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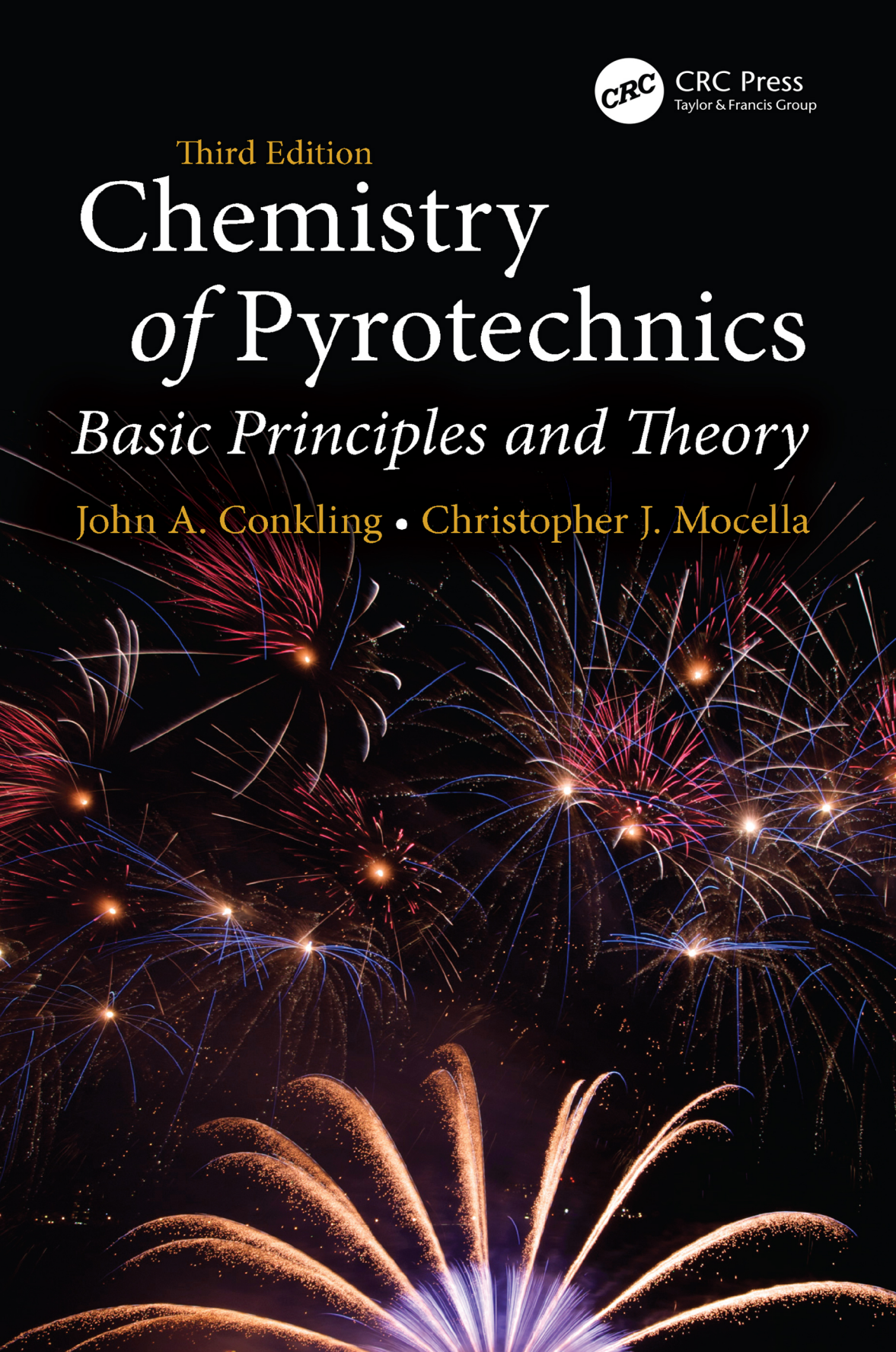
Third Edition

Chemistry *of* Pyrotechnics

Basic Principles and Theory

John A. Conkling • Christopher J. Mocella



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Preface to the Third Edition: 2019

This book is a continuation of the lifelong work and dedication of Dr. John Conkling, whom I have had the distinct honor to work for. While Dr. Conkling has "retired" from primary work on *The Chemistry of Pyrotechnics*, the reader should make no mistake that this is still entirely his work, and his are the shoulders that I stand on.

I met Dr. Conkling in 1999 while working at Washington College in Chestertown, MD (both our alma mater) between school years as I worked for the summer conferences held there, one of which was his legendary Summer Pyrotechnics Seminar. At that time a good friend of mine was also his research fellow and, seeing the opportunity, I inquired and later became Dr. Conkling's summer research fellow. I completed my undergraduate research under his tutelage, concurrently becoming a member of the pyrotechnics seminar instructional staff, and continued through its final 27th year in 2010. Dr. Conkling continues to advise on this project and many other pyrotechnics and fireworks ventures out there, and I cannot express my gratitude enough for his mentorship, both academic and professional, and continued friendship to this day.

In continuing Dr. Conkling's work with this text, I have strived to take the core discussion of chemistry and pyrotechnics and update the main themes with recent advancements since the previous version was published, most notably in the world of "green pyrotechnics" and finding new formulations with decreased toxic effects to humans and the environment around us. The amount of research going into new pyrotechnic study is extensive, and I was able to include only a small segment of what is out there. I hope the reader will be inspired to use the many references and ideas to continue their own research and advance the state-of-the-art of pyrotechnics well into the 21st century.

Christopher J. Mocella
Annapolis, MD

Preface to the Second Edition: 2010

In the twenty-five years that have passed since the first edition of this book was published, the world of pyrotechnics and high energy materials has continued to undergo significant changes. The changes have been driven primarily by concerns for safety - of personnel working with energetic materials, of the communities located near facilities producing energetic materials, as well as concerns for the environment. One result of the pressure for change has been the promulgation of new government regulations placing restrictions on the materials that may be used in energetic mixtures, mandating numerous training programs, and initiating other actions - such as OSHA's Process Safety Management Standard - intended to eliminate accidents and incidents. And almost all of the personnel who entered the field of energetic materials in the 1950's and 1960's have now retired and taken with them their years of hands-on, practical knowledge in the preparation of energetic mixtures.

The International Pyrotechnics Seminars have grown in frequency and significance since the first edition of this book was published in 1985. There is now at least one seminar a year, either in Colorado or a non-United States location, and the proceedings from these seminars continue to be a great source of information regarding ongoing pyrotechnic research. In addition, the International Symposium on Fireworks (ISF) continues to be held every other year in Canada or elsewhere and these sessions always produce an interesting blend of technical papers.

The Pyrotechnics Guild International (PGI) has matured into a respected group of pyrotechnics enthusiasts and researchers who are making significant contributions in the area of fireworks technology.

A new journal, appropriately named *The Journal of Pyrotechnics*, has provided a vehicle for the prompt publication of research and review papers in the broad field of pyrotechnics.

On the negative side, we in the United States continue to lack any organized, broad-range academic programs covering the science of energetic materials. The New Mexico Institute of Technology is offering a program in explosive technology, and this is a great first step. More and more, the field of pyrotechnics is interacting with and adapting to changing technology in areas such as obscuration science and low-signature flame emission. Greater academic interest in the science of pyrotechnics would be a valuable asset for this country.

I'd like to thank my numerous colleagues and co-workers over the past twenty-five years for their interesting discussions, helpful comments, and constructive criticism. First on the list is Joseph Domanico, my friend and colleague with the Summer Pyrotechnic Seminar program at Washington College since 1984 – Joe is truly a unique individual with a broad knowledge of the field of energetic materials.

I also want to thank Christopher J. Mocella, Washington College '01 for his assistance with, and contributions to, the second addition of this book. Chris also participates as an instructor in the Summer Pyrotechnic Seminars at Washington College, and has become a valuable member of the team.

The thank-you list includes Tom Shook and Loy Aikman at Pine Bluff Arsenal, who got me involved in the military side of pyrotechnics two decades ago. Another special acknowledgement goes to David Pier of MP Associates, with whom I have enjoyed debating a wide variety of topics covering many aspects of energetic material for many years. Other friends and colleagues who have contributed to my education include the late Fred McIntyre, and another former Washington College chemistry student Jeff Johnson, with Orion Safety Products. I'd also like to thank the American Pyrotechnics Association for allowing me time to pursue my scientific interests for many years, and to TNT Fireworks and Orion Safety Products for allowing me to assist them with interesting projects since my retirement for the APA. More thanks go to the participants in my Summer Pyrotechnic Seminar programs for the past 27 years, and to my friends at the Bureau of Alcohol, Tobacco and Firearms, and Judy LeDoux and Debra Satkowiak in particular, for allowing me to assist them with training for their personnel.

Finally, I must acknowledge the importance of my wife Sandra to this project, without whose persistent encouragement this second edition would have been delayed even more. Aiding her in this motivational effort have been my two children, Melinda Conkling Hart and John A. Conkling, Jr., who in addition have presented us with four wonderful Texas grandchildren – John Maxey Hart, Edward Austin Hart, Jr., Julia Valliant Conkling, and the newest arrival John A. Conkling III. Maybe one of them will go on to a career in this fascinating field.

This book continues to stress basic chemical principles, rather than serve as a "how-to" guide for pyrotechnics. There are detailed published works covering many areas of energetic materials in detail. This book is intended as a bridge to allow people to transition with confidence from a knowledge of chemistry to an ability to apply chemical principles and logic to energetic materials. Discussion of the historical past of the field of pyrotechnics is, regrettably, kept to a minimum. The history of this field - particularly the work in the 20th century - is another book waiting for someone to pursue, but there should be no doubt in anyone's mind that pyrotechnics - like any other field of science - can only grow and expand as a science by building on past accomplishments in the field. Everyone's goal must continue to be to make the field of energetic materials as productive and useful, and as safe, as we possibly can.

John A. Conkling
Chestertown, MD

Preface to the First Edition: 1985

Everyone has observed chemical reactions involving pyrotechnic mixtures. Beautiful 4th of July fireworks, highway distress signals, solid fuel boosters for the Space Shuttle, and the black powder used by muzzle-loading rifle enthusiasts all have a common technical background.

The chemical principles underlying these high-energy materials have been somewhat neglected in the twentieth century by academic and industrial researchers. Most of the recent work has been goal-oriented rather than fundamental in nature (e.g., produce a deeper green flame). Many of the significant results are found in military reports, and chemical fundamentals must be gleaned from many pages of test results.

Much of today's knowledge is carried in the heads of experienced personnel. Many of these workers acquired their initial training during World War II, and they are presently fast approaching (if not already past) retirement age. This is most unfortunate for future researchers. Newcomers have a difficult time acquiring the skills and the knowledge needed to begin productive experiments. A background in chemistry is helpful, but much of today's modern chemistry curriculum will never be used by someone working in pyrotechnics and explosives. Further, the critical education in how to safely mix, handle, and store high-energy materials is not covered at all in today's schools and must be acquired in "on-the-job" training.

This book is an attempt to provide an introduction to the basic principles of high-energy chemistry to newcomers and to serve as a review for experienced personnel. It can by no means substitute for the essential "hands on" experience and training necessary to safely work in the field, but I hope that it will be a helpful companion. An attempt has been made to keep chemical theory simple and directly applicable to pyrotechnics and explosives. The level approaches that of an introductory college course, and study of this text may prepare persons to attend professional meetings and seminars dealing with high-energy materials and enable them to intelligently follow the material being presented. In particular, the International Pyrotechnic Seminars, hosted biannually in the United States by the Illinois Institute of Technology Research Institute in conjunction with the International Pyrotechnics Society, have played a major role in bringing researchers together to discuss current work. The Proceedings of the nine seminars held to date contain a wealth of information that can be read and contemplated by persons with adequate introduction to the field of high-energy chemistry.

I would like to express my appreciation to Mr. Richard Seltzer of the American Chemical Society and to Dr. Maurits Dekker of Marcel Dekker, Inc. for their encouragement and their willingness to recognize pyrotechnics as a legitimate branch of modern chemistry. I am grateful to Washington College for a sabbatical leave in 1983 that enabled me to finalize the manuscript. I would also like to express my thanks

to many colleagues in the field of pyrotechnics who have provided me with data as well as encouragement and to my 1983 and 1984 Summer Chemistry Seminar groups at Washington College for their review of draft versions of this book. I also appreciate the support and encouragement given to me by my wife and children as I concentrated on this effort.

Finally, I must acknowledge the many years of friendship and collaboration that I enjoyed with Mr. Joseph H. McLain, former Chemistry Department Chairman and subsequently President of Washington College. It was his enthusiasm and encouragement that dragged me away from the norbornyl cation and physical organic chemistry into the fascinating realm of pyrotechnics and explosives. The field of high-energy chemistry lost an important leader when Dr. McLain passed away in 1981.

John A. Conkling
Chestertown, MD

Authors

Dr. John A. Conkling received his BSc degree from Washington College in Chestertown, Maryland, in 1965 and his PhD in chemistry from Johns Hopkins University in 1969. Dr. Conkling returned to Washington College as a chemistry professor and colleague of Dr. Joseph McLain, who at the time was studying energetic materials and pyrotechnics, which Dr. Conkling began to study for his career. As former executive director and technical director of the American Pyrotechnics Association, Dr. Conkling is widely regarded as one of the world's foremost experts in pyrotechnics. Dr. Conkling conducted "The Summer Pyrotechnic Seminar" at Washington College for 29 years, and he is the original author of *Chemistry of Pyrotechnics: Basic Principles and Theory* in 1985 and second edition in 2010. Dr. Conkling retired from Washington College in 2012 and was awarded the Alumni Service Award in 2013. Dr. Conkling currently splits his time between Chestertown and Texas to be with his family.

Christopher J. Mocella received his BSc degree in chemistry from Washington College in Chestertown, Maryland, in 2001, having studied as a research associate under Dr. John Conkling. Chris continued to work with Dr. Conkling at his Summer Pyrotechnics Seminar series and assisted with the second edition of the Chemistry of Pyrotechnics text. Following graduate studies in chemistry at the University of Virginia, Chris took a position as a chemist with the U.S. federal government where he continues his career today. Chris lives with his wife and son near Annapolis, Maryland.

1 Introduction

Red, white, and blue bursts highlight at 4th of July fireworks spectacular.

Welcome to the world of energetic materials. Few people plan to spend their professional careers in this field of science and technology, but there is an old saying that "once you smell the smoke," you are hooked.

A PRIMER ON ENERGETIC MATERIALS

This book is an introduction to the basic principles and theory of pyrotechnics, with a focus on the chemistry and chemical interactions of the materials involved.

The term "pyrotechnics" comes from the Greek noun *pyr* for "a fire," and *techne* for "art," "craft skill," or "technique," which today might also be thought of as "science." Therefore, we might think of pyrotechnics as the "art of fire" or the "science of fire" and, as the reader will see, both scientific principles as well as some artistic creativity go into all pyrotechnic work.

Much of the "pyrotechnics" material in this text is also applicable to the closely related areas of propellants and explosives, all of which fall under the broad umbrella of "energetic materials" as shown in Figure 1.1. *Propellants* are designed to "deflagrate," or burn considerably rapidly—but not quite explode—under the confinement of a rocket engine or a gun barrel (noting that many propellants burn rather mildly

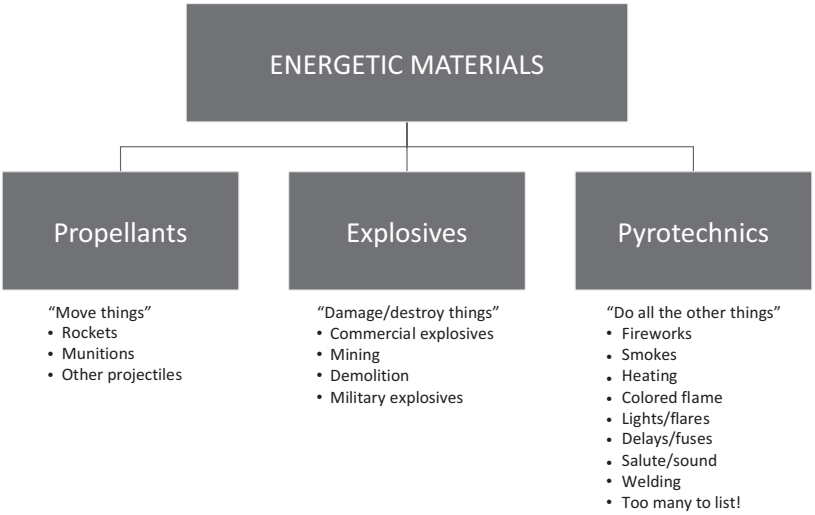

FIGURE 1.1 This chart shows a breakout of the disciplines of "energetic materials," classified as propellants (which move objects), explosives (which damage or destroy objects), and pyrotechnics (which is a catch-all for the many other functions that energetic materials can perform). While one could consider propellants and explosives types of pyrotechnics, the breadth and depth of the applications and study going into each affords them categories all their own.

in the open when unconfined). Propellants are formulated to maximize the volume of hot gas produced as the propellant material rapidly burns, pushing the hot gas out and, hopefully, the projectile in the intended direction. *Explosives* rapidly release large amounts of energy, and explosives engineers take advantage of this rapid release of energy, and the associated shock and pressure, to do work, often through a full "detonation" event (the difference between deflagrations and detonations will be discussed in a later chapter).

Pyrotechnic mixtures, our primary interest here, usually (but not always) react more slowly than explosive or propellant compounds, and the heat generated by the burning chemical mixture is used to produce combinations of light, color, smoke, gas, heat, and noise for a wide range of applications. Pyrotechnics, additionally, will combust as a smolder, as a fast burn, or as a full "deflagration" as opposed to a nearly instantaneous "detonation" of high explosives. Notably, a well-established research journal by the name *Propellants, Explosives, Pyrotechnics* has been publishing peer-reviewed research since 1976. The terms "high-energy chemistry" and "energetic materials" are also used to refer to these three closely related fields as a group.

The chemical reactions involved in pyrotechnics are of the classic electron-transfer or oxidation-reduction type (also colloquially referred to as "redox" reactions). Here, chemical species interact, exchange electrons, form new products, and release any excess energy. The mixtures to be studied are almost always solids at room temperature and are designed to function in the absence of external oxygen. Table 1.1 illustrates the reaction rates to be dealt with in that range along a continuum from very

TABLE 1.1
Classes of "High-Energy" Reactions

Class	Approximate Reaction Velocity	Example
Burning	Millimeters per second (mm/s)	Delay mixtures, colored smoke compositions
Deflagration	Meters per second (m/s)	Rocket propellants, confined black powder
Low-order detonation	>1 Kilometer per second (km/s)	Dynamite, TNT
High-order detonation	>5 km/s	Military explosives

slow burning to "instantaneous" detonations with rates greater than a kilometer/second. We should note that "detonation" refers to a specific, shock-propagated process for the reaction of an energetic material—the term "detonation" is *not* synonymous with "ignition" or "explosion." A detonation is an explosion, but so are high-rate deflagrations (especially when the material is confined).[1]

BLACK POWDER: THE ORIGINAL PYROTECHNIC

It is important to recognize early on that the same material may vary dramatically in its reactivity depending on its method of preparation and the conditions under which it is used. Black powder is an excellent example of this variability, and it is quite fitting that it serves as the first example of a "high-energy material" due to its historical significance (Kelly 2004; Buchanan 1996). Black powder is an intimate mixture of potassium nitrate (~75% by weight), charcoal (~15%), and sulfur (~10%), and its unique properties and characteristics continue to intrigue researchers even today (Brown and Rugunanan 1989; Hussain and Rees 1992; Maltitz 2001). A reactive black powder is no simple material to prepare and is a classic example of the "art" of manufacturing pyrotechnics. If one gently mixes the proper ratio of three components briefly, a powder is produced that is difficult to light and burns quite slowly. The same ingredients in the same proportions—when thoroughly mixed, moistened, and ground with a heavy stone wheel to achieve a high degree of homogeneity—become a mixture that readily ignites and burns rapidly. Particle size, purity of the starting materials, mixing time, and a variety of other factors—including the type of wood used to prepare charcoal—are all critical in producing high-performance black powder. Also, deviations from the 75/15/10 ratio of ingredients will lead to substantial changes in performance. Much of the early history of modern Europe is related to the availability of high-quality black powder for use in rifles and cannons. A good black powder manufacturer was essential to military success although he usually received far less recognition and decoration than the generals who used his product in their battles.

The burning behavior of black powder illustrates how a pyrotechnic mixture can vary in performance depending on the conditions of its use. A small pile of

[1] All detonations are explosions, but not all explosions are detonations!

loose black powder can be readily ignited by the flame of a match, producing an orange flash and a puff of smoke—but almost no noise. The same powder, tightly sealed in a strong paper tube but still in loose condition, will explode upon ignition by means of a fuse, rupturing the container with an audible noise. Black powder spread in a thin trail will quickly burn along the trail, a property used in making early fuses. Finally, if the powder is compressed in a tube, one end is left open, and that end is then constricted to partially confine the hot gases produced when the powder is ignited, a rocket-type device is produced. This varied behavior depending on confinement is quite typical of pyrotechnic mixtures and illustrates why one must be quite specific in giving instructions for preparing and using the materials discussed in this book.

Black powder is also a good example to use to illustrate the dramatic effect that moisture can have on pyrotechnic compositions. Damp powder is difficult to light and burns quite slowly—if at all—if ignition is successful. "Keep your powder dry" is still among the best pieces of advice for anyone making or using pyrotechnic materials, and hygroscopic chemicals—those that tend to rapidly pick up moisture in a humid environment—tend to be avoided by pyrotechnic formulators or kept in tight containers in environmentally controlled locations.

Why should someone working in pyrotechnics and related areas bother to study the basic chemistry involved? Throughout the 400-year "modern" history of the United States, many black powder factories have been constructed and put into operation. Although "smokeless powder" (a general term for propellants with more gaseous and less particulate combustion products than black powder, most commonly nitrocellulose-based) and other new materials have replaced black powder as a propellant and delay mixture in many applications, there is still a sizeable demand for black powder in both the military and civilian pyrotechnic industries due to its inexpensive ingredients and consistent properties when consistently prepared and stored. How many black powder factories are still operating in the United States today? Exactly one—GOEX Powder Inc., in Louisiana (GOEX, Inc. 2014). The remainder have been destroyed by explosions or closed because of the probability of one occurring: costs associated with critical worker safety are unable to compete economically with factories in other countries that are not subject to strict safety requirements, a potentially dangerous trade. In spite of a demand for the product, manufacturers are reluctant to engage in the production of the material because of the history of problems with accidental ignition during the manufacturing process. Why is black powder so sensitive to ignition? What can the chemist do to minimize the hazard? Can one alter the performance of black powder by varying the ingredients and their percentages, using theory as the approach rather than trial-and-error?

Black powder is not unique in its properties, however. High-energy materials like propellants and pyrotechnics are all designed to release energy in brief periods of time when an ignition stimulus is applied. New formulations continue to be developed, and new materials continue to be investigated for possible use in novel compositions. A pyrotechnic formulation consisting largely of magnesium powder and polytetrafluoroethylene (PTFE, also the chemical in the DuPont company's Teflon® product) is used to produce decoy flares for the protection of military aircraft from heat-seeking missiles. This material has acquired a "black powder"-like

reputation in recent years. Virtually every manufacturer of this material has suffered an incident producing magnesium-Teflon® composition, and the need to understand the basic science of the material has received much attention (Kubota and Serizawa 1987; Kuwahara, Matsuo and Shinozaki 1997). It is this type of problem and its analysis that we hope can be addressed a bit more thoroughly and scientifically with an understanding of the fundamental concepts presented in this book. If one accident can be prevented as a consequence of someone's better insight into the chemical nature of high-energy materials, achieved through study of this book, then the effort that went into its preparation was worthwhile.

A BRIEF HISTORY AND CULTURAL SIGNIFICANCE

The use of chemicals and chemical mixtures to produce heat, light, smoke, noise, and motion has existed for several thousand years, originating most likely in China or India. India has been cited as a particularly good possibility due to the natural deposits of saltpeter (potassium nitrate, KNO_3) found there (U.S. Army Material Command 1967).

Much of the early use of chemical energy involved military applications. "Greek fire," first reported in the 7th century AD, was probably a blend of sulfur, organic fuels, and saltpeter that generated flames and dense fumes when ignited. It was used in a variety of incendiary ways in both sea and land battles and added a new dimension to military science (U.S. Army Material Command 1967).

At some early time, most likely prior to 1000 AD, an observant scientist recognized the unique properties of a blend of potassium nitrate ("saltpeter"), sulfur ("brimstone"), and charcoal. Black powder was developed as the first "modern" high-energy composition. One interesting conjecture is that Chinese experimenters were searching for an elixir for immortality by mixing the "yin" of potassium nitrate and the "yang" of sulfur to create a "fire drug" (McLain 2017).

The Chinese were involved in pyrotechnics at an early date and had developed rockets by the 10th century (U.S. Army Material Command 1967) and were using black powder filled bamboo sticks thrown into fires to ward off evil spirits (McLain 2017). Fireworks followed, including firecrackers, and Chinese firecrackers became a popular item in the United States when trade was begun between the United States and China in the 1800s. Family correspondence passed down to Dr. John Conkling, the primary author of this book, shows that his great-great-grandfather, a merchant ship captain also named John Alexander Conkling, included "firecrackers" on his personal shopping list for a voyage to Canton, China (now Guangdong, China) in the 1830s. Dr. Conkling was not aware of this until after he had himself become involved in the field of pyrotechnics but was pleased to learn that the Conkling family was among the first importers of Chinese fireworks into the United States.

Chinese fireworks remain popular in the United States today, along with an assortment of other types of pyrotechnic articles that produce a wide assortment of visible and audible effects. The Japanese also produce beautiful fireworks, but, curiously, they do not appear to have developed the necessary technology until fireworks were brought to Japan around 1600 AD by an English visitor (Shimizu 1981). Many of the advances in fireworks technology over the past several centuries have come

from these two Asian nations, and China today is the world's primary supplier of both consumer and display fireworks.

The use of pyrotechnic and propellant mixtures for military purposes in rifles, rockets, flares, and cannons developed simultaneously with the civilian applications such as fireworks. Progress in both areas followed advances in modern chemistry, as new chemical compounds were isolated and synthesized and became available commercially to the pyrotechnician. Berthollet's discovery of potassium chlorate in the 1780s resulted in the ability to produce brilliant flame colors using pyrotechnic compositions, and color was added to the effects of sparks, noise, and motion previously available using potassium nitrate-based compositions.

The harnessing of electricity led to the manufacturing of magnesium and aluminum metals by electrolysis in the latter part of the 19th century, and bright white sparks and whiter light could then be produced. Strontium, barium, and copper compounds capable of producing vivid red, green, and blue flames also became commercially available during the 19th century, and modern pyrotechnic technology really took off.

Simultaneously, the discovery of nitroglycerine in 1846 by Sobrero in Italy, and Nobel's subsequent work with dynamite, led to the development of a new generation of true high explosives that were far superior to black powder for many blasting and explosives applications. These materials released their chemical energy through the *detonation* process, at rates much faster—and with greater accompanying blast pressure and shock—than the deflagration process by which propellants and pyrotechnics react upon ignition. The development of modern smokeless powder in the latter part of the 19th century—based on nitrocellulose and nitroglycerine—led to the demise of black powder as the main propellant for guns of all types and sizes.

Although black powder has been replaced in most of its former uses by newer and more energetic materials, it is important to recognize the important role black powder has played in modern civilization. Tenney Davis, addressing this issue in his classic book on the chemistry of explosives, wrote, "The discovery that a mixture of potassium nitrate, charcoal, and sulfur is capable of doing useful work is one of the most important chemical discoveries or inventions of all times... the discovery of the controllable force of gunpowder, which made huge engineering achievements possible, gave access to coal and to minerals within the earth, and brought on directly the age of iron and steel and with it the era of machines and of rapid transportation and communication" (Davis 1941). Black powder remains a viable energetic material today—it ignites readily and reliably and is quite stable in storage if kept dry, and it is commercially available in a range of grain sizes ranging from fine powder to granules the size of kernels of corn. Black powder is also fascinating because it is one of the very few materials produced by the chemical industry that is still made today using essentially the same materials and manufacturing process as it was produced 500 years ago.

Explosives are widely used today throughout the world for mining, excavation, demolition, and military purposes. Pyrotechnics are also widely used by the military for signaling, obscuration, and training simulators. Military technology is constantly striving to keep pace with advances in other areas of technology, such as thermal detection and "night vision" equipment. Civilian applications of pyrotechnics are

many and varied, ranging from the common match to highway warning flares ("fusees") to ever-popular fireworks and the spectacular "special effects" used to enhance movies, rock concerts, professional wrestling matches, sporting events, and theme park shows.

The fireworks industry remains perhaps the most visible example of pyrotechnics to the general public and also remains a major user of traditional black powder. This industry provides the pyrotechnician with the opportunity to fully display his skill at producing colors and other brilliant visual effects. The use of fireworks in the United States has not diminished. There has been a steady growth in consumption of fireworks from an estimated 30 million pounds in 1976 to over 285 million pounds in 2015, according to data compiled by the American Pyrotechnics Association (APA 2017).

Fireworks form a unique part of cultural heritage of many countries (Plimpton 1984). In the United States, fireworks have traditionally been associated with Independence Day—The Fourth of July. In England, large quantities are set off in commemoration of Guy Fawkes Day (November 5th), while the French use fireworks around Bastille Day (July 14th). Many countries use fireworks to celebrate the New Year on January 1st. Notably, in Germany, the use of fireworks by the public is limited to *one hour per year*: from midnight to 01:00 a.m. on January 1st—but it is reported to be quite a celebration. Much of the Chinese culture is associated with the use of firecrackers to celebrate New Year's and other important occasions, and this custom has been carried over to the Chinese communities throughout the world. The brilliant colors and booming noises of fireworks appear to have a universal appeal to our basic senses, eliciting "ooh's" and "aah's" from spectators regardless of where the fireworks are displayed—worldwide.

To gain an understanding of how these beautiful effects are produced, we will begin with a review of some basic chemical principles and then proceed to discuss various pyrotechnic systems.

2 Basic Chemical Principles

BLACK POWDER GRANULES: Black powder granules—the first commercial energetic material that has remained an article of commerce for over 1,000 years. This unique blend of potassium nitrate (saltpeter), charcoal, and sulfur (brimstone) has served as an explosive, a propellant, and a component in pyrotechnic devices such as safety fuses and squibs.

Most chemistry courses do not discuss energetic materials—explosives, propellants, and pyrotechnics—directly or by name. However, these materials all involve "chemistry in action" and produce their energetic output through chemical reactions. Many of the principles and logical thought processes that are taught in "Chem 101" directly apply to what will be covered in this book. Pyrotechnics are not magic, and the pyrotechnic chemist is no longer viewed as a wizard. When you are working in this field, and things seem to be making no sense, it's time to go back to the basics of science.

ATOMS AND MOLECULES

To understand the chemical nature of pyrotechnics and other energetic mixtures, one must begin at the atomic level. Two hundred years of elegant experiments and complex calculations have led to our present picture of the atom as the fundamental building block of matter. An atom consists of a small, dense nucleus containing

TABLE 2.1
Properties of the Subatomic Particles

Particle	Location	Charge	Mass, a.m.u.[a]	Mass, grams
Proton	In nucleus	+1	1.007	1.673×10^{-24}
Neutron	In nucleus	0	1.009	1.675×10^{-24}
Electron	Outside nucleus	−1	0.00549	9.11×10^{-28}

[a] a.m.u. = atomic mass unit, where 1 a.m.u. = 1.66×10^{-24} g.

positively-charged *protons* and neutral *neutrons*, surrounded by a large cloud of light, negatively-charged *electrons*. Table 2.1 summarizes the properties of these subatomic particles.

A particular *element* is defined by its *atomic number*—the number of protons in the nucleus (which will equal the number of electrons surrounding the nucleus in a neutral atom). For example, iron is the element of atomic number 26, meaning that every iron atom will have 26 protons in its nucleus. Chemists use a one or two-letter symbol for each element to simplify communication; iron, for example, is given the symbol Fe, from the old Latin word for iron, *ferrum*. The sum of the protons plus neutrons found in the nucleus is called the mass number. For some elements, only one mass number is found in nature. Fluorine (atomic number 9, mass number 19, symbol "F") is an example of such an element. Other elements are found in nature in more than one mass number. Iron is found as mass number 56 (91.52% abundance of all iron found in nature), 54 (5.90% abundance), 57 (2.245% abundance), and 58 (0.33% abundance). These different mass numbers of the same element are called *isotopes*[1] and vary in the number of neutrons found in the nucleus and therefore vary in their mass as well. *Atomic weight* refers to the average mass found in nature of all the atoms of a particular element; the atomic weight of iron is 55.847. For calculation purposes, these atomic weights are used for the mass of a particular element. Table 2.2 contains symbols, atomic numbers, and atomic weights for the elements. In practical terms, only elements 1–83 (hydrogen through bismuth) have use for "everyday" chemistry, since elements after bismuth are generally radioactive, expensive, inconvenient/unsafe to work with, or all three. Furthermore, the "transuranics" (beyond uranium) of 93 (neptunium) through 118 (oganesson) are either quite radioactive and unsafe to handle in normal circumstances or only exist for fractions of a second—after being synthesized in incredibly complex equipment—before decaying into lighter elements.

Chemical reactivity, and therefore pyrotechnic and explosive behavior, is determined primarily by the tendency for each element to gain or lose electrons during a chemical reaction. Calculations of theoretical chemists, with strong support from experimental studies, suggest that electrons in atoms are found in "orbitals" or

[1] The term "isotope" has been commonly and incorrectly used to mean "radioactive material" since certain isotopes of elements can be significantly radioactive, emitting gamma rays, neutrons, alpha particles, or beta particles. However, isotopes of elements are not necessarily radioactive, only those referred to as "radioisotopes" or "radionuclides."

TABLE 2.2
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Actinium	Ac	89	[227][b]
Aluminium	Al	13	26.9815386
Americium	Am	95	[243]
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	[210]
Barium	Ba	56	137.327
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	[272]
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Cesium	Cs	55	132.9054519
Calcium	Ca	20	40.078
Californium	Cf	98	[251]
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copper	Cu	29	63.546
Curium	Cm	96	[247]
Darmstadtium	Ds	110	[281]
Dubnium	Db	105	[268]
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	[252]
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	[257]
Fluorine	F	9	18.9984032
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	[270]
Helium	He	2	4.002602

(*Continued*)

TABLE 2.2 (*Continued*)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	[262]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	[276]
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	[237]
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	[259]
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.03588
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	[280]

(*Continued*)

TABLE 2.2 (*Continued*)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	[267]
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	[271]
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.94788
Technetium	Tc	43	[98]
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununbium[c]	Uub	112	[285]
Ununhexium	Uuh	116	[293]
Ununoctium	Uuo	118	[294]
Ununpentium	Uup	115	[288]
Ununquadium	Uuq	114	[289]
Ununtrium	Uut	113	[284]
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

This table is based on the 2005 table in *Pure Appl. Chem.,* **78**, 2051–2066 (2006).

[a] a.m.u. = atomic mass unit, where 1 a.m.u. = 1.66×10^{-24} g.

[b] Values enclosed in brackets are the mass number for the longest-lived isotope.

[c] Elements 112–118 were under review when the information from the academic journal *Pure and Applied Chemistry* published this technical information. They have since been named.