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The Chemistry of Explosives

2nd Edition

J. Akhavan

RSC Paperbacks

THE CHEMISTRY OF EXPLOSIVES

Second Edition

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RS•C

advancing the chemical sciences

WARNING STATEMENT

It is both dangerous and illegal to participate in unauthorized experimentation with explosives.

ISBN 0-85404-640-2

A catalogue record for this book is available from the British Library

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Published by The Royal Society of Chemistry, Thomas Graham House,
Science Park, Milton Road, Cambridge CB4 0WF, UK
For further information visit our web site at www.rsc.org

Typeset by Vision Typesetting Ltd, Manchester
Printed by TJ International Ltd, Padstow, Cornwall, UK

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Second Edition

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Preface

This book outlines the basic principles needed to understand the mechanism of explosions by chemical explosives. The history, theory and chemical types of explosives are introduced, providing the reader with information on the physical parameters of primary and secondary explosives. Thermodynamics, enthalpy, free energy and gas equations are covered together with examples of calculations, leading to the power and temperature of explosions. A very brief introduction to propellants and pyrotechnics is given, more information on these types of explosives should be found from other sources. This second edition introduces the subject of Insensitive Munitions (IM) and the concept of explosive waste recovery. Developments in explosive crystals and formulations have also been updated. This book is aimed primarily at 'A' level students and new graduates who have not previously studied explosive materials, but it should prove useful to others as well. I hope that the more experienced chemist in the explosives industry looking for concise information on the subject will also find this book useful.

In preparing this book I have tried to write in an easy to understand style guiding the reader through the chemistry of explosives in a simple but detailed manner. Although the reader may think this is a new subject he or she will soon find that basic chemistry theories are simply applied in understanding the chemistry of explosives.

No book can be written without the help of other people and I am aware of the help I have received from other sources. These include authors of books and journals whom I have drawn upon in preparing this book. I am also grateful for the comments from the reviewers of the first edition of this book.

I would particularly like to thank my husband Shahriar, who has always supported me.

Contents

<i>Chapter 1</i>	
Introduction to Explosives	1
Development of Blackpowder	1
Development of Nitroglycerine	2
Development of Mercury Fulminate	3
Development of Nitrocellulose	3
Development of Dynamite	4
Development of Ammonium Nitrate	4
Development of Commercial Explosives	5
Development of Permitted Explosives	5
Development of ANFO and Slurry Explosives	6
Development of Military Explosives	7
Development of Picric Acid	7
Development of Tetryl	8
Development of TNT	8
Development of Nitroguanidine	9
Development of PETN	9
Development of RDX and HMX	9
Polymer Bonded Explosives	11
Recent Developments	15
Insensitive Munitions	16
Pollution Prevention	16
 <i>Chapter 2</i>	
Classification of Explosive Materials	21
Explosions	21
Atomic Explosions	21
Physical Explosions	22

Chemical Explosions	22
Chemical Explosives	22
Classification of Chemical Explosives	23
Primary Explosives	24
Secondary Explosives	26
Propellants	27
Chemical Data on Explosive Materials	27
Primary Explosives	27
Mercury Fulminate	27
Lead Azide	28
Lead Styphnate	29
Silver Azide	30
Tetrazene	31
Secondary Explosives	32
Nitroglycerine	32
Nitrocellulose	33
Picric Acid	34
Tetryl	36
TNT	37
Nitroguanidine	39
PETN	40
RDX	41
HMX	42
TATB	43
HNS	44
NTO	45
TNAZ	46
Other Compounds used in Explosive Compositions	47

Chapter 3

Combustion, Deflagration and Detonation 49

Combustion	49
Physical and Chemical Aspects of Combustion	50
Combustion of Explosives and Propellants	50
Deflagration	50
Detonation	52
Burning to Detonation	53
Shock to Detonation	53
Propagation of the Detonation Shockwave	54
Effect of Density on the Velocity of Detonation	56

Effect of Diameter of the Explosive Composition on the Velocity of Detonation	59
Effect of Explosive Material on the Velocity of Detonation	60
Classification of Explosives	62

Chapter 4

Ignition, Initiation and Thermal Decomposition 63

Ignition	63
Hotspots	64
Mechanisms for the Formation of Hotspots	64
Ignition by Impact and Friction	66
Friction	66
Impact	66
Classification of Explosives	67
Initiation Techniques	70
Explosive Train	70
Detonators	71
Igniters	71
Thermal Decomposition	72

Chapter 5

Thermochemistry of Explosives 74

Oxygen Balance	74
Decomposition Reactions	77
Kistiakowsky–Wilson Rules	78
Modified Kistiakowsky–Wilson Rules	79
Springall Roberts Rules	80
Heats of Formation	81
Heat of Explosion	83
Effect of Oxygen Balance	87
Volume of Gaseous Products of Explosion	88
Explosive Power and Power Index	90
Temperature of Chemical Explosion	90
Mixed Explosive Compositions	94
Atomic Composition of the Explosive Mixture	94
Oxygen Balance	96
Decomposition Reaction	96
Heat of Explosion	97
Volume of Gaseous Products	98

Energized Explosives	98
Addition of Aluminium	99
Force and Pressure of Explosion	100

<i>Chapter 6</i>	
Equilibria and Kinetics of Explosive Reactions	103
Equilibria	103
Products of Decomposition	104
The Water–Gas Equilibrium	105
Heat of Explosion	105
Temperature of Explosion	110
Kinetics of Explosive Reactions	111
Activation Energy	111
Rate of Reaction	112
Kinetics of Thermal Decomposition	113
Measurement of Kinetic Parameters	114
Differential Thermal Analysis	114
Thermogravimetric Analysis	116
Differential Scanning Calorimetry	116

<i>Chapter 7</i>	
Manufacture of Explosives	118
Nitration	118
C-Nitration	119
Picric Acid	119
Tetryl	120
TNT	120
TATB	121
HNS	123
O-Nitration	125
Nitroglycerine	125
Nitrocellulose	126
PETN	129
N-Nitration	131
RDX	131
HMX	135
Nitroguanidine	137
Ammonium Nitrate	138
Primary Explosives	138

Lead Azide	138
Mercury Fulminate	139
Tetrazene	140
Commercial Explosive Compositions	141
Ammonium Nitrate	141
Ammonium Nitrate Slurries	141
Ammonium Nitrate Emulsion Slurries	142
Dynamite	142
Military Explosive Compositions	143
Casting	143
Pressing	144
Ram and Screw Extrusion	147

Chapter 8

Introduction to Propellants and Pyrotechnics 149

Introduction to Propellants	149
Gun Propellants	149
Performance	149
Composition	150
Single-base Propellants	151
Double-base Propellants	151
Triple-base Propellants	152
Propellant Additives	152
High Energy Propellants	152
Liquid Propellants	152
Composite Propellants	153
Rocket Propellants	154
Performance	154
Composition	154
Double-base Propellants	155
Composite Propellants	155
Liquid Propellants	156
Gas-generating Propellants	157
Introduction to Pyrotechnics	157
Heat-producing Pyrotechnics	158
Primers and First Fires	158
Heat-generating Devices	159
Delay Compositions	160
Smoke-generating Compositions	160
Light-generating Compositions	161

Coloured Light	162
White Light	162
Noise-generating Pyrotechnics	162
Bang	162
Whistle	163
Bibliography	165
Subject Index	168

Chapter 1

Introduction to Explosives

DEVELOPMENT OF BLACKPOWDER

Blackpowder, also known as gunpowder, was most likely the first explosive composition. In 220 BC an accident was reported involving blackpowder when some Chinese alchemists accidentally made blackpowder while separating gold from silver during a low-temperature reaction. According to Dr Heizo Mambo the alchemists added potassium nitrate [also known as saltpetre (KNO_3)] and sulfur to the gold ore in the alchemists' furnace but forgot to add charcoal in the first step of the reaction. Trying to rectify their error they added charcoal in the last step. Unknown to them they had just made blackpowder which resulted in a tremendous explosion.

Blackpowder was not introduced into Europe until the 13th century when an English monk called Roger Bacon in 1249 experimented with potassium nitrate and produced blackpowder, and in 1320 a German monk called Berthold Schwartz (although many dispute his existence) studied the writings of Bacon and began to make blackpowder and study its properties. The results of Schwartz's research probably speeded up the adoption of blackpowder in central Europe. By the end of the 13th century many countries were using blackpowder as a military aid to breach the walls of castles and cities.

Blackpowder contains a fuel and an oxidizer. The fuel is a powdered mixture of charcoal and sulfur which is mixed with potassium nitrate (oxidizer). The mixing process was improved tremendously in 1425 when the Corning, or granulating, process was developed. Heavy wheels were used to grind and press the fuels and oxidizer into a solid mass, which was subsequently broken down into smaller grains. These grains contained an intimate mixture of the fuels and oxidizer, resulting in a blackpowder which was physically and ballistically superior. Corned blackpowder gradually came into use for small guns and hand

grenades during the 15th century and for big guns in the 16th century.

Blackpowder mills (using the Corning process) were erected at Rotherhithe and Waltham Abbey in England between 1554 and 1603.

The first recording of blackpowder being used in civil engineering was during 1548–1572 for the dredging of the River Niemen in Northern Europe, and in 1627 blackpowder was used as a blasting aid for recovering ore in Hungary. Soon, blackpowder was being used for blasting in Germany, Sweden and other countries. In England, the first use of blackpowder for blasting was in the Cornish copper mines in 1670. Bofors Industries of Sweden was established in 1646 and became the main manufacturer of commercial blackpowder in Europe.

DEVELOPMENT OF NITROGLYCERINE

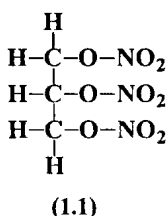
By the middle of the 19th century the limitations of blackpowder as a blasting explosive were becoming apparent. Difficult mining and tunnelling operations required a ‘better’ explosive. In 1846 the Italian, Professor Ascanio Sobrero discovered liquid nitroglycerine [$\text{C}_3\text{H}_5\text{O}_3(\text{NO}_2)_3$]. He soon became aware of the explosive nature of nitroglycerine and discontinued his investigations. A few years later the Swedish inventor, Immanuel Nobel developed a process for manufacturing nitroglycerine, and in 1863 he erected a small manufacturing plant in Helenborg near Stockholm with his son, Alfred. Their initial manufacturing method was to mix glycerol with a cooled mixture of nitric and sulfuric acids in stone jugs. The mixture was stirred by hand and kept cool by iced water; after the reaction had gone to completion the mixture was poured into excess cold water. The second manufacturing process was to pour glycerol and cooled mixed acids into a conical lead vessel which had perforations in the constriction. The product nitroglycerine flowed through the restrictions into a cold water bath. Both methods involved the washing of nitroglycerine with warm water and a warm alkaline solution to remove the acids. Nobel began to license the construction of nitroglycerine plants which were generally built very close to the site of intended use, as transportation of liquid nitroglycerine tended to generate loss of life and property.

The Nobel family suffered many set backs in marketing nitroglycerine because it was prone to accidental initiation, and its initiation in bore holes by blackpowder was unreliable. There were many accidental explosions, one of which destroyed the Nobel factory in 1864 and killed Alfred’s brother, Emil. Alfred Nobel in 1864 invented the metal ‘blasting cap’ detonator which greatly improved the initiation of blackpowder. The detonator contained mercury fulminate [$\text{Hg}(\text{CNO})_2$] and was able

to replace blackpowder for the initiation of nitroglycerine in bore holes. The mercury fulminate blasting cap produced an initial shock which was transferred to a separate container of nitroglycerine via a fuse, initiating the nitroglycerine.

After another major explosion in 1866 which completely demolished the nitroglycerine factory, Alfred turned his attentions into the safety problems of transporting nitroglycerine. To reduce the sensitivity of nitroglycerine Alfred mixed it with an absorbent clay, 'Kieselguhr'. This mixture became known as ghur dynamite and was patented in 1867.

Nitroglycerine (1.1) has a great advantage over blackpowder since it contains both fuel and oxidizer elements in the same molecule. This gives the most intimate contact for both components.



Development of Mercury Fulminate

Mercury fulminate was first prepared in the 17th century by the Swedish-German alchemist, Baron Johann Kunkel von Löwenstern. He obtained this dangerous explosive by treating mercury with nitric acid and alcohol. At that time, Kunkel and other alchemists could not find a use for the explosive and the compound became forgotten until Edward Howard of England rediscovered it between 1799 and 1800. Howard examined the properties of mercury fulminate and proposed its use as a percussion initiator for blackpowder and in 1807 a Scottish Clergyman, Alexander Forsyth patented the device.

DEVELOPMENT OF NITROCELLULOSE

At the same time as nitroglycerine was being prepared, the nitration of cellulose to produce nitrocellulose (also known as guncotton) was also being undertaken by different workers, notably Schönbein at Basel and Böttger at Frankfurt-am-Main during 1845-47. Earlier in 1833, Braconnot had nitrated starch, and in 1838, Pelouze, continuing the experiments of Braconnot, also nitrated paper, cotton and various other materials but did not realize that he had prepared nitrocellulose. With the announcement by Schönbein in 1846, and in the same year by

Böttger that nitrocellulose had been prepared, the names of these two men soon became associated with the discovery and utilization of nitrocellulose. However, the published literature at that time contains papers by several investigators on the nitration of cellulose before the process of Schönbein was known.

Many accidents occurred during the preparation of nitrocellulose, and manufacturing plants were destroyed in France, England and Austria. During these years, Sir Frederick Abel was working on the instability problem of nitrocellulose for the British Government at Woolwich and Waltham Abbey, and in 1865 he published his solution to this problem by converting nitrocellulose into a pulp. Abel showed through his process of pulping, boiling and washing that the stability of nitrocellulose could be greatly improved. Nitrocellulose was not used in military and commercial explosives until 1868 when Abel's assistant, E.A. Brown discovered that dry, compressed, highly-nitrated nitrocellulose could be detonated using a mercury fulminate detonator, and wet, compressed nitrocellulose could be exploded by a small quantity of dry nitrocellulose (the principle of a Booster). Thus, large blocks of wet nitrocellulose could be used with comparative safety.

DEVELOPMENT OF DYNAMITE

In 1875 Alfred Nobel discovered that on mixing nitrocellulose with nitroglycerine a gel was formed. This gel was developed to produce blasting gelatine, gelatine dynamite and later in 1888, ballistite, the first smokeless powder. Ballistite was a mixture of nitrocellulose, nitroglycerine, benzene and camphor. In 1889 a rival product of similar composition to ballistite was patented by the British Government in the names of Abel and Dewar called 'Cordite'. In its various forms Cordite remained the main propellant of the British Forces until the 1930s.

In 1867, the Swedish chemists Ohlsson and Norrbín found that the explosive properties of dynamites were enhanced by the addition of ammonium nitrate (NH_4NO_3). Alfred Nobel subsequently acquired the patent of Ohlsson and Norrbín for ammonium nitrate and used this in his explosive compositions.

Development of Ammonium Nitrate

Ammonium nitrate was first prepared in 1654 by Glauber but it was not until the beginning of the 19th century when it was considered for use in explosives by Grindel and Robin as a replacement for potassium nitrate in blackpowder. Its explosive properties were also reported in 1849 by

Reise and Millon when a mixture of powdered ammonium nitrate and charcoal exploded on heating.

Ammonium nitrate was not considered to be an explosive although small fires and explosions involving ammonium nitrate occurred throughout the world.

After the end of World War II, the USA Government began shipments to Europe of so-called Fertilizer Grade Ammonium Nitrate (FGAN), which consisted of grained ammonium nitrate coated with about 0.75% wax and conditioned with about 3.5% clay. Since this material was not considered to be an explosive, no special precautions were taken during its handling and shipment – workmen even smoked during the loading of the material.

Numerous shipments were made without trouble prior to 16 and 17 April 1947, when a terrible explosion occurred. The SS Grandchamp and the SS Highflyer, both moored in the harbour of Texas City and loaded with FGAN, blew up. As a consequence of these disasters, a series of investigations was started in the USA in an attempt to determine the possible causes of the explosions. At the same time a more thorough study of the explosive properties of ammonium nitrate and its mixtures with organic and inorganic materials was also conducted. The explosion at Texas City had barely taken place when a similar one aboard the SS Ocean Liberty shook the harbour of Brest in France on 28 July 1947.

The investigations showed that ammonium nitrate is much more dangerous than previously thought and more rigid regulations governing its storage, loading and transporting in the USA were promptly put into effect.

DEVELOPMENT OF COMMERCIAL EXPLOSIVES

Development of Permitted Explosives

Until 1870, blackpowder was the only explosive used in coal mining, and several disastrous explosions occurred. Many attempts were made to modify blackpowder; these included mixing blackpowder with ‘cooling agents’ such as ammonium sulfate, starch, paraffin, *etc.*, and placing a cylinder filled with water into the bore hole containing the blackpowder. None of these methods proved to be successful.

When nitrocellulose and nitroglycerine were invented, attempts were made to use these as ingredients for coal mining explosives instead of blackpowder but they were found not to be suitable for use in gaseous coal mines. It was not until the development of dynamite and blasting