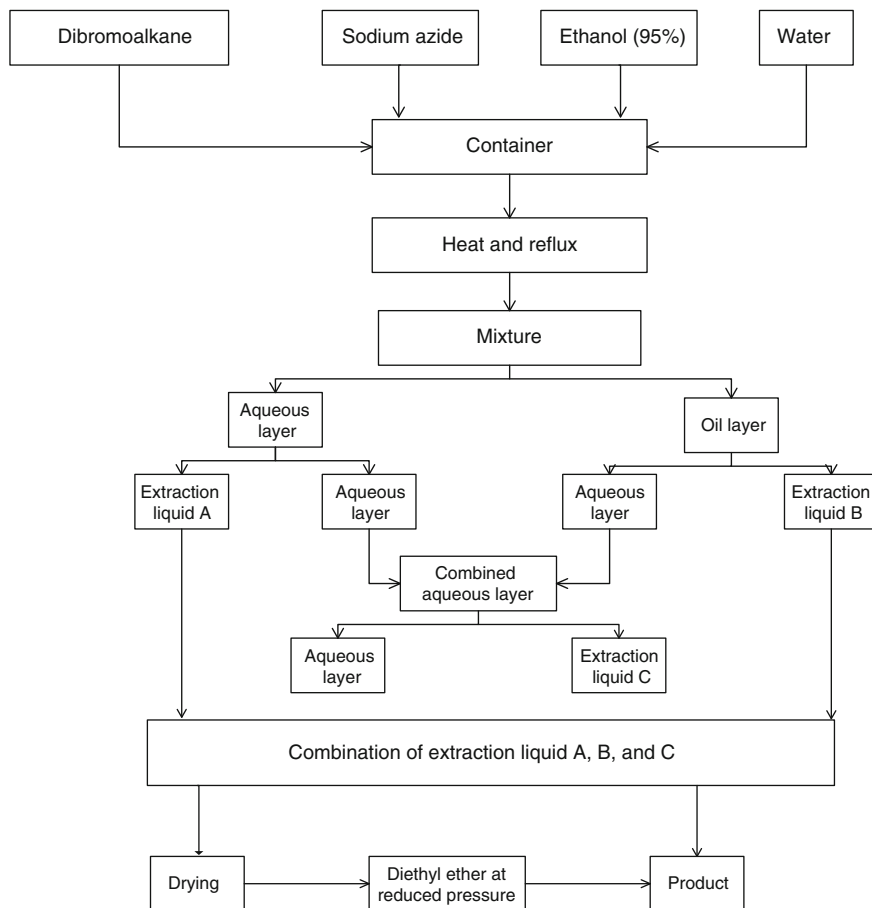
Fig. 6.1 synthesis and preparation processes of 1,3-diazidopropane

Table 6.5 Reaction time versus yield of 1,3-diazidopropane at 30 °C

Project	1	2	3	4	5	6	7	8	9	10
Temperature	30	30	30	30	30	30	30	30	30	30
Time (h)	5	10	15	20	25	30	40	50	60	100
Yield (%)	10	11.2	11.8	16	17.2	18.9	22	24	25	25.3

Table 6.6 Reaction temperature versus yield of 1,3-diazidopropane at 30 °C

Project	1	2	3	4	5	6	7	8	9	10
Time (h)	4	4	4	4	4	4	4	4	4	4
Temperature	40	45	50	55	60	65	70	75	80	85
Yield (%)	23.2	24.3	27.6	31.3	47.8	68.8	79.5	81.3	88.6	88.7

Table 6.7 The element analysis of 1,3-diazidopropane

	C	H	N
Theory	28.57	4.76	66.67
Experiment	28.68	4.73	66.33
	28.62	4.75	66.41
Error (%)	0.28	−0.42	−0.45

Fig. 6.2 IR spectra of 1,3-diazidopropane
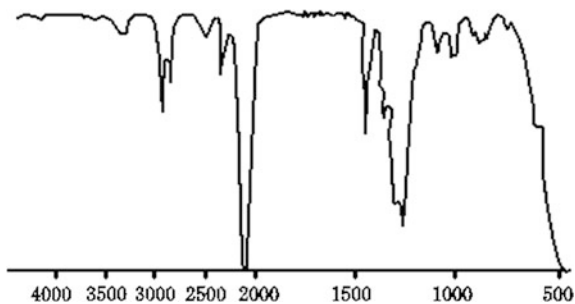
Fig. 6.3 1H-NMR spectra of 1,3-diazidopropane
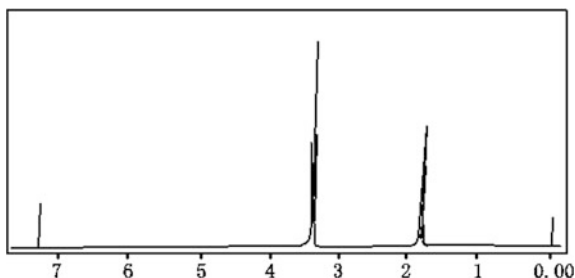
6.2.6 1,5-Diazido-3-Nitraza Pentane

The molecular formula: $C_4H_8N_8O_2$

The chemical structure:

$$N_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-CH_2-\overset{\displaystyle NO_2}{N}-CH_2-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-N_3$$
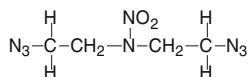
The molecular weight: 200.16

The oxygen balance: −79.93 % (calculated according to the production CO_2)

The nitrogen content: 55.89 %

The relative density: 1.33

Table 6.8 The saturation pressure of 1,3-diazidopropane at different temperature

T/(°C)	20.4	30	40	50.2	60	70	80	90.5
P (mmHg)	0.5	0.9	1.6	2.2	4.7	10.6	20.1	36.8

Fig. 6.4 DSC of 1,3-diazidopropane
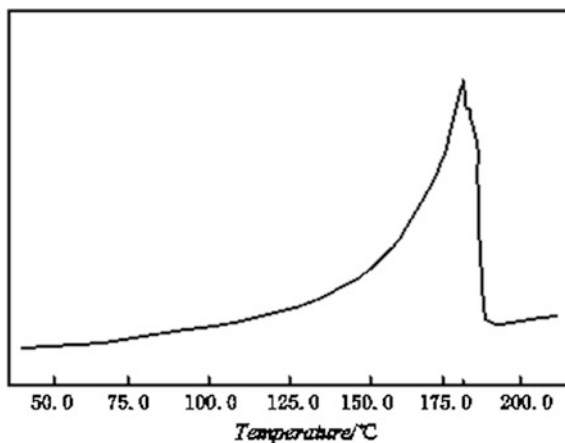
Chemical and physical properties: colorless liquid; dissolved in acetone, methanol, DMF, dimethylsulfide, ethyl acetate, benzene, and nitrocellulose; partially dissolved in ethanol, propanol, and iso-propanol

The standard heat of formation: (s) 539.74 kJ/mol, (s) 2696.54 J/g

The combustion heat: (s) −3265.29 kJ/mol, (s) −16313.42 J/g

The decomposition temperature: 246 °C (DSC)

The frozen point: −20 °C.

6.2.7 Triazidomethane

The molecular formula: CHN_9

The chemical structure:

$$N_3-\underset{\underset{N_3}{|}}{\overset{\overset{H}{|}}{C}}-N_3$$
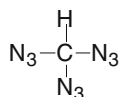
The molecular weight: 139.05

The nitrogen content: 90.64 %

6.2.8 3,3-Bis(Azidomethyl)Oxetane [3]

The chemical code: BAMO
   The molecular formula: $C_5H_8N_6O$
   The chemical structure:
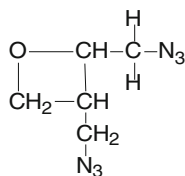
   The molecular weight: 168.2
   The oxygen balance: −123.66 % (calculated according to the production CO_2)
   The nitrogen content: 50 %
   The relative density: 1.34
   Chemical and physical properties: colorless liquid; melting point (−78.0 °C); boiling point (67 °C)
   The standard heat of formation: (l) 518.82 kJ/mol, (l) 3084.54 J/g
   Application: additives of propellants and gas generants

6.2.9 3-Azidomethyl-3-Methyloxetane [3]

The chemical code: AMMO
   The molecular formula: $C_5H_9N_3O$
   The chemical structure:
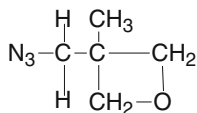
   The molecular weight: 127.07
   The oxygen balance: −170 % (calculated according to the production CO_2)
   The nitrogen content: 33 %
   The relative density: 1.30
   Chemical and physical properties: melting point (−50 °C); glass transition temperature (−45 °C)
   The standard heat of formation: (l) 11.60 kJ/mol, (l) 91.3 J/g

6.3 Azidoalcohol and Azidoesther

6.3.1 2-Azidoethanol

The molecular formula: $C_2H_5N_3O$
   The chemical structure:

$$\underset{\underset{H}{|}}{\overset{\overset{N_3}{|}}{H-C}}-CH_2OH$$
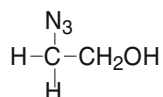
   The molecular weight: 87.08
   The oxygen balance: -101.06 % (calculated according to the production CO_2)
   The nitrogen content: 48 %
   The standard heat of formation: (l) 94.4 kJ/mol, (l) 1084.06 J/g

6.3.2 Glycerol Triazidoacetate

The chemical code: GTAA
   The molecular formula: $C_9H_{11}N_9O_6$
   The chemical structure:

   The molecular weight: 341.2
   The oxygen balance: -82.06 % (calculated according to the production CO_2)
   The nitrogen content: 37 %
   The standard heat of formation: (l) -139.75 kJ/mol, (l) -409.58 J/g
   The combustion heat: (l) -4985.65 kJ/mol, (l) -14612.1 J/g

6.3.3 Pentaerythritol Tetrakis

The chemical code: PETKAA
  The molecular formula: $C_{13}H_{16}N_{12}O_8$
  The chemical structure:
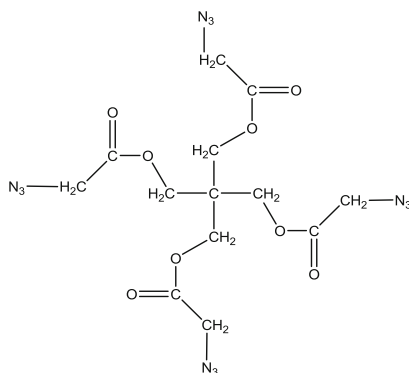
  The molecular weight: 468.35
  The oxygen balance: −88.82 % (calculated according to the production CO_2)
  The nitrogen content: 36 %
  Chemical and physical properties: relative density (1.39)
  The friction sensitivity: 360 N
  The impact sensitivity: 60 Nm

6.4 Azidonitrate Ester

Azidonitrate ester is a kind of liquid-rich nitrogen compounds, which have not only properties of nitrate ester, but also the energy of azides. They are regarded as high energy adhesion agents and plasticizers, optimized materials of future propellants and polymer-bonded explosives. They have wide application foreground.

6.4.1 Properties and Preparation of Pentaerylthritol Diazido Dinitrate

Diazidoneopentyl nitrate is pentaerylthritol diazido dinitrate. Its chemical code is PDADN.

6.4.1.1 Properties of Pentaerylthritol Diazido Dinitrate

The molecular formula: $C_5H_8N_8O_6$

The chemical structure:

$$CH_2ONO_2$$
$$N_3H_2C-\overset{|}{\underset{|}{C}}-CH_2N_3$$
$$CH_2ONO_2$$
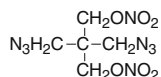
The molecular weight: 276.14

The oxygen balance: −46.35 % (calculated according to the production CO_2)

The nitrogen content: 40.57 %

Physical properties: wax-like white solid with low melting point; melting point (32–34 °C); density (1.507 g/cm³); dissolved in chloroform; not dissolved in water

The mechanical sensitivity: impact sensitivity (50 %) with falling height 15.4 m; friction sensitivity 4 % (25 kg, swing angle 66°)

The decomposition temperature: 179 °C (activation energy E = 123.33 kJ/mol, A = $10^{11.44}$)

The combustion heat: 14,259 J/g

The standard heat of formation: 825.42 kJ/mol

The flash point: 225 °C (5 s)

The frozen point: −20 °C.

The compatibility: good with NG, NC, polyether, and GAP

6.4.1.2 Preparation of Pentaerylthritol Diazido Dinitrate [3]

Since America first reported the synthetic method of PDADN [36] in 1987, the five-step processes have been used until now. These five steps include chlorination of pentaerythritol, cyclization, azido reaction, nitrolysis, and nitrification. The writer first brominated, then azidized, and finally nitrificated pentaerythritol. The three-step process to produce PDADA has fewer steps with high yield (up to 78.62 %). It is easier to be applied in industry.

The three-step process uses pentaerythritol as the original materials, bromination, azidization, and nitrification to produce PDADN. Its mechanism is below.

CH₂OH   CH₂OH   CH₂OH   CH₂ONO₂

HOH₂C–C–CH₂OH →(HBr) BrH₂C–C–CH₂Br →(NaN₃) N₃H₂C–C–CH₂N₃ →(HNO₃) N₃H₂C–C–CH₂N₃

CH₂OH   CH₂OH   CH₂OH   CH₂ONO₂

                                (PB)   (PA)   (PDADN)

CH₂OH   CH₂OH   CH₂OH   CH₂ONO₂

HOH₂C–C–CH₂OH →(HBr) BrH₂C–C–CH₂Br →(NaN₃) N₃H₂C–C–CH₂N₃ →(HNO₃) N₃H₂C–C–CH₂N₃

CH₂OH   CH₂OH   CH₂OH   CH₂ONO₂

                                (PB)   (PA)   (PDADN)
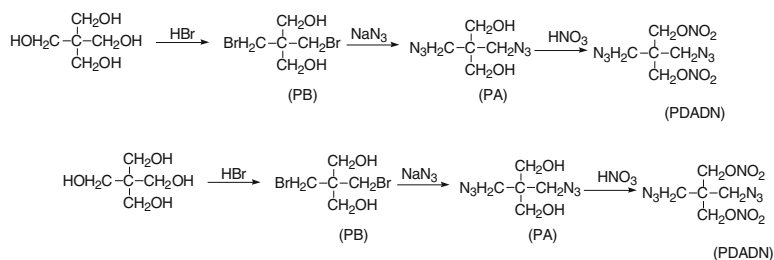
28 kg pentaerythritol, 100 kg 45 % HBr solution and 20 kg acetate acid are added into the reactor with mechanical stirring, thermometer and reflux condenser, heated to 115 °C, and reluxed for 6 h. After reaction, water and excess HBr are evaporated under reduced pressure. The mixture is cooled down to room temperature, neutralized by base, and treated by the solution of methylbenzene and water. 49 kg pentaerythritol dibromohydrin (PB) is obtained after filtration and drying with melting point 108–109 °C. The yield is 94.26 %.

131 kg PB, 72.5 kg NaN₃ and 175 DMF are added into a 250 L reactor, heated to 120 °C, and react 2–5 h. After reaction, DMF is evaporated under reduced pressure. 100 L dichloromethane is added. After filtration, the dichloromethane mother liquid with PA is collected for next reaction. The yield of this step is up to 97 %.

The dichloromethane with PA is added into the reactor with thermometer and mechanical stirring, and statistic HNO₃ is added drop by drop at 10–15 °C. After 10–15 min reaction, the mixture is poured into ice water, and organic layer is separated. The organic products are first washed two times by 100 L water, then one time by 50 L of 2 % NaHCO₃, finally DI water to be neutral. The dichloromethane with PDADN is dried using anhydrous MgSO₄. After solvent evaporation, 12.64 kg PDADN is obtained with yield 93.5 %. It has melting point of 39–41 °C and purity of 98.55 %.

There are some challenging technical problems in the synthesis and preparation, which are discussed below.

(1) PB separation in the synthesis processes

There are probably nonreactant pentaerythritol, bromopentaerythritol, tribromopentaerythritol, tetrabromopentaerythritol, etc. PB is not dissolved in water and methylbenezene; while pentaerythritol and bromopentaerythritol are dissolvable in water, and tribromopentaerythritol and tetrabromopentaerythritol are dissolved in toluene. PB is conveniently separated using the same volume of toluene and water mixture, and purified using recrystallization in hot water.

(2) The influence of nitrification coefficient for the yield of PDADN

Because nitrification coefficient influences the yield of nitrification reaction, the yield is studied under different nitrification coefficient and the same reaction temperature. The results are in Table 6.9.

The data in Table 6.9 indicates that the yield of PDADN increases following the increment of nitrification coefficient. When the nitrification coefficient is larger than

Table 6.9 The influence of reaction temperature for the yield of PDADN

Number	Nitrification coefficient	Reaction temperature/°C	Yield/%
1	2	15–20	50.45
2	4	15–20	70.35
3	6	15–20	80.36
4	8	15–20	82.10
5	10	15–20	82.10
6	12	15–20	82.09

8, the yield does not increase any more. So the best nitrification coefficient is 8, the mole ratio of HNO_3 to PA is 8:1.

(3) The influence of reaction temperature for the yield of PDADN

Nitrification reaction is heavily influenced by temperature. The nitrification yield is studied with fixed nitrification coefficient and under different temperatures. The results are in Table 6.10.

From Table 6.10, the yield of PDADN rises following the temperature increase. But after the temperature is higher than 20 °C, the yield does not increase any more. Study also found that when the temperature is higher than 25 °C, the yield decreases a little. According to the literature, when 1,3-diazido-2,2-propandiol is nitrificated under high temperature, the azido groups react to nitrate groups. −5 to 5 °C is the proper temperature range to obtain 1,3-diazido-2,2-diitrate propane. It is predicted that when temperature is higher than 25 °C, azido groups of PA probably change to nitrate groups. The best nitrification temperature of PA is 15–20 °C.

6.4.2 Properties and Preparation of 1,3-Diazido-2-Nitryloxypropane

The danger level of nitroglycerine is very high. NG is the only way, and there is no researcher to reform NG now [37], especially the further azidization.

Table 6.10 The influence of reaction temperature for the yield of PDADN

Number	Nitrification coefficient	Reaction temperature/°C	Yield/%
1	8	0–5	50.38
2	8	5–10	72.87
3	8	10–15	80.25
4	8	15–20	82.10
5	8	20–25	82.06
6	8	25–30	81.50
7	8	30–35	80.48

6.4.2.1 Properties of 1,3-Diazido-2-Nitryloxypropane

The molecular formula: $C_3H_5N_7O_3$
    The chemical structure:

$$N_3H_2C-\underset{\underset{ONO_2}{|}}{\overset{\overset{H}{|}}{C}}-CH_2N_3$$
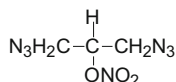
    The molecular weight: 187.09
    The oxygen balance: -47.04 % (calculated according to the production CO_2)
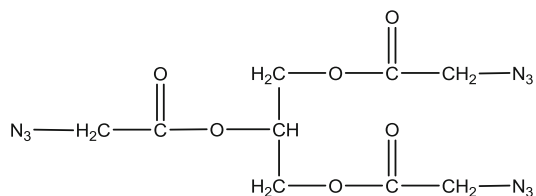   The nitrogen content: 52.34 %
    The freezing point: <-15 °C
    The melting point: 154 °C
    The relative density: 1.0059 (20/4)
    The color and appearance: light yellow oily liquid
    The refraction: 1.435820
    The solubility: soluble in water, alcohol, and ether
    The decomposition temperature: 188 °C (a second endothermic peak at 149.5 °C)
    The friction sensitivity: 90 %
    The impact sensitivity: 50 % with limit drop height 31.5 m (drop weight: 1.2 kg); while nitroglycerine is 100 % with 2 kg drop weight with 25 cm drop height; DANG reacts 12–13 h at 90 ± 3 °C; the intermediates (azido alcohols) does not decompose at 90 °C for 10 h.

6.4.2.2 Preparation of 1,3-Diazido-2-Nitryloxypropane

The theoretical analysis of 1,3-diazido-2-nitryloxypropane syntheses indicates that the azidization replacement reaction of nitroglycerine derives three new azido nitrates. This study voided the danger of NG raw materials, and designed other three routes to synthesize azido nitroglycerine.
    (1) 1,3-dichloropropanol as raw materials

(2) 2-chloro-1,3-propandiol as raw materials

$$\text{HOCH}_2\text{CH}-\text{CH}_2\text{OH} \xrightarrow{\text{NaN}_3} \text{HOCH}_2\text{CH}-\text{CH}_2\text{OH} \xrightarrow{\text{Nitrification}} \text{O}_2\text{NOCH}_2\text{CHCH}_2\text{ONO}_2$$

Cl → (under first) ; N$_3$ (under second) ; N$_3$ (II. MANG-1)

HAc ↓ ; Hysrolysis ↓

$$\text{OAc}-\text{CH}_2-\text{CH}-\text{CH}_2\text{OAc} \xrightarrow{\text{NaN}_3} \text{AcOH}_2\text{C}-\text{CHCH}_2\text{OAc}$$

Cl ; N$_3$
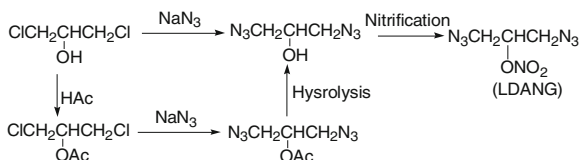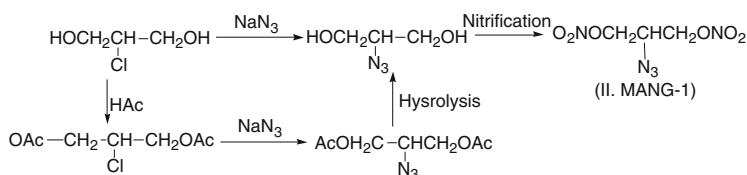
(3) epoxy chloropropane as raw materials

$$\text{H}_2\text{C}\overset{\text{O}}{-\!\!-}\text{CHCH}_2\text{Cl} \xrightarrow{\text{NaN}_3} \text{CH}_2\text{CH}-\text{CH}_2\text{N}_3 \xrightarrow{\text{Ring opening with diluted acid}} \text{HOH}_2\text{C}-\text{CH}-\text{CH}_2\text{N}_3$$

O ; ONO$_2$

$$\xrightarrow{\text{Nitrification}} \text{O}_2\text{NO}-\text{CH}_2\text{CH}-\text{CH}_2\text{N}_3 \quad \text{(III. MANG-2)}$$

ONO$_2$
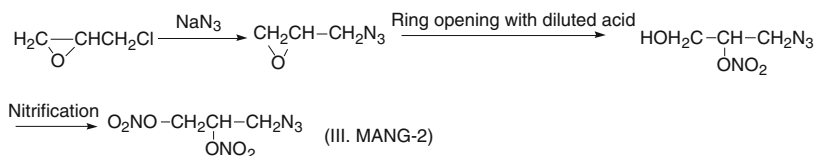
(1) Reaction mechanism of 1,3-diazido aminopropanol

$$\text{ClCH}_2\text{CHCH}_2\text{Cl} \xrightarrow[\text{DMF}]{\text{NaN}_3} \text{N}_3\text{CH}_2\text{CHCH}_2\text{N}_3$$

OH ; OH
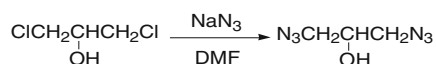
1,3-dichloropropan-2-ol (76 g, 0.6 mol) and 150 mL DMF are added into a 500-mL three-neck bottle with stirring and thermometer. NaN$_3$ (108 g, 1.66 mol) is added under stirring. The mixture is heated to 95 ± 2 °C and react for 90 min, then cooled down to room temperature. CH$_2$Cl$_2$ is used to extract for three times. The extraction liquids are combined and washed three times. The separated organic layer is dried using MgSO$_4$. After filtration, solvent CH$_2$Cl$_2$ is evaporated; finally 1,3-diazido propan-2-ol (66.06 g) is obtained. The yield is 82 % with purity 99.2 %.

(2) Preparation of 1,3-azido-2-nitripropane

CH$_2$Cl$_2$ (200 mL) and 1,3-dichloropropan-2-ol (46 g, 0.112 mol) are added into a 1,000 mL three-neck bottle, and cooled down to 0 °C. HNO$_3$ (38 mL) is added drop by drop in about 25 min. After 150 min reaction at 0–5 °C, H$_2$O is added and stirred 15 min to separate the organic layer, which is washed 4 times using water. After drying by MgSO$_4$ and filtration, CH$_2$Cl$_2$ is evaporated. The final product 1,3-azido-2-nitripropane (16.68 g, 0.087 mol) is obtained and the yield is 79.46 %.

Nitrification of 1,3-azido-2-nitripropane at 15–75 °C produces nitroglycerine, which is not the target product. Following the reaction temperature increase, the purity of NG rises.

Experiments (Table 6.11) indicate that if nitrification is conducted at high temperature, azido group (–N$_3$) turns to nitrate group (–ONO$_2$) gradually. The target product is produced only under proper temperature range (−5 to 5 °C). Experiments

Table 6.11 Relationship of reaction temperature and purity of NG

Number	Reaction temperature/°C	Reaction time/h	Purity of NG/% (HPLC)
1	15	–	8.25
2	30	1–3	27
3	40	–	50
4	50	–	61
5	55	–	69.4
6	65	1–3	87.3
7	70	–	90
8	75	–	93

under high temperature indicate that at 75 °C 93 % NG does not decompose within 1–3 h. It supplies a valuable reference data for the safe treatment of NG.

The above exploration and study indicated the product 1,3-azido-2-nitripropane (DANG) of azidization and nitrification of 1,3-dichloropropan-2-ol raw materials is the target. The melting point of DANG is obviously lower than that of NG, which means that the partial replacement of azido group to nitrate group can produce lower melting products than maternal nitrates. The sensitivity is equal or a little lower to that of NG. Azido nitroglycerine is not more dangerous than traditional nitroglycerine. New materials with better comprehensive properties from analog may be discovered after further exploring and study.

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Chapter 7
Liquid Explosive Mixtures

Liquid explosive mixtures are one of the most important liquid explosives developed thus far [1]. Currently, they are widely used in various areas including manufacturing, mining, agriculture, and military. The mixture of nitric acid and aromatic nitro compounds is the earliest liquid explosive mixture documented in the literature [2]. Later on, the Maide Ang technology explosives that utilized potassium chlorate as the oxidant were invented and extensively used in Germany, Poland, and Russia during the World War I. In addition, La Stead liquid explosives composed of nitrogen oxides and fuel oil were developed and broadly used in many kinds of bombs [3]. Liquid explosives play important roles in combat fields, for instance, French researcher invented the Miro dynamite for bombs, which is a liquid explosive composed of methyl nitrate and methanol [4]. In addition, liquid explosives containing nitromethane and ammonium nitrate as well as the mixture of oxidizers and fuels have been extensively used as warhead ammunitions [5]. Since late 1980s, research on liquid explosives began to thrive all over the world [6]. Thickened nitrate liquid explosives and their application technologies were successfully developed, and they have been effectively employed in the field of overload blasting in mine [7]. However, it is comparatively difficult for mining industry to use nitric acid-type explosives, because they are generally corrosive and have strong odors. With further research on nitric acid-type explosives, especially in the past decade, significant progress has been made to improve the corrosivity, development of thickeners and adhesives, as well as compatibility. Therefore, this type of explosives are being used as versatile temporary charge in combat fields [8–11]. Imperial Chemical Industries Co., Ltd. successfully developed blasting agents containing nitric acid, and the free acid incorporated in the thickened liquid explosives can be well controlled, which allows them to be employed as propellants, detergents, etchants, oil well treatment agents, and so forth [12, 13]. In addition, emulsion-type nitrate-based liquid explosives were also reported [14, 15]. Japan, the Czech Republic and other countries had invented and manufactured insensitive nitrate liquid explosives in succession [16]. Specifically, Japanese researchers developed a liquid explosive composed of nitroglycerin and ethylene glycol dinitrate that are very insensitive to transportation, storage, usage and disposal; scientists in the Czech Republic found that adding polymers to nitroglycerine can produce insensitive colloidal liquid

explosives. Adding ammonium nitrate sensitizer into nitroalkanes can generate high-power liquid explosives [17]. Specifically, the gelatinous nitroalkane explosives containing ammonium nitrate or other sensitizers have developed [18–20], and they can be employed as loose powder, or for the construction of individual bunkers, trenches, fortifications, and firing shields [21]. Hydrazine-based liquid explosives are widely used in both military and civilian projects [22]. Particularly, the hydrazine nitrate-hydrazine system is called "Astralite," which frequently leads to engine explosion when it was used as the liquid propellant for rockets. Encouraged by the fact that these explosions are extremely violent, researchers have gradually developed "Astralite" system into liquid high explosives [23, 24]. Generally, such explosives tend to possess advantages such as high energy, excellent detonation properties, ease to process, and fine adaptability. The key to prepare liquid explosives featuring excellent detonation properties and high energy is the development of oxidants. Prior to this, the most frequently used oxidants in liquid explosives are concentrated nitric acid, hydrogen peroxide, liquid nitrogen oxide, multi-nitromethane, et al., which often have poor stability and are difficult to use, mostly due to a number of practical problems such as corrosivity and odor. Consequently, the design and synthesis of novel high-energy oxidants have become one of the most important tasks in the research of liquid explosives.

Fujiwara et al. [25, 26] found that some polar organic compounds and nitro compounds can dissolve in saturated aqueous solution of perchloric acid urea at room temperature to afford homogeneous perchloric acid urea liquid explosives, which can stably transmit detonation waves and are suitable for underwater blasting operations. Japanese industrial company also developed a liquid explosive containing barium perchlorate with a detonation velocity up to 6,230 m/s [27]. South Africa Dow Chemical Company invented a liquid explosive composed of calcium nitrate and water-soluble organic fuels, which can remain as liquid even at −12 °C and produce brisance similar to TNT [28]. Japan patented the usage of perchlorate-aqueous hydrogen peroxide solution as the oxidant for liquid explosives [29]. Yokokawa [30] reported that liquid explosives can be prepared by using aromatic sulfonic acids or organic plasticizers as primary fuels and high concentration of hydrogen peroxide as oxidizing agent.

In summary, liquid explosive mixtures include the aliphatic nitro compounds, nitric acid and nitrate series, the perchloric acid hydrazine series, the hydrogen peroxide series and the N_2O_4 series. Besides, two-component liquid explosives and emulsion liquid explosives were also reported. Consequently, the rapid development on liquid explosive mixtures has led to many different explosive types that found broad applications in various areas. For instance, liquid explosives can be used as ordinary chemical raw materials, employed in mining and underwater blasting operations, or serve as temporary fillings for firearms. Naturally, they are deemed as emergency explosives suitable for both civilian and military applications. In this chapter, we will thoroughly discuss the properties and preparative methods of liquid explosive mixtures.

7.1 Nitro Liquid Explosive Mixtures

7.1.1 Nitromethane-Based Liquid Explosives

Nitromethane was only recognized as an explosive featuring typical explosion characteristics in the past 30–40 years. Particularly, in 1958, two explosion incidents took place in the railroad tank cars that were transporting nitromethane in the US, proving that nitromethane could be a liquid explosive with strong power.

Nitromethane is a colorless transparent liquid with a boiling point of 101.2 °C and freezing point of −28.55 °C. Its density is 1.138 and 1.124 g/cm^3 at 20 and 30 °C, respectively. The temperature coefficient of the density of nitromethane (dρ/dt) is −0.001377 g/cm^3 °C^{-1}.

The heat of combustion for nitromethane is 708.1 kJ mol^{-1} under standard conditions, and the enthalpy of formation for liquid nitromethane at 25 °C is −112.99 ± 0.63 kJ mol^{-1}, whereas the one for gaseous nitromethane is only −74.65 kJ/mol^{-1} at the same temperature.

Nitromethane can form azeotrope with many organic solvents. Additionally, it can dissolve certain polymers, nitro compounds, and nitrate compounds. Nitromethane is partially miscible with water; at 20 °C, the solubility of nitromethane in water is 9.5 % (by volume) or 10.5 % (by mass), meanwhile, the solubility of water in nitromethane is 1.75 % (by mass). Generally, the miscibility of nitromethane increases with the rise of temperature. Dry nitromethane is a neutral substance, thus it possesses excellent storage stability. After being stored for certain period of time, wet nitromethane will become acidic, which making it capable of corroding metals, however, adding a small amount of phosphoric acid or phosphate can effectively inhibit corrosion.

Low-carbon nitroalkanes have similar physical properties as nitromethane, but they are comparatively more difficult to detonate, exhibiting inferior detonation properties, therefore, they are mainly used in liquid explosive mixtures to lower the freezing point of nitromethane. Table 7.1 listed the physical properties of four low-carbon nitroalkanes including nitromethane (NM), nitroethane (NE), *iso*-nitropropane, and nitropropane.

As shown in Table 7.1, increasing the number of carbon atoms in nitroalkanes can lead to the rise of density, which in turn would increase the difficulty of detonation, ultimately dampening detonation properties.

Nitromethane is an extremely insensitive explosive. Heating or burning nitromethane in thin-walled containers would not lead to detonation. Explosion would only take place when nitromethane is heated to 300 °C or above in a sealed thick-walled container. The sensitivity of nitromethane to mechanical shock is closely related to whether it contains bubbles. Using no.8 detonator alone cannot detonate nitromethane at ambient temperature, and booster pellets must be employed. The detonation sensitivity of nitromethane increases with the rise of temperature, while its critical diameter is reduced. Figure 7.1 showed the effects of temperature on critical diameter and detonation velocity of nitromethane sealed in tubes [31].

Table 7.1 Physical properties of four nitroalkanes [1]

Properties	CH_3NO_2	$C_2H_5NO_2$	$CH_3CH_2CHNO_2$	$(CH_3)_2CHNO_2$
Mt	61.04	75.07	89.09	89.09
θ_b/°C	101.2	114.0	131.6	120.3
θ_a/°C	−28.55	−90	−108.0	−93.0
ρ/g cm^{-3}	1.139	1.052	1.033	0.992
$\sigma(20°C)$/N.m^{-1}	3.78	3.19	3.06	3.06
θ_f/°C	44.4	41.1	48.9	39.5
θ_D/°C	420.0	414.4	420.6	427.8
Low explosive limit of mixture in air × 100	7.3	4.0	2.6	2.6

Apparently, it appears that the detonation velocity decreases with the increase of temperature, which mainly should be due to the reduced density.

Because the detonation velocity of nitromethane is highly dependent on temperature, experimental conditions (tube constraining strength, detonation capability, etc.), experimental errors and others, results reported in the literature appeared to be substantially different. Table 7.2 showed the detonation velocity of nitromethane reported by Urbanski et al. [32]. In addition, it was found that the detonation pressure of nitromethane is 13 GPa, detonation reaction time is $(22 \pm 3) \times 10^{-9}$ s, explosion heat is 5141.4 kJ kg^{-1}, and explosion product volume is 936 L kg^{-1}. As nitromethane is not easy to detonate, strong boosters were often used under dramatically different experimental conditions, therefore, its power data documented in the literature are largely discrepant. At this stage, the lead block expansion value of nitromethane has been determined to be about 400 mL. Based on these results, one can conclude that nitromethane is a high explosive with strong power, and its detonation velocity is approximately equal to the one of RDX with the same density.
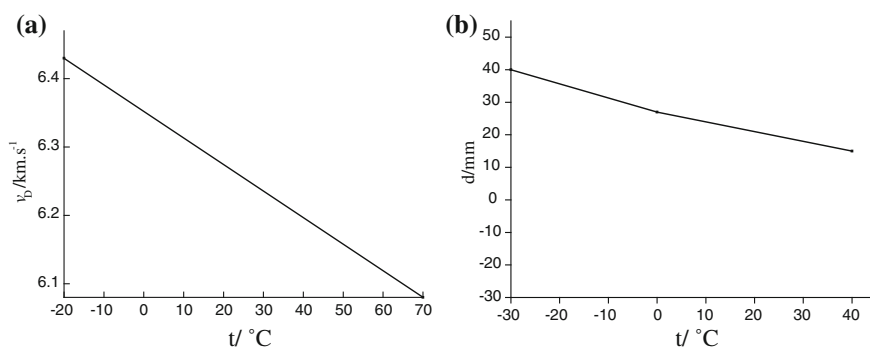
Fig. 7.1 Effect of temperature on critical diameter and detonation velocity of nitromethane [1], **a** detonation velocity (brass tube φ50.9 × 3.2 mm),**b** critical diameter (glass tube)

Table 7.2 Detonation velocity of nitromethane [1, 32]

Tube parameter			Booster	v_D/ms^{-1}	Measurement method
Material	External diameter/mm	Internal diameter/mm			
Copper	20	18	No. 8 detonator and (1–5) g CE	6,190	Blasting fuse
Copper	25	23	Same as above	6,270	Same as above
Steel	27	22	Same as above	6,360	Same as above
Copper	20	18	No. 8 detonator and 6.2 g CE	6,405	Electronic timer

Nitromethane is usually not sensitive to heat or mechanical impact, exhibiting stability to some extent. The starting materials for the production of nitromethane are adequately abundant and inexpensive, and nitromethane itself is a noncorrosive chemical that can be safely transported or handled, thus, it is an important component for the preparation of liquid explosives.

The major hurdle to directly use pure nitromethane as liquid explosives is that its detonating sensitivity is too low. Consequently, a large number of researchers have devoted enormous efforts to the integrated and comprehensive studies aiming to solve this problem. As a result, it was found that adding other liquids into nitromethane can produce a wide variety of liquid explosive mixtures.

7.1.1.1 Explosion Characteristics for the Mixture of Nitromethane and Aromatics, Alcohols and Esters

To decrease the detonation sensitivity of nitromethane, higher nitroalkanes, benzene, xylene, *n*-butanol, methanol, *n*-butyl acetate, amyl acetate, di-butyl phthalate, di-butyl sebacate, and other substances can be added. However, when the amount of additives reaches certain degree, detonation waves cannot be transmitted steadily.

7.1.1.2 Explosion Properties of Nitromethane with Basic Additives

Adding aniline, ethylenediamine, morpholine, methylamine, NH_4OH, KOH, Na_2CO_3, formic acid, nitric acid, sulfuric acid, phosphoric acid, and other substances into nitromethane can increase its detonation sensitivity [33]. Specifically, acids can act as weak sensitizer whereas basic substances are strong sensitizer. As a matter of fact, adding a suitable base into nitromethane can enable its detonation with no. 8 detonator, especially after ethylenediamine has been added. Table 7.3 showed the effect of ethylenediamine content on the detonation sensitivity of nitromethane.

Table 7.3 The effect of ethylenediamine content on the detonation sensitivity of nitromethane [1]

Ethylenediamine content × 100	Diameter of plastic tube/mm		Detonation experiment (pressure needed for 50 % explosion)/GPa	V_L/ml
	Explosion	No explosion		
0	24	21	3.4	400
1	4	2.5	2.6	350
5	2.5 (1.2)	–	1.9	305
10	–	–	1.6	275
20	–	–	1.3	235

As illustrated in Table 7.3, adding 1 % of ethylenediamine into nitromethane can significantly increase its detonation sensitivity. When the content of ethylenediamine reaches 5 %, however, even a thin layer liquid with a thickness of 1.2 mm (data shown in parentheses) can be detonated to afford stable explosion. In the presence of basic or acidic substances, nitromethane can partially convert to its acid form that is supposedly more sensitive than regular nitroalkanes, which certainly would improve its sensitivity of detonation [34, 35]. However, one must note that adding ethylenediamine can substantially reduce the explosive power of nitromethane.

7.1.1.3 Detonation Properties of the Mixture of Nitromethane and Dichloromethane

Adding dichloromethane to nitromethane can reduce its freezing point. Particularly, adding 2–12 % of diethylenetriamine ($NH_2C_2H_4NHC_2H_4NH_2$) as a sensitizer can produce liquid explosive mixture suitable to low temperature usage [35]. For example, when 2–12 % diethylenetriamine was added into the mixture of nitromethane and dichloromethane (70/30), the explosive mixture does not freeze at −40 °C and still can transmit detonation in a stable manner. When 10–12 % of diethylenetriamine was employed, the explosive mixture can detonate even at −51.1 °C. Table 7.4 showed the detonation properties of the mixture of nitromethane and dichloromethane (70/30) with 2 % sensitizer.

Table 7.4 Detonation properties of the mixture of nitromethane and dichloromethane (70/30) with 2 % diethylenetriamine

Experiments	Results
Detonation velocity at −40 °C (φ32 mm)	5,312 m/s
Friction and impact sensitivity at −40 °C	Negative (no explosion)
Friction and impact sensitivity at ambient temperature	Negative (no explosion)
Limiting diameter at −40 °C	32 mm

Table 7.5 Detonation properties of the mixture illustrated in Table 7.4 but containing 12 % diethylenetriamine

Experiments	Results
Detonation velocity at −40 °C (φ228.6 mm)	6,044 m/s
Detonation velocity at ambient temperature (φ228.6 mm)	6,950 m/s
Friction and impact sensitivity at ambient temperature	Negative (no explosion)
Limiting diameter at ambient temperature	12.7 mm
Over-blasting effect at −50 °C	Normal detonation
Over-blasting effect at −60 °C	Normal detonation

Notably, it appears that the properties of explosive changed significantly after the content of diethylenetriamine was increased to 12 %. Specifically, it was found that this explosives is able to detonate under low temperature conditions, and its properties were shown in Table 7.5.

7.1.1.4 Explosion Characteristics of Nitromethane Sensitized by Amines

(A) Explosion properties of nitromethane sensitized by ammonium salts

Runge et al. [36] proposed to use ammonium salts that possess the following molecular structure to sensitize nitromethane explosives

$$RCOOH \cdot \underset{\underset{R^3}{|}}{\overset{\overset{R^1}{|}}{N}} - R^2$$
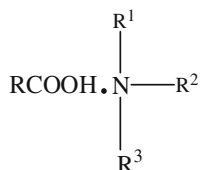
Here R is hydrogen or alkyl group with 1–4 carbon atoms; R1 and R2 are hydrogen or alky groups with 1–5 carbon atoms, which may be the same or different; R3 is alkyl or aryl groups with 1–5 carbon atoms.

Using ammonium salts as the sensitizer for nitromethane-based explosives appears to be an advantageous approach. First of all, ammonium salts usually are not very toxic, thus they would not impose toxicity-related health risks on operation staffs. Second, unlike amine sensitizers that often lead to damaged explosive properties, the explosion properties of nitromethane with ammonium salt sensitizers are almost the same as plain nitromethane. Detonation distance of nitromethane with different sensitizers was shown in Table 7.6.

Table 7.7 showed the mass fraction of liquid explosives composed of nitromethane and other substances. Notably, the critical diameter of such mixed

Table 7.6 Effects of organic acids and ammonium salts on detonation distance of nitromethane [1]

| No. | Content of nitromethane × 100 | Content of methanol × 100 | Content of sensitizer × 100 | | | | | | Ratio of sensitizer to nitromethane × 100 | Diaphragm detonation transmission distance /mm | Increase of detonation transmission distance /mm |
			Methyl ammonium acetate	Butylammonium acetate	Piperidine acetate	Butyl ammonium formate	Dimethyl ammonium acetate	Trimethyl ammonium acetate			
0	100								0	30	–
1–1	90	5	5						5.5	43	13
1–2	77.5	7.5	15						19.4	43	13
1–3	70	10	20						286	39	9
2–1	92.5	2.5		5					5.4	44	14
2–2	88.75	3.75		7.5					8.4	45	15
2–3	85	5		10					11.8	47	17
2–4	85[a]	6		7.5					8.8	45	15
2–5	85	7.5		7.5					8.8	42	12
2–6	81.25	6.25		12.5					15.4	46	16
3	85	5			10				11.8	43	13
4	85	5				10			11.8	43	13
5	90	5					5		5.6	51	21
6	90	5						5	5.6	47	17

[a] Contains 1.5 % water

Table 7.7 Typical formulation of liquid explosives containing nitromethane and metal powder

Raw material	Formulation				
	1	2	3	4	5
Nitromethane	66	69	68	61	60
Nitroglycerine	10				
RDX	9	7			
HMX			7	Potassium nitrate 20	Sodium nitrate 22
Aluminum powder	12		11	12	
PETN		10			
Magnesium powder		11			1.2
Cellulose acetate		1			
Diethylene glycol dinitrate			9.5	2	4
Nitrocellulose	1		1	2	
Resorcinol		1	1.5		
White yin	1				
Cav-o-sil	1	1	2	3	2

Table 7.8 Properties of liquid explosives described in Table 7.7

Properties	1	2	3	4	5
Charge density (g/cm^3)	1.416	1.363	1.379	1.472	1.521
Minimum critical detonating diameter (inch)	1/64	1/32	1/32	1/2	1/2
Detonation velocity (m/s)	6,230	7,140	6,190	5,120	5,200
Explosion rate initiated by 5,000 g hammer (%)	0–8	8–12	0–8	0–8	0–8
Charge mode and detonation mode	Filling, directly initiated by no. 8 detonator	Filling, directly initiated by no. 8 detonator	Filling, directly initiated by no. 8 detonator	Filling, with booster pellet	Filling, with booster pellet
Storage time (year)	10	8	5	3	3

explosives is only 0.4 mm or so, thus they are not only useful for military purposes but also can be employed as explosives for oil wells (Table 7.8).

(2) Adding sensitizers to nitromethane to prepare thermobaric explosives

Adding certain amounts of fuels such as RDX and aluminum flakes into nitromethane can significantly improve the detonation outcome. Chunhua Bai in Beijing Institute of Technology [37] developed a liquid-solid type slurry explosive by mixing nitromethane with metal powder, which was found to possess excellent detonation properties. The formulation of this explosive was shown in Table 7.9.

Table 7.9 Thermobaric explosive composed of nitromethane and aluminum flakes

Formulation composition and content (%)				Properties				
Nitromethane	RDX	Aluminum flakes	Ethyl ether	Viscosity	Density	Detonation velocity	Detonation temperature	Detonation pressure
40	30	20	10	160–200 (paint viscosity flow cup-4)	1.61–1.65	5,800–6,200 m/s		

The detonation experiments of nitromethane/aluminum explosive were conducted under equivalent concentration ratio conditions with an ignition delay of 380 m/s. Total 15 explosion pressure sensors were placed at different points of the leveled combustion area, and their distance from the explosion end is 2.45, 3.85, 5.25, 6.65, 8.05, 9.45, 10.85, 12.25, 13.65, 17.15, 19.25, 21.35, 23.45, 25.55, and 27.65 m, respectively. The transient pressure during the detonation transition process has been determined, and the results were summarized in Table 7.10.

Table 7.10 revealed the pressure and explosion characteristics produced in the transition process from combustion to detonation of the three-phase suspension clouds of nitromethane/aluminum/air. Based on these results, he went ahead to study general rules involved in the explosion of the mixture of nitromethane and ethylene oxide [38, 39].

When propylene oxide clouds are ignited by spark, the cloud particles surrounding the spark are in their high temperature states, thus the surface of particles might peel, crush, and atomize, followed by evaporation and diffusion. This type of explosive seems to combust in the form of gas-phase reaction, thus the ignition process is transmitted automatically. At the beginning, combustion proceeds in a

Table 7.10 Detonation combustion results collected from the mixture of nitromethane and aluminum powder

No.	x/m	p/MPa	t/ms	D_v/(km/s)
1	2.45	0.09	74.11	0.14
2	3.85	0.17	84.32	0.46
3	5.25	0.35	87.36	0.99
4	6.65	0.85	88.77	1.08
5	8.05	1.32	90.07	1.35
6	9.45	1.65	91.10	2.13
7	10.85	1.12	91.76	1.77
8	12.25	1.76	92.55	1.62
9	13.65	2.93	93.42	1.67
10	17.15	3.02	95.51	1.34
11	19.25	3.43	97.08	1.94
12	21.35	3.85	98.16	1.59
13	23.45	3.14	99.48	1.65
14	25.55	2.98	100.75	1.80
15	27.65	2.83	101.92	

very low speed. Subsequently, compression waves are generated in front of the combustion array due to the expansion of combustion products, affording a two wave, three-zone structure composed of precursor compression wave front and flame array front. Since this is a spark ignition, flame and precursor compression wave both transmit outward spherically. When they finally reach the wall, the motion of precursor compression wave is blocked, thus the turbulence intensity of flow field near the wall will increase suddenly to generate a recirculation zone, which can dramatically deform the flame surface. In the form of reflection wave, the flame surface can quickly pass through the unburned area below the ignition head, and then flow toward the three-phase suspension clouds of nitromethane/aluminum/air as planar wave.

It was found that an attenuated transmission wave can be formed when the combustion compression plane wave generated by propylene oxide precursor enters the area of three-phase suspension mixture of nitromethane/aluminum/air. After the departure of transmission wave, the droplets and nitromethane aluminum flake particles are effectively compressed, which would further atomize nitromethane droplets until evaporation. At this stage, aluminum flakes will undergo melting and vaporization on the surface, resulting in the combustion of mixture in the form of gas phase reaction. Subsequently, combustion products can either expand or compress surrounding media to produce compression waves, which can be strengthened via integrating with chemical reactions.

Therefore, the pressure in the area distant from the ignition end 2.45–6.65 m should increase due to the formation of compression wave; however, it should do so slowly. At 6.65 m, the pressure is only 0.85 Mpa; when the compression wave approaches 8.05 m, the pressure jumps to 1.32 MPa, at which the compressive wave has been adequately enhanced. When the wave reaches 9.45 m area, the pressure is 1.65 Mpa with a speed of 1.35 km/s. At this moment, the reaction compression process is complete and the transition process starts. Afterward, the combustion process gradually moves from the slow reaction compression stage into the transition process, and the combustion speed is suddenly increased from 1.35 to 2.13 km/s. The rapid expansion of combustion products results in the reduction of reaction zone pressure from 1.65 to 1.12 MPa, marking the end of transition process. Subsequently, the combustion process enters the rapid reaction shock stage. Due to enhanced integration between chemical reactions and shock waves, the reaction has been substantially accelerated, while the pressure in the combustion tube will be gradually increased. At the measuring point of 21.35 m, the peak overpressure reaches its maximum of 3.85 MPa, and the detonation wave velocity is 1.94 km/s, suggesting the occurrence of detonation overvoltage status. Subsequently, the detonation wave velocity seems to be gradually stabilized, so that flame front can catch up on the detonation wave front, affording a stable detonation process.

As shown in Table 7.10, the peak explosion overpressure reaches its maximum of 3.85 MPa at 21.35 m (aspect ratio L/D = 107), exhibiting typical detonation characteristics. Meanwhile, under the same experimental conditions, the blasting experiments of the three-phase mixtures of isopropyl nitrate/aluminum/air and ether/aluminum/air were carried out with equivalent ratio. The results obtained

clearly indicated that the transition process from combustion to detonation for the gas/solid/liquid three-phase mixture mainly involves reaction compression process, transition process, reaction shock process, and detonation process.

7.1.1.5 Explosion Characteristic of the Mixture of Nitromethane and Other Explosives

Aside from the sensitizers described above, nitrate and ammonium nitrate can also be employed as explosive sensitizer for nitromethane. In addition, adding metal powder (e.g., Al powder) into nitromethane can increase the corresponding explosion energy and detonation sensitivity. To prevent potential separation of solid components, nitrocellulose or cellulose acetate may be used as thickener [40, 41].

Nitromethane itself is a liquid explosive, and the mixture of nitromethane with nitroglycerin, ethylene glycol dinitrate, as well as other nitrate esters are also novel liquid explosives. In addition, nitromethane can dissolve nitrate salts such as sodium nitrate and potassium nitrate, aromatic nitro compounds such as TNT and nitro naphthalene, and the liquid explosive mixture of RDX and HMX, which can effectively decrease the critical diameter until it is extremely small. Generally, small critical diameter is beneficial for well sinking process because the explosion properties are not confined by any factor under these circumstances. When nitromethane is used as the liquid wax component for nitro explosives, the critical diameter of explosive liquid can be decreased to 1/64. Therefore, carefully selecting a liquid explosive composition can minimize the production and perseverance of nitrogen dioxide at high temperature. When it is in use, one can properly adjust the pump speed to make sure that explosives are poured into the borehole to obtain a continuous flow while preventing the occurrence of autogenous ignition due to friction [42].

The large-caliber weapon system Laboratory of US Army Ordnance Research and development board [1] evaluated five kinds of explosives for the purpose of mining single bunker, and they recommended three nitromethane-containing liquid explosive mixtures. The compositions were shown in Table 7.11.

Depending on technical requirements, explosives that can be used for individual bunkers must meet two important criteria: (I) at −40 °C, the explosive should still have excellent charge properties with decent mobility, plus, it should be easy to handle; (II) the explosive should be able to work well, easy to detonate and transmit

Table 7.11 Composition of nitroalkane explosive mixtures [1]

Consistency	75 nitromethane/25 nitroethane	RDX		Aluminum (type 3 or 7)	Nitrocellulose (N 12.5 %)	Cab-O-Sil (M5)
		Level E	Level A			
Liquid	59.5	30	–	10	–	0.5
Slurry	48	30	–	20	2	–
Creamy	24	15	60	–	1	–

detonation, exhibiting desired explosion properties. Nitromethane has ideal explosion properties and it can serve as a RDX carrier, however, the freezing point of nitromethane is higher than −30 °C. When 25 % of nitroethane is added to nitromethane, the freezing point of resulting mixture is reduced to −68.3 °C, perfectly meeting the requirement of lower than −40 °C. The first liquid explosive that meets the technical specifications of temperature range was listed in Table 7.11. This explosive can be detonated directly by a detonator. When charged in small diameters, this liquid explosive still displayed excellent initiation and detonation properties, thus it should work effectively on wet ground and other abnormal conditions. Because this explosive is easy to charge and meets most safety requirements, it has become a preferred explosive [42, 43].

7.1.1.6 Explosion Characteristics of the Liquid Explosive Composed of Nitroalkanes and Nitrate

It was found that adding trinitroethanol orthocarbonate into nitroalkane can produce a liquid explosive with high detonation velocity, excellent detonation properties and remarkable ability to transmit detonation [44, 45]. Table 7.12 showed the composition of liquid explosive mixture of nitroalkanes with TNEOC and TNEOF.

Because there are multiple nitro groups in the molecular structure of TNEOF and TNEOC, they are highly explosive organic oxidants and extremely sensitive to mechanical shock, essentially similar to PETN. TNEOF and TNEOC both have great solubility in nitroalkanes, in which their impact sensitivity can be significantly reduced. Therefore, it appears that combining these two oxidants with nitro compounds to produce liquid explosives is a clever approach.

The liquid explosives mixture of trinitroethanol orthocarbonate and nitroalkanes have decent chemical stability, which allows them to be stored in glassware for 6 month at room temperature, or for 5 days at 60 °C. In these cases, neither decomposition nor change of explosive properties was observed. The density and detonation velocity of such explosives are close to nitroglycerine, and they can be detonated by No.6 detonators to afford stable detonation transmission with critical diameter less than 4 mm. In addition, their impact sensitivity is also very low, and

Table 7.12 Liquid explosive mixture of nitroalkanes with TNEOC and TNEOF [1]

No	$\omega_i \times 100$				$\rho/\text{g cm}^{-3}$	v_D/ms^{-1}
	TNEOF	TNEOC	NM	NE		
1	50	–	50	–	1.356	7,075
2	66.7	–	33.3	–	1.416	7,357
3	77.1	–	22.9	–	1.533	7,575
4	66.7	–	–	33.3	1.406	7,067
5	77.0	–	–	23.0	1.496	7,440
6	–	69.7	30.3	–	1.480	7,350
7	–	66.1	33.9	–	1.433	7,098

no explosion has been observed in the impact experiment of 5 kg hammer with 50 cm height. These liquid explosives are not corrosive, not very volatile, and produce less-toxic gases upon explosion. Therefore, this class of explosives is convenient and safe in terms of handling and utilizing; however, they can only be used on special occasions due to the high price.

7.1.2 Tetranitromethane-Based Liquid Explosives

Tetranitromethane appears as a type of heavy oil liquid with freezing point of 13.0 °C and boiling point of 126 °C. It is highly volatile but not decomposed during the boiling, and is insoluble in water but soluble in organic solvents, e.g., alcohol, benzene, and kerosene as well as nitro compounds. In addition, it can form the eutectic mixture with specific nitro compounds (see Table 7.13). Tetranitromethane has pungent order as the nitrogen dioxide with density of 1.65 g/cm^3 at 20 °C.

Tetranitromethane is of explosion whose oxygen balance is 49 % with explosion heat of 1,892 J/g. The pure tetranitromethane is of poor sensitivity that cannot be detonated by even 10 g special as booster. However, it is violently explosive when it is mixed with combustible material at almost zero oxygen balance, and it has a small critical diameter (thickness) and significant detonation and shock sensitivity. Such explosives are generally prepared when they are needed and the quantity addresses the requirement exactly regarding the safety considerations. Table 7.14 lists the detonation properties of tetranitromethane and certain combustible compounds at zero oxygen balance.

The liquid explosive consisting of 86.5 tetranitromethane to 13.5 toluene has a density of 1.45 g/cm^3, explosion heat of 7,114 J/g, explosion temperature of 6,673 K, and explosion velocity of 9,000 m/s which is one of fast explosion velocity explosive so far [40].

The mixture of Tetranitromethane and poly butyl methacrylate can be used as a viscous liquid explosive. The poly butyl methacrylate can reduce the volatility of

Table 7.13 General eutectic mixture formed by tetranitromethane

Nitro compounds	C(NO$_2$)$_4$ content (%)	θs/°C	Nitro compounds	C(NO$_2$)$_4$ content (%)	θs/°C
Benzene	70.0	−16.1	Dinitrobenzene	97.0	11.3
Nitrobenzene	57.0	−19.1	2,4,6-trinitrotoluene	97.0	12.3
O-nitrotoluene	41.5	−28.5	α-nitrobenzene	90.0	9.3
Internitrotoluene	47.5	−24.0	Special Kuehl	Limited solubility	–
Right-nitrotoluene	81.5	1.5	RDX	95.0	12.5
Aviation kerosene	65.0	−18.6	*n*-heptane	95.0	17.6

Table 7.14 Composition and explosion performance of $C(NO_2)_4$

Composition			ρ/g cm^{-3}	v_D/ms^{-1}	V_L/ml
Combustible compound	Combustible compound content (%)	$C(NO_2)_4$ content (%)			
Benzene	13.75	86.25	1.47	7,180	520
Nitrobenzene	23.15	76.85	1.53	7,430	470
O-nitrotoluene	21.30	78.70	1.52	7,770	480
Right-nitrotoluene	21.30	78.70	1.52	8,170	495
Dinitrobenzene	34.05	65.95	1.53	6,670	650
TNT	39.85	60.15	1.58	6,670	565
α-nitronaphthalene	19.70	80.30	1.57	8,160	490
Special Kuehl	51.00	49.00	1.63	7,100	570
Aluminum flakes	25.00	75.00	1.79	7,420	690
RDX	30.00	70.00	1.67	–	–
n-heptane	5.00	95.00	1.63	6,700	*Note* 10 g special Kuehl Booster

Note The detonation velocity was measured in φ20 glass tube using 8th detonators with 10 g TNT as booster

tetranitromethane significantly, especially in sealed condition where no evaporation loss would occur. Usually, the composition of such explosives would be 90:10 (tetranitromethane: poly butyl methacrylate, w/w). With the density of 1.50 g/cm^3, the explosion velocity is 7,400 m/s whose poser is 119 % TNT equivalent and the shock sensitivity is 88 % that can be used for industrial blasting.

7.2 Nitrate-Based Liquid Explosives

Nitrate-based liquid explosives mainly refer to liquid explosives composed of nitrate and nitrate, nitrate and oxidizer, nitrate and sensitizers. Such mixtures are fundamental liquid explosives which can prepare other complicated liquid explosives with regarding to specific purposes.

7.2.1 Characteristics of Nitrate-Based Liquid Explosives

Nitroglycerin (NG) is one of most widely used liquid explosives, but also an important mining explosive. Nitroglycerin was applied for mining by Alfred Nobel who is a Swedish engineer [46], which led to the development of nitrate. Nobel established the first factory of 'oil explosive' in 1862 and used nitro and sulfonitric acid to generate Nitroglycerin that can be extracted from water-alcohol solution.

According to a large amount of experiments, Nitroglycerin can be adsorbed by diatomaceous earth to formalize diatomite explosive. The first diatomite explosive consisting of 75 % Nitroglycerin and 25 % diatomaceous earth (w/w) was produced by Nobel in 1867.

Russian engineers [47] mixed Nitroglycerin and magnesium carbonate, a type of solid adsorbent, such formulation has been used for gold mining in Trans-Baykal of Siberia, Upper-Uspleaskii [48].

Theoretically speaking, nitroglycerin can mix with nitric acid ester, ethylene glycol dinitrate, diethylene glycol dinitrate, glyceryl dinitrate, glycerol trinitrate isobutyl nitro, azido nitrate, nitric acid hydroxyl ester at any ratio, respectively. The chemical equation of nitroglycerine can be described as follows:

$$C_3H_5(ONO_2)_3 \rightarrow 3CO_2 + \frac{5}{2}H_2O + \frac{3}{2}N_2 + \frac{1}{4}O_2$$
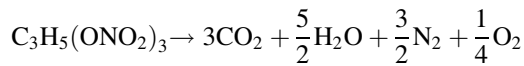
For nitroglycerin explosion, the explosion heat is 6,231 J/g, explosion volume V_0 is 715.7 mL/g, explosion temperature is 4,250 °C, and explosion force f_0 is 9,292 m.

The stability of nitroglycerin is generally realized using filtered water, since it can be detonated by 200 Hz vibration. However, the stabilized nitroglycerin can be preserved safely even under 800 Hz vibrations.

Nitroglycerin is sensitive to shock, and the shock sensitivity increases when the nitroglycerin is absorbed into solid. The liquid nitroglycerin has the most significant shock sensitivity. The shock sensitivities of different nitroglycerin forms are given in Table 7.15.

Nitroglycerin easily explodes by mechanic force and heat, but this explosion is incomplete. 100 % explosion rate of nitroglycerin can be achieved by gun shot. The water fill lead block expansion value of nitroglycerin is determined by detonation performance, and Table 7.16 lists the water fill lead block expansion values generated by different detonators.

Single-used nitroglycerin could be difficult to realize stable detonation, however, mixture of nitroglycerin and diatomaceous earth at 75:25 (w/w) could increase the

Table 7.15 Shock sensitivities of different nitroglycerin forms

Nitroglycerin form	Impact force (kg m/cm^2)	Explosion rate (%)
Liquid	0.08	10
	0.11	50
	0.40	100
Stable crystalline	0.51	10
	0.65	50
	0.82	100
Unstable crystalline	0.63	10
	0.78	50
	0.93	100

Table 7.16 Water fill lead block expansion values generated by different detonators

Detonators	Water fill lead block expansion (cm)
1	190
2	225
6	460
8	590

explosive strength. For example, the water fill lead block expansion of no. 1 detonator was 285 cm while the no. 8 detonator's was 305 cm.

The detonation of nitroglycerin related to its charge configuration, experimental results demonstrate that steel column with 5 mm thickness filled with nitroglycerin can be detonated stably by no. 1 detonator.

The explosive strength of mixture of methyl nitrate and nitroglycerine at 1:1 (w/w) is greater than the nitroglycerine only. Further experiments showed that the mixture of 75 % methyl ester of nitric acid and 25 % 1,3-propanediol dinitrate can produce stronger explosion using 3.0 % second aniline as the stabilizer, and the shock wave overpressure is 1.6 times of TNT.

7.2.2 Detonation Velocity of Nitrate-Based Liquid Explosives

The detonation velocities of nitrate-based liquid explosives could vary in a wide range. Different formulations can have different critical explosive diameters indicating different detonation velocities. Taking liquid nitroglycerin as an example, detonation velocity relates to charge diameter and configuration. Based on the writer's studies, the detonation velocity would increase when the configuration diameter increasing. For 5 mm configuration diameter, the limitation of detonation velocity is 920 m/s. The information of charge configuration and detonation velocity is given in Table 7.17.

The emulsion formalized by nitroglycerin and water could produce a certain detonation velocity, for example, the emulsion consisting of 100 nitroglycerin and 150 water (w/w) can be exploded by no. 8 detonator for a stable detonation. The detonation velocities of nitroglycerin and water elusions are given in Table 7.18.

The elusion whose ratio of nitroglycerine and water is greater than 2:1 cannot be exploded. The detonation velocity of nitroglycerine is impacted by charge configuration significantly, and it varies under different detonation conditions. For low detonation velocity, the reaction of nitroglycerine can be described as follows:

$$C_3H_5(ONO_2)_3 \rightarrow 2CO + CO_2 + 2\frac{1}{2}H_2 + 1\frac{1}{2}N_2O + 1\frac{3}{4}O_2 + 87.86 \text{ kJ}$$
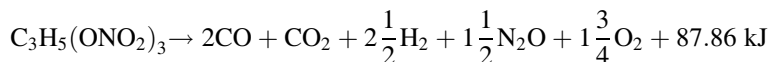
Above reaction usually occurs under following conditions, e.g., unsealed explosive device, no booster, incomplete detonation reaction, such reaction may produce half-burst phenomenon and release a large amount of N_2O. The reaction of nitroglycerine without any condition above can be described as follows:

Table 7.17 Charge configuration, detonation conditions, and velocity of liquid nitroglycerin explosive

Charge media	Charge (mm)	Detonation condition	Detonation velocity (m/s)
Lead pipe	30	Detonated by no. 8 detonator	1,560
Lead pipe	3.0	Detonated by no. 8 detonator	915
Lead pipe	9.0	Detonated by no. 8 detonator	1,130
30CrMnSi pipe	30	Detonated by no. 8 detonator	3,780
Glass tube (thickness 3.0 mm)	22	Detonated by no. 8 detonator	1,165
Plexiglass tube	28	Detonated by no. 8 detonator, 15 Kurt Kuehl Booster	7,800
30CrMnSi pipe (thickness 1.0 mm)	37.5	Detonated by no. 8 detonator, 2 Craig mercury booster	8,520
Plexiglass tube	25	Detonated by no. 8 detonator, 15 Kurt Kuehl Booster	7,410
30CrMnSi pipe	22	Detonated by no. 8 detonator, 75 Kurt Kuehl Booster	7,760
no. 12-rust aluminum pipe	40	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	8,560
no. 12-rust aluminum pipe	35	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	7,830
no. 12-rust aluminum pipe	30	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	6,970
no. 12-rust aluminum pipe	25	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	6,100
no. 12-rust aluminum pipe	20	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	5,870

Table 7.18 Detonation velocities of nitroglycerine and water

H_2O: NG	Detonation condition	Detonation velocity (m/s)
0.75:1	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	6,370
1:1	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	5,520
1.5:1	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	5,150
2:1	Detonated by no. 8 detonator, 20 Kurt Kuehl Booster	4,300

$$C_3H_5(ONO_2)_3 \rightarrow 3CO_2 + 2\frac{1}{2}H_2O + 1\frac{1}{2}N_2 + \frac{1}{4}O_2 + 1334.7 \text{ kJ}$$
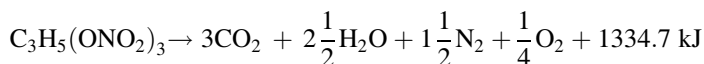
The final products are carbon dioxide and vapor indicating high detonation velocity.

The detonation capacity of ethylene glycol dinitrate and nitroglycerin methyl nitrate are different with nitroglycerin, they can achieve complete explosion even if

weakly detonated. The mixture of 70 % nitroglycerine and 30 % nitroglycerine formyl glycerol dinitrate (w/w) was used as the additive to nitroglycerine to produce "dynamite" explosive, and its detonation performance equals to 90 % of nitroglycerin.

The mixed explosives consisting of 75 % nitroglycerine and 25 % dinitroglycerine have the same explosion heat as pure nitroglycerine. The advantages of dinitroglycerine has insensitive shock, and the characteristic drop height is 8–10 cm (2 kg drop hammer). The explosive reaction of dinitroglycerine can be described as follows:

$$C_6H_{10}N_4O_{13} \rightarrow 2CO_2 + 4CO + 5H_2O + 2N_2 + 5564.7 \text{ J/g}$$
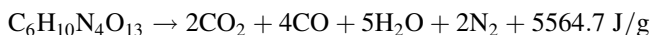
Dinitroglycerine can be used to produce "dynamite" explosive with low freezing point or other liquid explosives, and has better performance than chlorinated glycerol dinitrate since its explosive products do not contain hydrogen chloride and it is insoluble in water. The mixture of diglycerin and nitroglycerin is easy to prepare which has the advantage of low cost of raw material. Using the mixture of dinitroglycerine, ethylene glycol dinitrate, and other group glycol dinitrate as well combustible agents as explosives have been applied for building and mine blasting in many countries. The explosion performances of nitrate acid ester-based explosives are given in Table 7.19 [49].

Table 7.19 Explosion performances of nitrate acid ester-based explosives

Nitric acid ester (concentration)	Additives (concentration)	Density (g/cm^3)	Detonation velocity (m/s)
Nitroglycerine 60 %	Methyl nitrate 40 %	1.46	7,600
Isopropyl nitrate 60 %	Ethylene glycol dinitrate 40 %	1.28	5,970
Nitroglycerine 50 %	Ethyl nitrate 50 %	1.36	6,850
Isopropyl nitrate 50 %	Nitroglycerine isobutyl 50 %	1.34	7,130
Isopropyl nitrate 90 %	1,3-azido propane 10 %	1.12	6,920
Nitroglycerine 60 %	Nitromethane 40 %	1.44	7,330
1,2-propanediol dinitrate 60 %, nitrocellulose 8 %	Propylene oxide 20 %, aluminum flake 12 %	1.53	8,170
Isopropyl nitrate 50 %	1,2-ethane azide 10 %, aluminum powder 40 %	1.43	7,800
Nitric acid, *n*-butyl 60 %	Hydrogen peroxide 40 %	1.43	7,790
Ethylene glycol dinitrate 50 %	Hydrazine perchloric 50 %	1.51	8,320
Ethylene glycol dinitrate 50 %	Dimethyl carbonate of the original 50 %	1.43	7,910
1,3-propylene glycol dinitrate 50 %	Hydrazine nitrate 40 %, nitric acid 10 %	1.57	8,320

Based on Table 7.19, nitrate acid ester can be mixed with various inorganic materials that usually produce high energy. Another characteristic of these explosives is significantly high charge density, and the mixture of nitrate acid ester and metal powders are also considerable explosives.

7.3 Nitrate Nitrogen Oxide Based Liquid Explosives

7.3.1 Nitric Acid Liquid Explosives

Liquid nitrate-based explosives have high detonation velocity, strong detonation strength, and strong shock sensitivity. Although these characteristics would not be good as tetranitromethane-based explosives, they could make them still suitable for general applications. In order to enhance the shock sensitivity of nitrate-based explosives, dissolving a specific amount of tetranitromethane in nitric acid would be available. These two chemicals are well miscible, and the tetranitromethane is not coagulated and precipitated at $-10\ °C$ and its solubility can still achieve 20 %.

Nitric acid serves as oxidizing agent, and its concentration should be above 95 % to ensure the oxidation effect. The formulations of nitrate-based liquid explosives with their performance are given in Table 7.20.

7.3.1.1 Nitrate-o-Ethylbenzene Liquid Explosives [50]

Nitrate-o-ethylbenzene nitrate explosives are prepared by mixing of nitrate acid as oxidant and o-ethylbenzene as a flammable agent at specific weight ratios. The reaction of nitric acid and o-ethylbenzene can be described as follows:

$$C_8H_9NO_2 + 7.4\,HNO_3 \rightarrow 8CO_2 + 8.2H_2O + 4.2N_2$$
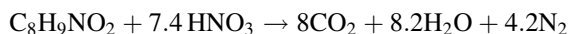
(1) Raw materials
(2) Nitric acid (industrial grade), concentration: 90 and 85 % (w/w)
(3) O-ethylbenzene (ONEB) formula: $C_8H_9NO_2$
(4) Structure.
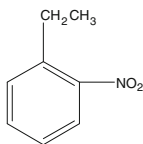
Table 7.20 Formulations of nitrate-based liquid explosives with their performance

Serial No.	Formulations		Combustion agent	Concentration (%)	Critical detonation thickness (mm)	Detonation velocity[a] (m/s)	Brisance[b] 25 g (mm)
	Oxidant	Concentration (%)					
1	Tetranitromethane	83.3	Kerosene	16.7	0.5	7,700–7,800	23.6
2	Nitric acid (95 %)	71.7	Nitrobenzene	28.3	6-7	6,980	21
3	Nitric acid (95 %)	58.3	Nitrobenzene	27.1	5	6,840	
	Tetranitromethane	14.6					
4	Nitric acid (95 %)	61.3	Ortho-nitro-ethylbenzene	23.4	6-7	7,250	22
	Tetranitromethane	15.3					
5	Nitric acid (95 %)	75.6	Ortho-nitro-ethylbenzene	24.4	8-10	7,130	20.7

[a] Detonation velocity was measured in the glass tube with inner diameter 10 mm
[b] Brisance was measured in the flat glass container and the explosive dosage was 25 g

O-ethylbenzene is a yellow transparent oily liquid, and its density is 1.126 g/ cm³, freezing point is below −40 °C, flashing point is 110 °C, and boiling point is 223–224 °C. It is not combusted even the air temperature achieves 250 °C, but detonation occurs contacting with fire. It is corrosive and toxic, the maximum allowable concentration is 0.005 mL/kg in the air and the LD50 value of oral acute toxicity test in mice (the lowest dose to cause of half death of animals) is 4.2 mg/kg. Hence, it is a low toxic substance based on the chemicals toxicity grading standards.

The formulations of different ONEB are:

Nitric acid 90 %, nitric/o = 77.5/22.5 (w/w);
Nitric acid 85 %, nitric/o = 78.5/21.5 (w/w).

Preparation of nitrate-o-ethylbenzene explosives requires adding nitric acid into ONEB slowly and stirring them as homogeneous mixture. The formulations and temperatures are given in Table 7.21.

(2) Basic Properties of Explosives

O-nitrate explosives is a corrosive and homogeneous transparent yellow liquid with a pungent odor as nitric acid. The density of explosives may vary with the concentration, weight of nitric acid and temperature, and such information is indicated by Fig. 7.2

O-nitrate explosives have good resistance of low temperature. Table 7.22 lists the results of low temperature resistance.

(3) Safety Performance of Nitrate-o-Ethylbenzene Explosives

1. Storage safety performance test: nitrate-o-ethylbenzene explosives were sealed in polyethylene plastic bottles for 2 months, the physical and chemical properties were consistent without any change, no decomposition occurred, and the liquid were still homogenous.
2. Drop test: nitrate-o-ethylbenzene explosives sealed into plastic bottles and iron pipes were dropped from 100 m height, the bottles broke and the explosives were splashed out but no explosion occurred.
3. Flame sensitivity test: single and a bunch of four fuses were hung vertically above the nitrate-o-ethylbenzene explosives, the distance between fuses and explosives were 5 mm and reduced gradually until they were contacted. Making

Table 7.21 80/20 nitrate explosives preparation and reaction temperature [50]

Material temperature (°C)		Environmental temperature (°C)	Highest reaction temperature (°C)	Reaction phenomenon
Concentration 90 % HNO₃	Concentration 98 % HNO₃			
60	15–17	About 17	About 105	Intense boiling, releasing a large amount of NO₂
30	−2	−1 to 2	About 100	Same above
15	15–17	About 17	About 85	Gentle boiling, releasing NO₂
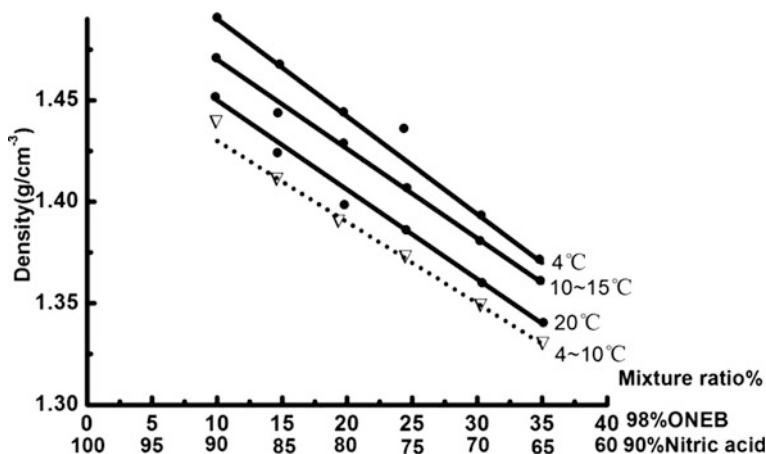
Fig. 7.2 Densities of nitrate-o-ethylbenzene explosives generated under different temperatures [50]

Table 7.22 80/20 nitrate-o-ethylbenzene explosives low-temperature resistance test results [50]

Nitrate acid concentration (%)	Experimental conditions		Observations
	Recorded unfrozen temperature (°C)	Crystallization temperature (°C)	
90	−55	–	Not congealing, viscosity increased significantly
85	−35	−43	Two temperatures were measures in the same container, −43 °C was measured at the bottom where columnar transparent crystals formalized

the flame spray of fuses contact with explosives, no combustion and explosion were observed, and also no decomposition.

4. Resistance wire heating test: a resistance wire was placed in an open container containing nitrate-o-ethylbenzene explosives, the wire was charged for 3 min, and no combustion and explosion occurred but evaporation and decomposition.
5. Shooting sensitivity test: no combustion and explosion occurred.
6. Nitrate-o-ethylbenzene explosives should not be contacted with other explosive equipment if it is used with other explosive materials in order to prevent accidents.

(4) Detonation Performance

Nitrate-o-ethylbenzene explosives have desirable explosive performance. The detonation velocity of nitrate-o-ethylbenzene placed in glass tubes with different

inner diameters and wall thicknesses were tested using no. 8 detonator. The results are given in Table 7.23.

Above results demonstrate that detonation velocity were within the range between 6,700 and 7,100 m/s for charge diameter 13.5 mm. The detonation performances were compared with other condensed explosives, and the results are given in Table 7.24.

The detonation velocity of nitrate-o-ethylbenzene explosives is stable at low temperature (dry ice frozen to −30 °C, velocity was 7,070 m/s at glass tube with inner diameter 19 mm and wall thickness 1.5 mm), and the velocity will not change after 1 month storage (tests were conducted in a glass tube with 10 mm inner diameter and 1 mm wall thickness, and the detonation velocities were measured as 6,840 and 6,770 m/s). The formulations of nitrate-o-ethylbenzene and their brisance are given in Fig. 7.3.

From above figure, the maximum brisance values of both explosives, i.e., 23.5–24.5 mm, were obtained by 80/20 and 75/25 accordingly, and these results corresponds to the theoretical calculation of zero oxygen balance.

The brisance results were conducted among various condensed explosives which demonstrate that nitrate-o-ethylbenzene explosive performs better. The results are given in Table 7.25

O-nitrate explosives have excellent resistance to low temperature. Brisance of O-nitrate explosive was not decreased after 1 month storage. The results are given in Table 7.26.

In order to improve the detonation performance of slurry explosives, nitrate-o-ethylbenzene, 40 % gum explosive, and 60/40 RDX were used as detonation agents, separately, and the comparison results of detonation in blasting crater with different sizes are given in Table 7.27. The results demonstrate that performance of nitrate-o-ethylbenzene using as detonation agent would be worse than 60/40 RDX but better than 40 % gum explosive. The results also show that the power of nitrate-o-ethylbenzene is greater than no. 2 ammonium nitrate explosive up to 70 %. The experimental results are given in Table 7.28.

Table 7.23 Detonation velocities generated from different glass tubes [50]

Nitrate acid concentration (%)	Composition (w/w)		Glass tubes (mm)		Detonation velocity (m/s)
	Nitrate acid	ONBE	Inner diameter	Wall thickness	
90	80	20	10.0	1.0	6370
			19.0	1.5	6850
			13.5	1.0	6500, 6670
	75	25	13.5	1.0	6890, 7140
85	80	20	13.5	1.0	7100, 6770
	75	25	13.5	1.0	6770, 6670

Table 7.24 The detonation velocities comparison between nitrate-o-ethylbenzene and other explosives [50]

Explosives	Shell size (mm)	Charge density (g/cm^3)	Detonation velocity (m/s)
O-nitrate	Φ38, 长500	About 1.40	7720, 7360, 8190
Nitroguanidine	Φ38, 长500	About 0.88	4780, 3890, 4570
2nd rock dynamite	Φ38, 长500	About 0.75	3520, 3760, 3770
ANFO	Φ38, 长500	About 0.67	2640, 2650, 2640

Note Detonation velocity of detonating cod is 6,896 m/s
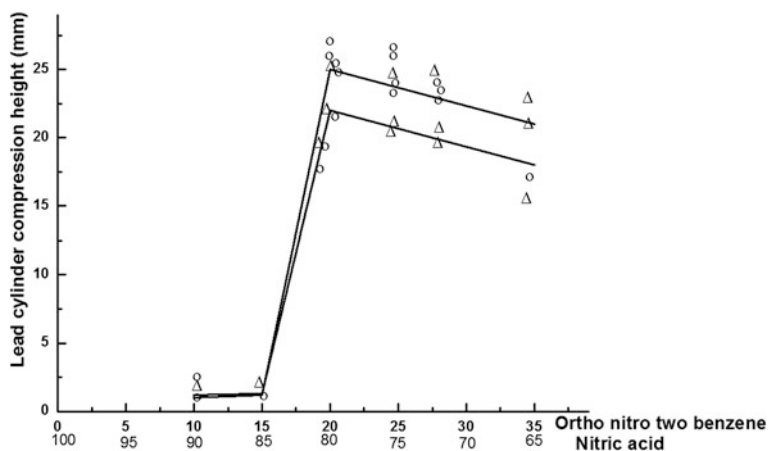
Fig. 7.3 The relationship between nitrate-o-ethylbenzene formulations and their brisance [50]

Table 7.25 Brisance values of different explosives

Explosives	Brisance (mm)	
	Paper tube	Φ38 mm, wall thickness 4 mm seamless steel pipe
O-nitrate explosives		27.00, 26.55, 27.00
Nitroguanidine	23.72, 22.70, 21.95	20.52, 20.80, 20.60
ANFO (cold milled)	6–8	15.45, 16.10, 17.33
no. 2 Ammonium nitrate explosive	About 10.5	18.40, 18.45, 20.90
RDX	22.17 (white), 18.55 (orange)	–
Scaly TNT (density 0.85/cm^3)	8	–

Table 7.26 Brisance of 80/20 nitrate-o-ethylbenzene explosives at low temperature

Nitrate acid concentration (%)	Experimental conditions	Brisance (mm)
90	Not storage, temperature +6 °C	24.00
90	Not storage, temperature −35 °C (with dry ice to −55 °C)	24.05
90	Storage for one month	23.50

Table 7.27 Comparison results of nitrate-o-ethylbenzene, 40 % gum explosive, and 60/40 RDX used as detonation agents in blasting crater with different sizes [50]

ID	Detonation agents		Explosives to be detonated		Blasting crater size (m)		Detonation medium
	Name	Quantity (g)	Name	Quantity (g)	Diameter	Visible depth (m)	Hard tack loess
1	40 % gum explosive	800	no. 4 slurry explosive	4,000	1.95	0.65	Dense wet tailings
					2.20	0.75	
2	80/20 O-nitrate explosive	400	no. 4 slurry explosive	4,000	2.35	0.81	Dense wet tailings
					2.25	0.78	
3	80/20 O-nitrate explosive	400	no. 4 slurry explosive	3,600	2.50	0.76	Dense wet tailings
					2.18	0.71	
4	80/20 O-nitrate explosive	400	no. 4 slurry explosive	3,600	2.38	0.79	Dense wet tailings
					2.28	0.73	
5	60/40 RDX	400	no. 4 slurry explosive	3,600	3.15	0.94	Dense wet tailings
		200		3,800	2.80	0.88	
		100		3,900	2.50	0.75	

(5) Detonation Effect of Nitrate-o-Ethylbenzene

80/20 nitrate-o-ethylbenzene is placed in the oxidize iron stair holes to detonate 4th slurry explosives, the results are compared with results generated by ANFO under the same conditions. Experimental conditions: The height of mining stair is 12 m, the depth of hole is 14.5–16 m, the charge amount of slurry explosives is 350–400 kg. 1.5 kg Nitrate-o-ethylbenzene are placed into plastic bottle, each relay initiating explosive kit is placed at the top, middle, and bottom of the hole, and each kit consists of four to five bottles that are tied together, and the detonating cord circle one of kit as the initiation source. The whole instrumentation is given in Fig. 7.4.

Good detonation results were generated using the nitrate-o-ethylbenzene as the relay initiating explosives to detonate slurry explosives, and it indicates that nitrate-o-ethylbenzene can replace RDX.

Table 7.28 Detonation results of nitrate-o-ethylbenzene and no. 2 ammonium nitrate explosive at blasting crater [50]

Conditions	Explosives	Results	ID								Average volume (m³)
			1	2	3	4	5	6	7	8	
Test dose is 1 kg, the depth of test hole is 1 m, and detonation medium is homogeneous loess	no. 2 ammonium nitrate explosive	Crater diameter (m)	2.48	2.17	2.12	2.31	2.23	2.18	7	–	0.83
		Crater visible depth (m)	0.69	0.69	0.52	0.60	0.62	0.64	–	–	
	O-nitrate explosive	Crater diameter (m)	2.34	2.32	2.12	2.23	2.24	2.16	2.40	2.16	1.39
		Crater visible depth (m)	0.58	0.69	0.68	0.73	0.52	0.58	0.64	0.55	
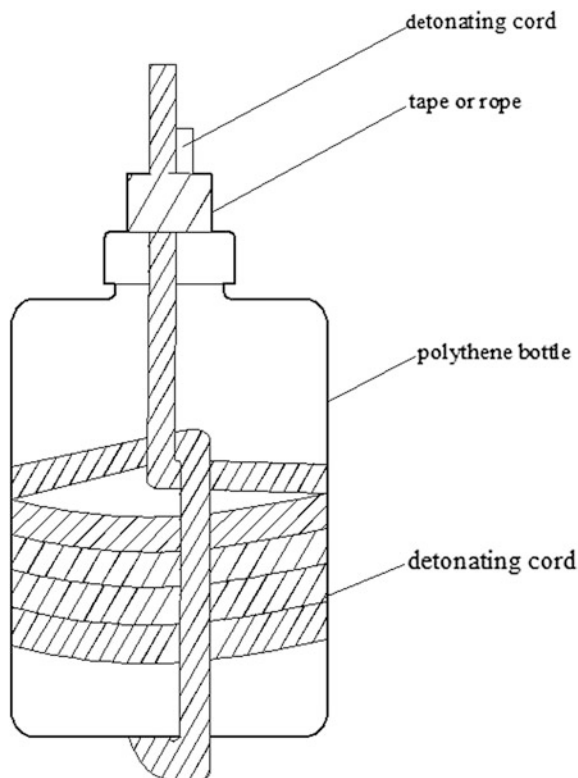
Substantial studies have been done using full-length polyethylene plastic bags
(bottom sealed) which are fullfilled with nitrate-o-ethylbenzene explosives to do
deep hole detonation, and results show that it performs better detonation effect than
other explosives regarding same charge quantity. Such information indicates that
the nitrate-o-ethylbenzene explosives have better explosive parameters that can
save the consumption during the practical implementations.

7.3.1.2 XJ-I Liquid Explosives Prepared from Nitric Acid and Toluene

XJ-I are liquid explosives prepared by mixing nitric acid and toluene in certain
ratios, and they possesses a number of advantages like high explosive power, ease
of preparation, and cost-effectiveness [51].

(1) Determination of the Formulation of XJ-I Liquid Explosives

① Effect of Nitric Acid Concentration on Explosion Properties

An amount of 80, 85, 90, or 95 % nitric acid was allowed to combine with
toluene in a ratio near to zero oxygen balance, affording a series of XJ-I liquid

explosives. Subsequently, these explosives were subject to explosion brisance tests and blasting power tests, and the results were shown in Table 7.29.

As shown in Table 7.29, the brisance and blasting power of liquid explosives seem to increase with the rise of nitric acid concentration. Notably, the explosives prepared with more than 85 % nitric acid concentration can be detonated with no. 8 detonator, whereas the explosives prepared with less than 80 % nitric acid concentration do not possess stable explosion properties; instead, they tend to separate into layers after being stored for a short period of time. Moreover, layer separation turned out to be worse for explosives prepared with lower concentration nitric acid. The no. 8 detonator is not able to detonate explosives with separated layers.

② Effect of Oxygen Balance on the Properties of Explosives

To understand the effect of oxygen balance on the properties of explosives, the concentration of nitric acid was maintained at constant, while the oxygen balance has been changed gradually, and the results were shown in Table 7.30.

As shown in Table 7.30, the optimal outcome is obtained when the oxygen balance in XJ-I type explosives is close to zero. When oxygen balance is too high or too low, the explosion properties seem to be inferior. Particularly, severe layer separation is evident in the liquid explosives when the value of oxygen balance is adequately negative, which certainly would prohibit the full usage of the work capacity of explosives. Based on these results, two formulations which have been primarily considered for the production of XJ-I explosives were illustrated in Table 7.31.

(2) Preparation of XJ-I Explosives

① Determination of Conditions used in Preparation Process

(1) Effect of different charging sequence on explosion properties

Under stirring conditions, toluene is slowly added into nitric acid while the addition speed and reaction temperature are effectively controlled.

Alternatively, toluene can be first charged into a reaction flask, and then nitric acid is added portion-wise with stirring and cooling. Initially, the reaction rate is slow, and it dramatically increases when the temperature of reaction solution reaches certain values like 30–40 °C, which in turn would increase the reaction temperature enormously. However, if too much nitric acid is added at the beginning, it will be extremely difficult to control the reaction rate and temperature. The explosion properties of explosives prepared through different charging sequences appear to be quite similar, as illustrated in Table 7.32.

Table 7.29   Effect of nitric acid concentration on explosion brisance and blasting power

| No. | Concentration of nitric acid (%) | Ratio% (mass) | | Oxygen balance (%) | Brisance (mm) | Explosion crater volume in refine ore (L) |
		Nitric acid	Toluene			
1	80	86	14	−0.132	21.46	10.2
2	85	85	15	−1.061	22.18	16.5
3	90	84.5	15.5	−0.223	22.56	17.6
4	95	84	16	+0.57	24.29	22.5

Table 7.30 Effect of oxygen balance on explosion brisance and blasting power

No.	Concentration of nitric acid (%)	Ratio% (mass)		Oxygen balance (%)	Brisance (mm)	Explosion crater volume in refine ore (L)
		Nitric acid	Toluene			
1	90	86	14	+5.3	20.34	18.6
2	90	85	15	+1.6	21.32	21.2
3	90	84	16	−2.2	21.93	21.5
4	90	83	17	−6.1	20.19	13.5

Table 7.31 Formulation of XJ-I explosives

No.	Concentration of nitric acid (%)	Ratio% (mass)		Oxygen balance (%)
		Nitric acid	Toluene	
1	90	84	16	−2.2
2	98	83	17	+1.56

Table 7.32 Explosion properties of explosives prepared by different charging sequence

Nitric acid concentration (%)	Amount of nitric acid (%)	Amount of toluene (%)	Charging sequence	Brisance (mm)	Explosion crater volume (L)
90	84	16	Toluene is added into acid	20.75	19.9
90	84	16	Acid is added into toluene	20.38	20.1

② The Effect of Reaction Temperature on Explosion Properties

Due to the hydration reaction, nitration reaction, and oxidation reaction between toluene and nitric acid, significant amount of heat is often released after toluene and nitric acid are mixed, which naturally makes the reaction temperature rise sharply. At the same time, reaction temperature can not only contribute to the composition of final products, but also affect their explosion properties. Table 7.33 showed the explosion properties of explosives prepared between 75–80 °C and below 50 °C.

As shown in Table 7.33, when the reaction temperature is below 80 °C, the effect of reaction temperature on the explosion properties is negligible. Generally, the reaction temperature for the preparation of XJ-I type explosive in laboratory is controlled between 70 and 80 °C, whereas the temperature in industrial production is maintained less than 100 °C.

③ The Effect of Stirring Conditions on Explosion Properties

It appears that stirring conditions have marginal impact on the heat dissipation of reaction process, mass transfer between components, as well as production safety. Related experiments suggested that the only difference between the stirred

Table 7.33 Effect of reaction temperature on explosion properties

Concentration of nitric acid (%)	Ratio% (mass)		Reaction temperature (°C)	Brisance (mm)	Explosion crater volume (L)
	Nitric acid	Toluene			
90	84	16	50 °C以下	22.1	24.5
90	84	16	75–80 °C	22.04	25.5

processes and nonstirred one is production time, and the explosion properties of products obtained from both processes are slimier. Therefore, the industrial production of XJ-I explosives can be implemented by either continuous feeding or pipeline production.

Currently, reactor or pipeline production has been employed in the industrial production of XJ-I explosives. Specifically, nitric acid and toluene in high-dosage barrels are allowed to continuously flow into a reactor in certain ratio controlled via individual valve, in which they are allowed to mix and react. Subsequently, the reaction solution flows into a 35 m long coiled tube for cooling, in which the reaction is allowed to continue followed by cooling down. The effluent flowing out of coiled tubes is the desired explosive product, which can stay for some time in a temporary storage tank before being moved into the permanent storage container. The continuous production process has been illustrated in Fig. 7.5.

Nitric acid and toluene are continuously added in certain ratios: nitric acid and toluene are both placed in high-dosage barrels, respectively, and then they can be added into a sealed crater in a proper ratio via valves and pipes, in which they will be mixed and allowed to react. After that, the resulting reaction solution can be cooled down by passing a multisegment condensing tube. This approach is safe, reliable, easy to control, highly efficient, and capable of continuous production.

(3) Applications of XJ-I Explosives [52]

To obtain realistic evaluation about the effect of XJ-I liquid high-power explosives, blasting experiments have been conducted in open iron ore mining fields and underground construction sites. Specifically, total 39 blasting has been performed to afford 339 deep holes, which consumed 188 tons of explosives and covered more than 100 million tons of ores and rocks. This result clearly indicated that XJ-I explosives possess excellent blasting properties as well as pronounced economic advantages.

① Experimental Conditions and Charging Process

XJ-I explosives are mainly used for stope −8 to 20 m platforms with ore-rock hardness $f = 10$–18. Generally, blast holes tend to accumulate water, and some even have flowing water, thus it is extremely difficult to blast with powder explosives such as ammonium pine wax. When XJ-I explosives are used for this purpose, a long polyethylene bag (bag length should be 1m longer than cannon hole depth, and blast hole diameter should be greater than the diameter) with detonating cords or detonating kits should be first placed in boreholes. Subsequently, liquid explosives are streamed into the bag through meters and delivery tubes. After the plastic bag has been sealed, boreholes can be filled and then detonated.
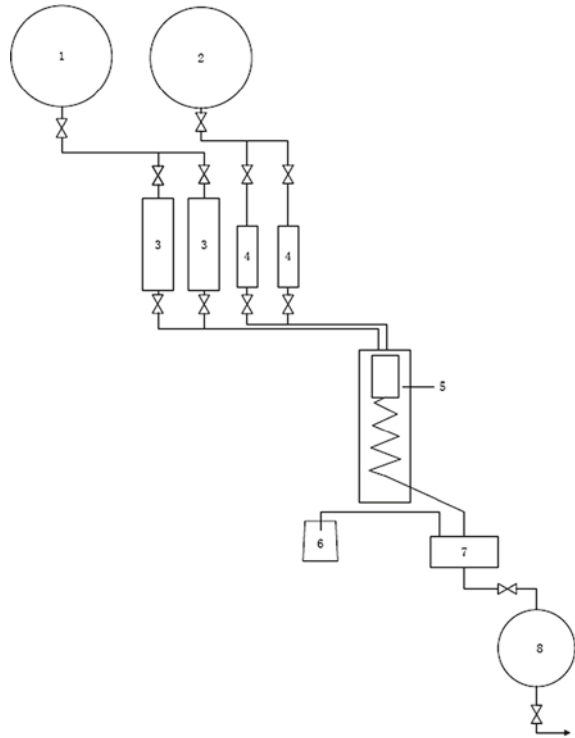
1-Nitric acid storage tank; 2-Toluene storage tank; 3-Nitric acid measuring
barrel; 4-Tolune measuring barrel; 5-Reaction mixing cooler; 6-Waste
container; 7-Temperaory storage tank; 8-Storage tank

② Effect of Application

Initially, detonators and water-proof detonating kits were used to afford reliable
initiation, later, detonating cords were employed for safety purpose. Butter can be
applied on the surface of detonating cord to ensure the water-proof-ness of detonate
kits. XJ-I explosives have been employed in iron-ore blasting experiments,
affording interesting results as follows: decent blasting effect is evident in hard rock
blasting and water hole blasting, and the costs of transmitting detonation has been
reduced up to 22 %; problems involved in the hard rock blasting and water-rich
hole blasting have been solved, and the labor intensity needed for the processing
and operation of explosives is also reduced, which ultimately improve working
conditions and are welcomed by mining fields all over the world.

Nitric acid can also be combined with other substances to afford liquid explosive
mixtures, and their composition and explosion properties are described as follows:
for the mixture of 33.5 % di-nitrotoluene, 50.0 % nitric acid and 16.5 % H_2O, the
detonation velocity is 6,700 m/s in a 30 mm diameter glass tube; for the mixture of
47.0 % TNT, 50.0 % nitric acid, and 3.0 % H_2O, the detonation velocity is 7,500 m/
s in a 40–50 mm diameter aluminum tube; for the mixture of 79.5 % nitrate and

Table 7.34 Properties of explosive mixtures composed of nitric acid and combustible substances

Component	Combustible substance content (%)	Heat of reaction (J/g)	Density (g/cm^3)	Burning pressure (atm)	Flashing point (°C)	Specific impulse (s)
Nitric acid	Hydrazine 38.5	–	1.28	21	–	243
Nitric acid	Furyl alcohol 34.5	–	1.37	21	2,620	214
Nitric acid	Aniline 26.6	6024.96	–	21	2,760	218
Nitric acid	NO$_2$ 39, aniline 1	6422.44	1.45	20	2,707	225

20.5 % acetonitrile, the blasting heat is 6987.28 kJ/L, specific volume is 708.0 mL/g, detonation temperature is 4,200 K, and lead block expansion value is 450 cm^3; the mixture of 22.0 % DME, 77.0 % nitric acid, and 1.0 % H$_2$O; for the mixture of 24.4 % nitrobenzene, 62.6 % nitric acid, and 13.0 % H$_2$O, the detonation velocity is 6,430 m/s in a 40 mm diameter glass tube.

In addition, nitric acid can also be combined with combustible substances to produce novel liquid explosives, and their composition and properties were summarized in Table 7.34.

7.3.2 Liquid Explosives Based on Nitrogen Dioxide

Nitrogen dioxide exists as N$_2$O$_4$ dimers at low temperature but monomers at high temperature. The boiling point of nitrogen dioxide is 21 °C, with a relatively high freezing point of −10.2 °C. Its density at 0 °C is 1.49 g/cm^3. The properties of nitrogen dioxide are fairly similar to concentrated nitric acid, even though the former is easier to decompose and evaporate, making it more difficult to use.

Nitrogen dioxide can be used in the liquid explosives containing aliphatic hydrocarbons (excluding aromatic compounds), carbon disulfide, nitrobenzene, and other combustible substances. To prevent the solidification of nitrobenzene at low temperature, the concept of two-component flammable substances has been attempted, for instance, combing nitrobenzene with carbon disulfide. The explosion properties of such liquid mixtures have been studied and found to be close to nitroglycerine, exhibiting high impact sensitivity [53]. For this reason, French researchers adopted a bomb design suitable to two-component liquid explosives while using nitrogen dioxide as warhead fillings. In other words, the flammable agent and oxidant of explosive are first placed in two chambers separated by a partition, which can be opened after the bomb is dropped to allow these agents to be mixed. Via this approach, the direct handling and transporting of explosive mixture has been avoided, which would ensure the safe and reliable use of such bombs.

The explosive mixture composed of 79NO$_2$/21 gasoline has a detonation velocity of 7,100 m/s. The detonation velocity of 64.5NO$_2$/35.5 is 7,650 m/s.

7.4 Hydrazine Liquid Explosives

7.4.1 Hydrazine Liquid Explosives Contain Nitric Acid

Hydrazine nitrate is a chemical does not contain carbon atoms, thus its explosion would not produce smoke, making it excellent smokeless explosive. In the 1960s, inspired by a rocket propellant explosion incident, USA developed a new class, hydrazine nitrate-based high-power explosives "Astrolite," which have been widely used in military operation, civilian blasting as well as ammunition. Among them, some belong to the liquid explosives. As they have high energy, decent explosion properties, and wide applicability, after the United States, the former Soviet Union, Japan and other countries have also carried out research on the development and manufacturing of such explosives.

7.4.1.1 Astrolite Explosives

There are four types of Astrolite explosives, A, G, P, and K. Type A and type P explosives are plastic explosives.

The G-type Astrolite explosive is a clear and transparent liquid explosive with high detonation velocity and explosion power. One of the major characteristics of such liquid explosives is that they can be readily absorbed by soil and still maintain detonation capability. When G-type Astrolite explosives are directly poured on the ground, they can be rapidly absorbed by soil, and their explosive properties can be retained for a long time, thus they can be detonated with either pressure detonators or ordinary detonator, serving as "shell-less" or "liquid" mines. The sensitivity of G-type Astrolite explosives to mechanical shock and adiabatic compression shock is almost the same as their A-type counterparts. In addition, such explosives can be easily produced in battle field or factory, and reliably packed to afford explosive packages. G-type Astrolite explosives are mainly used for large area rapid mine placing to damage or destroy armored vehicles, clearing minefields, and opening up forward path. Plus, they can be used to dig bunkers and fortifications.

A- and G-type Astrolite explosives are usually composed of hydrazine nitrate, perchlorate, hydrazine, ammonia, and others. Table 7.35 included two Astrolite explosives and a few other explosives for comparison [54]. It appears that the properties of both Astrolite explosives are superior to the reference. In particular, Astrolite G is the most typical liquid explosive, and its compositions were summarized in Table 7.36.

The explosives described above are all liquid at room temperature, and their physical properties such as melting point, density as well as viscosity are closely related to the content of nitrogen, as illustrated in Table 7.37.

Astrolite G explosives generally utilize hydrazine nitrate and/or hydrazine perchlorate as the oxidant, and hydrazine as the combustible. To improve the physical properties of such liquid explosives, ammonia is often added to decrease the

Table 7.35 Property comparison between Astrolite explosives and others [1]

Properties	A-1-5	G	TNT + Al	Nitromethane	TNT	RDX
Physical state	Liquid or solid	Liquid or solid	Solid	Liquid	Solid	Solid
Power factor $(Q_v.V_e)$	1,600	1,175	792	1,133	675	1,162
ρ/g cm^{-3}	1.6	1.41	1.70	1.14	1.57	1.65
Shock sensitivity/ N m	900	820		280	–	–
Effect of blasting cone comparison (relative value)	3–4.0	1.1–1.3	1.5–2.0	1.0	1.0	–
v_D/ms^{-1}	–	8,600	6,800	6,210	6,900	8,180

Table 7.36 Composition of Astrolite G [1]

No.	Hydrazine nitrate × 100	Hydrazine perchlorate × 100	Hydrazine × 100	Ammonia × 100
1	91	0	7	2
2	88	0	7	5
3	84	0	7	9
4	79	0	7	14
5	79	0	13	8
6	68	19	9	7
7	59	24	10	7
8	42	40	11	7

Table 7.37 Physical properties of some Astrolite G explosives [1]

| No.	Nitrogen content × 100	ρ/g cm^{-3}	v_D/ms^{-1}	θ_s/°C	μ_m/mPa.s
1	2	1.42	8,600	14.5	22
2	5	1.39	8,500	3.3	20
3	9	1.35	8,200	−9.5	16
4	14	1.31	8,100	−22.2	12

freezing point and viscosity, thus the solid explosives at ambient temperature will become liquid even at very low temperatures. However, if the ratio of ammonia is excessive, the density of liquid mixture will decrease, thus the explosion velocity and power will be reduced. Hydrazine perchlorate can serve as a sensitizer for these explosives to improve their ability to transmit detonation, while the impact sensitivity is increased simultaneously. For this reason, the ratio of hydrazine perchlorate in the liquid explosive mixtures is generally maintained less than hydrazine nitrate.

Aside from using ammonia to prevent the freezing of liquid explosives, adding thiocyanate hydrazine (N_2H_5SCN) or methyl hydrazine ($CH_3N_2H_3$) can achieve similar or even better results. The mass percentage of the former can be up to 30 %, whereas the mass percentage of the latter can be up to 50 %.

To obtain the "optimal" explosion properties, the ratio between oxidants and flammable agent hydrazine should be maintained near zero oxygen balance; however, ammonia should not be included in the consideration of oxygen balance relationship. When hydrazine nitrate is used as the sole oxidant, the theoretical explosion equation can be described as follows:

$$N_2H_5NO_3 + 0.25N_2H_4 + 0.5NH_3 \rightarrow 3H_2O + 2N_2 + 0.75H_2$$

When the mixture of hydrazine nitrate and hydrazine perchlorate is used as the oxidant, the explosion reaction equation can be described as follows:

$$2N_2H_5NO_3 + N_2H_5ClO_4 + 1.5N_2H_4 + NH_3 \rightarrow 10H_2O + HCl + 6N_2 + 1.5H_2$$
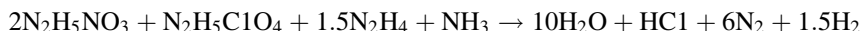
Based on the theoretical explosion reaction equation, the optimal ratio (mass fraction) for the former should be 85.2 hydrazine nitrate/7.2 hydrazine/7.6 ammonia, whereas the optimal ratio for the latter should be 49.05 hydrazine nitrate/34.17 perchloric acid hydrazine/12.40 hydrazine/4.38 ammonia.

Preparation of Astrolite G: first, determine the amount of each chemical component according to the formulation; second, hydrazine nitrate (or together with hydrazine perchlorate) is allowed to mix with liquid hydrazine, and then ammonia can be flushed into the solution until hydrazine salt is completely dissolved in hydrazine solution. By controlling the amount of ammonia added, one should be able to obtain Astrolite G liquid explosives.

If this liquid explosive is employed for land casting applications, a 0.5–3 % Guartec503 water-proof agent or Oxirane resin can be added to prevent explosives from being soaked due to moisture, which often lead to failed blasting (Guartec503 is a water-proof agent).

The formulations of Astrolite explosives usually include anhydrous hydrazine, a strong reducing substance, thus the mixture of which with air is prone to explosion and combustion. Plus, anhydrous hydrazine is expensive and toxic. Consequently, other combustible substances such as hydrazine hydrate and fatty acids have been employed to substitute anhydrous hydrazine, affording excellent results in practical applications.

7.4.1.2 Hydrazine Nitrate and Hydrazine Hydrate Liquid Explosives

Hydrazine nitrate itself is a powerful high explosive. It is usually prepared through the low-temperature salinification of either anhydrous hydrazine or hydrazine hydrate with nitric acid 65 % in the presence of methanol as the medium. This approach, however, suffers from the high cost of anhydrous hydrazine and the

toxicity of methanol. The efficient way of production concerns the reaction between nitric acid and hydrazine hydrate, that is simple but requires a salinification process at low temperatures.

(1) Synthesis of Hydrazine Nitrate

Hydrazine hydrate is the key material for the preparation of this type of explosive. Hydrazine dinitrate has to be first prepared following the production of hydrazine nitrate through the recrystallization of hydrazine hydrate. As shown in Fig. 7.6, the preparation involves nitric acid 65 % and hydrazine hydrate 50 %, of which an equimolar mixture in methanol stirred at room temperature and ambient pressure. Upon the reaction, the mixture is aged and filtered before white hydrazine dinitrate precipitation is received. Adding hydrazine hydrate 85 % then leads to the dissolution of precipitation. Tuning the solution to a PH level of 8 can induce recrystallization at temperatures lower than 10 °C where white needle like or rod like hydrazine nitrate.

The structure and properties of hydrazine nitrate agree with reported value in the literature. The melting points for hydrazine nitrate and hydrazine dinitrate are found to be 69–71 °C and 116.5–118.5 °C, respectively, according the measurement with a X-6 detector. Elemental analysis for both compounds shows the full details for each element, as presented in Tables 7.38 and 7.39.

Figures 7.7 and 7.8 show the corresponding infrared spectra for the hydrazine materials.

All the above results point to the chemical and chemical structure for hydrazine dinitrate to be $H_6N_4O_6$ and $N_2H_4 \cdot 2HNO_3$, respectively, and $H_5N_3O_3$ and $N_2H_4 \cdot HNO_3$ for hydrazine nitrate.

(2) Production of Hydrazine Nitrate Liquid Explosives

Hydrazine nitrate represents the major component material in hydrazine nitrate liquid explosive which is a composite explosive and its full composition consists of
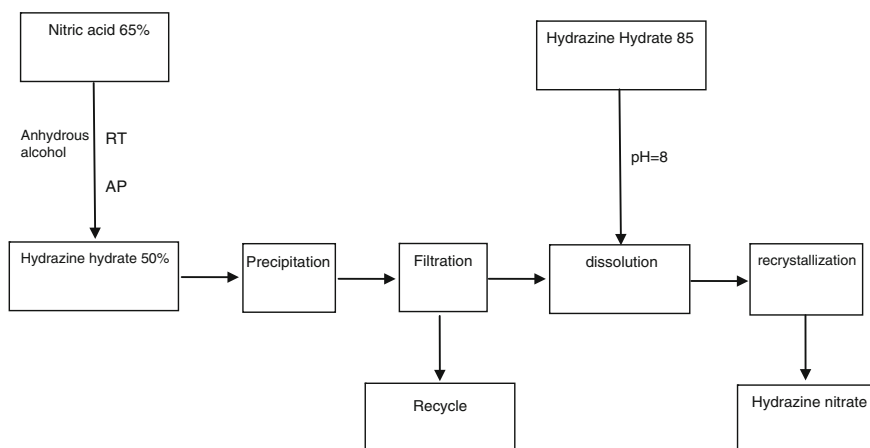

Fig. 7.6 Scheme for the production of hydrazine nitrate from nitric acid and hydrazine hydrate [64]

Table 7.38 Elemental results for hydrazine dinitrate [64]

Concentration/%	N	H	O
Theoretical value	35.43	3.83	60.74
Observed value	35.63	3.5	60.87

Table 7.39 Elemental results for hydrazine nitrate [64]

Concentration/%	N	H	O
Theoretical value	44.21	5.30	50.49
Observed value	44.36	5.43	50.49

Fig. 7.7 Observed infrared spectrum for hydrazine nitrate
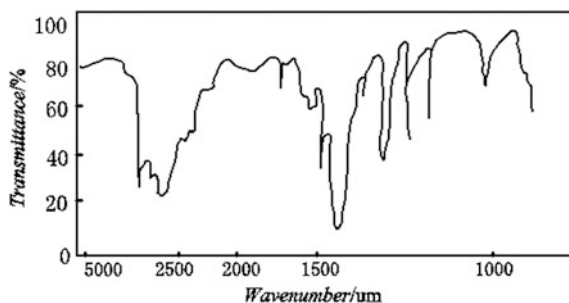
Fig. 7.8 Observed infrared spectrum for hydrazine dinitrate
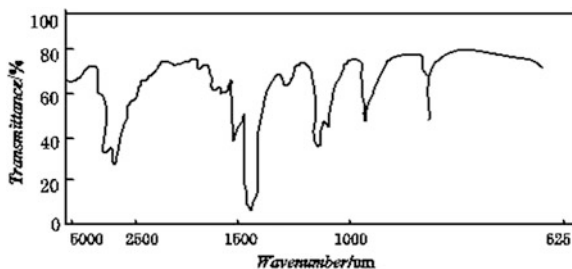
hydrazine hydrate 85 % and additives in addition to hydrazine nitrate. In producing such explosives, it is important to maintain the oxygen balance and consider the explosion strength as well as the environmental impact. A series of calculation and experimental work gives rise to the optimal composition that includes hydrazine nitrate in account of 70 % and hydrazine hydrate of 20 % and remaining additives (such as toluene, petrol and kerosene). The titled explosive is colorless and transparent liquid with density of 1.31 g/cm^3 and oxygen partial pressure of -0.2 and pH level of 9.0. This liquid explosive can be directly detonated using either no. 8 detonator or a small booster pellet.

(3) Detonation Properties [55]

Hydrazine nitrate liquid explosive could not be detonated by lighting the fuse. When heated by a naked flame, the explosive would burn but not explode. Loading

Table 7.40 Properties for hydrazine nitrate liquid explosives and a few other condensed explosives

Properties	Liquid explosive	TNT	TNT/ hexogen 40/60	Passivated hexogen (9 % paraffin)	HMX/ TNT75/ 25
Density/g cm^{-3}	1.31/ 20°C	1.59	1.61	1.59	1.81
Detonation velocity/ ms^{-1}	7,246	6,825	7,900	8,100	8,480
Brisance/mm (lead block compression test)	35.3 (half weight)	12.5 (full weight)	–	–	–

100 g of such liquid explosives into a plastic bottle could generate a sensitivity to rifle bullet impact of propellants and explosives that means no combustion and explosion. Be noted that the detonation velocity is 7,246 m/s ($\rho = 1.31$ g/cm^3) and the shock sensitivity from the standard experiment with a land impact testing machine is 0 %. The brisance is 35.3 mm according to the lead block compression test. The characteristic parameters for hydrazine nitrate liquid explosive and other condensed explosives are compared and tabulated in Table 7.40.

These experimental results indicate the characteristic features for hydrazine nitrate liquid explosive, that include the ease in production, good access to the raw materials, and readiness for manufacturing. Such liquid explosives have both civil and military use. Studies show that the alkaline substance generated after the explosion would react with some toxic chemicals to break the P–H bond and trigger the alkali catalytic hydrolysis. Such reactions are effectively a detoxication process and therefore hydrazine nitrate liquid explosive opens a new way for decontamination, that is quite unique.

7.4.2 Hydrazine Nitrate Liquid Explosives Containing Hydrazine Hydrate and Aliphatic Amine

Hydrazine nitrate shows high solubility in the hydrazine hydrates aqueous solution. Dissolving hydrazine nitrate into hydrous hydrazine hydrate can also produce liquid explosives with good performance. For example, the liquid explosive from a mixture of 77.8 % Hydrazine nitrate, 20.1 % hydrazine hydrate, and 2.1 % water can achieve a high detonation velocity of 8,370 m/s at the density of 1.42 g/cm^3. Moreover, it is not sensitive to mechanical shock and shows good reliability and full detonation [56]. The freezing point for this liquid explosive, however, is high [57]. Table 7.41 compares the component and properties for some hydrazine nitrate and hydrazine hydrate liquid explosives.

Aqueous solution of most aliphatic compounds can also dissolve hydrazine nitrate. The mixture aqueous solution of aliphatic amine and hydrazine nitrate

Table 7.41 Component materials and properties for hydrazine nitrate and hydrazine hydrate liquid explosives [1]

$\omega_i \times 100$		$\rho/g\ cm^{-3}$	v_D(observed)[a]$/ms^{-1}$	v_D(max)[b]$/ms^{-1}$	v_D(calculated)$/ms^{-1}$
Hydrazine nitrate	Hydrazine hydrate				
40	60	1.176	–	–	7,312
55	45	1.267	7747.1	7792.7	–
60	40	1.293	7893.3	7952.1	7,904
65	35	1.325	8050.0	8058.3	–
75	25	1.387	8327.1	8339.2	–
80	20	1.421	8473.5	8491.9	8,363

[a] The inner diameter is 31 mm for the polyvinyl chloride tube used for the detonation velocity measurement
[b] The theoretical steady detonation velocity when the diameter is beyond the maximum value

works well as liquid explosives. Table 7.42 shows the component and properties of one group of liquid explosives with aliphatic amine as the combustible agent [58].

In Table 7.42, hydrazine nitrate serves as the oxidation agent. Actually, nitrate for alkaline metals or alkaline earth metals should also be added to form water-soluble composite oxidizers. Content of hydrazine nitrate is required to be over 60 %. Some aliphatic amines can be used as combustible material, such as ethanolamine, diethylenetriamine, methylamine, and methylamine.

Table 7.42 Component and properties for the liquid explosive with aliphatic amine as the combustible agent [1]

$\omega_i \times 100$	$\rho/g\ cm^{-3}$	v_D/ms^{-1}	Impact sensitivity	
			Explosion rate	Height/cm
$85H_5N_3O_3$/15 Ethanolamine/$5H_2O$	1.42	7,810	0/6	60
$70H_5N_3O_3$/10 Ethanolamine/ $5.8N_2O_4$/$14.2H_2O$	1.35	7,770	0/6	60
$75H_5N_3O_3$/20 Diethylenetriamine/ $5H_2O$	1.37	7,520	0/6	60
$80H_5N_3O_3$/16 Ethylenediamine/ $4H_2O$	1.41	7,990	0/6	60
$65H_5N_3O_3$/8 methylamine/$5N_2O_4$/ $22H_2O$	1.28	7,280	0/6	60
$65H_5N_3O_3$/10$Ca(NO_3)_2$/10 methyl-amine/$15H_2O$	1.34	7,130	0/6	60
$65H_5N_3O_3$/10$Na(NO_3)_2$/10 methyl-amine/$15H_2O$	1.36	7,460	0/6	60
$75H_5N_3O_3$/6 methylamine/4 Oma-flora/$15H_2O$	1.40	7,670	0/6	60
NG	1.59	7,500	416	5

Note For explosion rate, denominator represents the experiment counts and numerator represents the number of explosion

Water as the component material is able to not only enhance the solubility of aliphatic amine towards hydrazine nitrate, but also reduce the shock sensitivity. In the presence of water, the explosion power does not decrease. Generally, a reasonable concentration range of 5–30 % applies to the composite liquid explosive with respect to the water content.

This type of explosive is odorless. Upon a full dissolution of hydrazine nitrate, the strongly irritating odor from hydrazines or amines would be completely removed. This explosive is not volatile or toxic, nor is corrosive. Furthermore, its easy to synthesize and user-friendly to use all afford compelling attributes for industrial production and other practical utilization.

7.5 Perchloric Acid Urea Liquid Explosive

A liquid explosive made from condensed perchloric acid aqueous solution and nitrate compounds was proposed in Japan in 1975 [25, 59]. Table 7.43 shows the component and properties for the liquid explosive that is prepared by adding nitrate compounds to 85 % perchloric acid solution.

The best combustible agent is nitromethane for perchloric acid urea liquid explosives as it can be mixed to form solution under any molar ratio. Different liquid explosives become available in terms of the ratio between perchloric acid urea and water and nitromethane. See Table 7.44 for component and explosion properties.

Nitromethane is indeed a liquid explosive of high energy output, however, its poor initiation sensitivity leads to the difficulty in detonation. If mixed with perchloric acid urea, this explosive could be detonated easier with noticeably decreased critical diameter and increased density. All lead to better detonation velocity and brisance.

Table 7.43 Component and property for the liquid explosive consisting of perchloric acid urea and nitrate compounds

$\omega_i \times 100$	$\rho / g\ cm^{-3}$	v_D / ms^{-1}	Shock sensitivity (drop hammer: 5 kg)	
			Explosion rate	Height/cm
$95CH_5N_2ClO_5^a/5PA$	1.60	6,520	0/6	50
$90CH_5N_2ClO_5/10PA$	1.603	6,890	0/6	50
$85CH_5N_2ClO_5/15PA$	1.609	7,370	0/6	50
$90CH_5N_2ClO_5/10C_6H_3N_2Cl_4$	1.593	5,680	0/6	50
$90CH_5N_2ClO_5/10CE$	1.601	6,850	0/6	50
$87CH_5N_2ClO_5/4THT/9C_6H_5NO_2$	1.504	5,720	0/6	50
$80CH_5N_2ClO_5/6PA/10TNT/4$ Polyacrylamide	1.512	5,480	0/6	50
$72CH_5N_2ClO_5/8PA/9KNO_3/10Si$-Fe Powder/4Polyacrylamide	1.69	6,100	0/6	50

a   The concentration for all perchloric acid urea solutions is 85 %

Table 7.44 Liquid explosive made from perchloric acid urea and nitromethane [65]

$\omega_i \times 100$						$\rho/\text{g cm}^{-3}$	$v_\text{D}/\text{ms}^{-1}$	Shock sensitivity (drop hammer: 5 kg)	
Perchloric acid urea	Nitromethane	Hexanitroethane	Sec-nitropropane	TNEOF	Water			Explosion rate	Height/cm
20	80					1.24	6,560	0/6	60
40	60					1.31	6,720	0/6	60
60	40					1.40	6,950	0/6	60
70	30					1.46	7,070	0/6	60
35	62				3	1.28	6,590	0/6	60
78	20				2	1.51	7,220	0/6	60
70	20				10	1.44	7,040	0/6	60
78	10				12	1.49	7,210	0/6	60
20	60	20				1.20	6,300	0/6	60
60	16	24				1.38	6,720	0/6	60
61	26		13			1.38	6,730	0/6	60
10	40			50		1.44	7,330	0/6	60
85		15				1.48	7,150	0/6	60
85			15			1.47	7,080	0/6	60
Nitroglycerin						1.59	7,500	4/6	30
Nitromethane						1.13	6,270	0/6	60

The characteristic of this explosive is to use water as the additive and its detonation sensitivity can be adjusted at will due to the ease in mixing nitroalkane with perchloric acid urea. The detonation velocity can also further increased, if additional organic oxidizer is used such as orthoester. The good chemical stability, easy in manufacturing and handling safety in addition of the feature of being free of odor, smoke, and volatility make perchloric acid urea explosive one the best choices. The disadvantage associated is related to the corrosion to metals. Particularly, when nitro compounds are present, the corrosivity is more serious. Therefore, the containers used for storage and transfer have to be made from such materials as polyethylene and glass which are corrosion resistant.

Liquid explosives with both insensitivity and high energy can be prepared by reacting metal perchlorate with ethanol, nitroalkane, and DMF. For instance, explosive from the composition of barium perchlorate, nitromethane, methanol, and DMF in the ratio 52:20:20:8 can be detonated at either 0 or 20 °C with a no. 6 detonator showing a detonation velocity of 6,230 m/s ($\rho = 1.92$ g/cm^3) at 20 °C and a freezing point of −28 °C.

Similarly, in the case of composition where iron perchlorate: lithium perchlorate: sec-nitropropane: methanol: formamide = 15:30:30:15:10, detonation is possible at the same temperatures with detonation velocity of 6,250 m/s ($\rho = 1.56$ g/cm^3) at 20 °C and a freezing point of −19 °C. When cations in perchlorates such as Ba, Li, Fe, or Sr become high in concentration, the explosives exhibit high sensitivity and explosion performance. Likewise, when the concentration is low, poor sensitivity and performance would be observed. The best content is 20–70 %, although it allows a large range of 10–80 % for optimization. This explosive tolerates some water for better explosion parameters. However, excess water would dissolve component materials bar nitroalkane so that nitroalkane precipitate from the oxidizer solution and the explosibility is disabled. This principle is utilized in the destruction of such explosives.

## 7.6 Liquid Explosives with Hydrogen Peroxide

7.6.1 Properties of Hydrogen Peroxide Containing Liquid Explosives

Oxygen makes up most molecular weight of hydrogen peroxide and it is around 47 % if only oxygen that could be utilized is considered. Density of 80 % H_2O_2 solution is 1.34. Pure H_2O_2 is stable at room temperature, and decomposes only at elevated temperature. To enhance the stability, one effective way is to add phosphoric acid/phosphate or 8-Hydroxyquinoline. With many combustible substances, H_2O_2 can be used to form high-force liquid explosive. On the other hand, powerful explosion occurs to H_2O_2 when induced by strong external factors. The major parameters for H_2O_2 of 90 % purity are listed in Table 7.45.

Table 7.45 Parameters for high purity H_2O_2

Parameters	Values
Relative density at 20 °C	1.39
viscosity at 18 °C (cps)	11.62
vapor pressure at 30 °C (mmHg)	5
solidifying point (°C)	−11.1
Boiling point (°C)	175
Enthalpy of formation $(-\Delta H_f)$	–
Liquid (kJ mol^{-1})	188.95
Gas (kJ mol^{-1})	139.29
Capacity (0–18.5 °C) cal/g °C	0.58
vaporization heat (J/g)	138.72
Surface tension at 18 °C (dyn/cm)	75.53
Conductivity at 25 °C	–
chemically pure	2×10^{-6}
Industrial grade	10×10^{-6}
Refractivity at 20°C	1.398
Residue	0.005 %

Hydrogen peroxide can be used as a monopropellant by taking advantage of the decomposition reaction triggered by catalysts. 80–85 % concentration hydrogen peroxide can be used not only as liquid explosives, but also in the launch of unmanned aerial vehicle (UAV). Oxidizers and fuels from respective tanks are injected into the combustion chamber for reaction that generates thrust to engine for the launch of rocket and other aircraft. These applications are based on the following reaction where hydrogen peroxide decomposes to form water and oxygen.

$$H_2O_2 + H_2O + \frac{1}{2}O_2 + 98.116 \, \text{kJ/mol} \, (2886.96 \, \text{J/g})$$
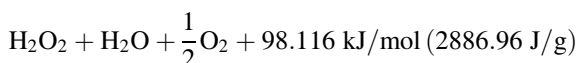
Adding calcium permanganate and sodium permanganate aqueous solutions to hydrogen peroxide can trigger its decomposition. Potassium permanganate, in contrast, is not a right choice as its solubility in water is so weak that not sufficient amounts of MnO_4^- are present to induce the reaction.

The working principle for the rocket booster is similar to that of the engine. The former allows 280 L H_2O_2 and 20 L solutions of permanganates to be loaded. Replacing these propellants with hydrazine and nitric ether gives rise to comparable performance. Shown in Table 7.46 is the thermochemical energy in the H_2O_2 monopropellant.

According to Table 7.46, for H_2O_2 its heat of decomposition is much larger than the heat of vaporization and hence the steam generated stays in high temperature that effectively give high pressures. It means that H_2O_2 can serve as both propellant and liquid explosive. In fact, the specific impulse for H_2O_2 propellant is found not larger than 232 s.

Table 7.46 Thermochemical performance of hydrogen peroxide

Parameters	Concentration of H_2O_2 (%)	
	86	100
Decomposition heat (J/g)	2510.4	2886.96
Enthalpy of vaporization (J/g)	1652.68	1548.08
Adiabatic decomposition temperature	650	980
Volume after full adiabatic decomposition (L/kg)	4,900	6,400

Extensive experimental studies over the decomposition mechanism have shown that the low thermodynamic energy for the reaction between H_2 and O_2 in boric acid-coated old containers can be only understood by considering the chemical inertness of the surface to water and H_2O_2 [60]. It is reported that in such conditions the decomposition of H_2O_2 occurs in the temperature range of 260–520 °C and the parameters suggest a first-order reaction.

The following reaction occurs spontaneously when H_2O_2 is mixed with hydrazine:

$$2H_2O_2 + NH_2NH_2 \cdot H_2O \rightarrow 5H_2O + N_2 + 786.59 \text{ kJ}$$
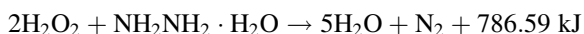
There is hysteresis in reaction, but copper salts if added, such as in the form of $K_3Cu(CN)_4$ can help catalyze the reaction and the salt dissolves into hydrazine hydrate. It was further confirmed that $K_3Cu(CN)_4$ reacts with hydrazine at room temperature to form copper metals whose accumulation could block hydrazine from entering combustion chamber. To remove such a possibility, before entering combustion chamber hydrazine hydrate should go through a cartridge of copper nitrate which are able to accelerate the reaction.

The hydrogen peroxide solution treated with ammonium nitrate has been used as the oxidant [61]. A solution of 40 % ammonia nitrate in 60 % H_2O_2 is compelling as the solidifying point is around −30 °C.

7.6.2 Explosion Properties of H_2O_2 and Its Mixtures

(a) Explosion Properties of H_2O_2

The exothermic decomposition reaction of hydrogen peroxide indicates the possibility to be used as explosive. In fact, lead block expansion value for 99.6 % concentration H_2O_2 is 75–80 cm^3. In a steel tube of a diameter of 34–40 mm, 94–100 % of H_2O_2 can be fully detonated with 50 g pentaerythritol tetranitrates. However, for 92 % H_2O_2, the detonation can propagate 100 mm away from the detonator.

No detonation occurs to 90 % concentration H_2O_2 [61]. There are interesting studies over the explosion properties of ternary mixture including H_2O_2, water, and possible organic substances. There results [62] give the possibility that the ternary

diagram on H_2O_2, water, and organic materials such as ethanol, glycerol, and propyl alcohol can be built. There could exist other ternary systems. In general, only the mixture with limited water can show explosibility.

All three organic substances mentioned above can be dissolved in 80 % H_2O_2 form mixtures whose velocity of detonation is around 7,000 m/s when detonated by detonator and booster pellet. If the concentration of H_2O_2 is reduced, the velocity decreases to 2,300 m/s. With low initiation energy, the velocity is further weakened to as low as 750 m/s [63].

(b) Oxidation of Hydrazine with H_2O_2

The most important reaction concerning hydrazine that is the oxidation process is not fully understood yet. Prior studies were mainly focused on the oxidation dynamics in the diluted solutions. There was a report finding that the rate of reaction largely depends on pH, for instance at a pH level of 10–11, there is a maximum.

Adding cobalt sulfate to the reaction can increase the rate. In contrast, addition of copper salts can fully remove the hysteresis and sodium nitrate works equally effectively. The reaction between H_2O_2 and a mixture of hydrazine and methanol represents the principle for a liquid explosive. Table 7.47 shows the parameters for a liquid explosive using 80 % H_2O_2 as oxidizing agent.

Be noted that 0.11 % $K_3Cu(CN)_4$ should be used a stabilizing agent for the explosive in Table 7.47. Table 7.48 shows the physical and chemical properties for the liquid explosive from a mixture of equimolar 80 % H_2O_2 and methanol.

Because the decomposition heat of hydrazine hydrate is large, it is possible to use it as a single-component propellant. The energy and gas products are provided by the reactions induced by permanganate salt (generally using solid permanganate salt). The combustible fuels can be nitrate esters, nitroalkanes, alkyl azides, etc. To provide the energy, the hydrogen peroxide and hydrazine nitrate oxidation systems were also used.

Table 7.47 Liquid explosives made from hydrogen peroxide and hydrazine hydrate

Component	Content (%)
Hydrazine hydrate	30
Methanol	57
Water	13

Table 7.48 Physical and chemical properties of hydrazine hydrate diluted by equimolar 80 % hydrogen peroxide and methanol

Parameters	Values
Reaction heat (J/g)	4267.68
Relative density	1.30
Gas volume (mL/g)	940
Explosion heat (J/g)	9,877
Detonation temperature (K)	3,328
Specific impulse (s)	243

7.6.3 Toxicity and Control Measure for H_2O_2 Liquid Explosives

As exposure of skin to H_2O_2 leads to irritation, in handling large amount of H_2O_2, goggles and lab coats (made of such protective fibers as polyvinyl chloride) should be worn, together with rubber gloves and laboratory boots.

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