Journal of Pyrotechnics

Issue Number 1, Summer 1995

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Observations on the Heights Attained by Spherical Firework Shells

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ABSTRACT

This paper examines previously published information on the heights attained by spherical firework shells and proposes some empirical relationships that enable rough estimates to be made of the height attained from knowledge of either the mass or the diameter of the shell.

Keywords: shell height, shell mass, lift charge mass, shell diameter

Introduction

Shimizu[1] has discussed factors that can be important in determining the height attained by shells launched from mortars, and has presented some data illustrating the relationships between height and the mass of both the shell and its lift charge.

Related work from Contestabile and co-workers[2] has also provided some information, and studies of this general type have helped to identify a number of variables that can be important in determining shell height. For example, the fit of the shell in the tube, the composition and grain size of the lift charge, the mass of the lift charge, the type of shell, its density, the mass of the shell, and the length of the mortar are all factors that can exert an influence.

Kosanke and Kosanke have also reported work that has examined the role of mortar tilt angle and wind speed in determining the height attained by shells.[3] Additionally, they have examined the lateral drift of shells from their predicted paths caused by the tumbling motion in flight.[4]

As well as the factors affecting shell height identified above, the burning time of the fusing arrangement (delay time) will also be important in determining the height at which the burst occurs.

A recent paper[5] reported noise measurements for a range of fireworks and also contained some information, see Table 1, relating to the heights that can be attained by various spherical shells. These results were examined initially by plotting the height of burst of each shell against

Table 1. Heights Attained by Various Spherical Fireworks Shells.

Shell	Gross Mass, M_1 (g)	Lift Charge Mass, M_2 (g)	Height (m)		
			Test 1	Test 2	Test 3
125 mm Green Peony	763.7	76.3	129	190	175
125 mm Purple Peony	754.6	49.4	224	168	195
125 mm Spanish White	767.6	93.0	106	73	109
100 mm Spanish White	527.4	72.0	62	68	70
100 mm Red Silk	246.4	50.3	98	96	71
100 mm Purple Peony	429.8	37.8	146	132	152
75 mm Spanish White	240.4	38.1	68	62	76
75 mm Purple Peony	176.9	20.9	121	94	118

both the gross mass (M_1) and the mass of the lift charge (M_2). The forms of dependence found prompted the examination of literature data presented in this paper.

Much of the published data on shell heights relates to experimental shells which may not always fit generally accepted design criteria. These are included in this paper because of the lack of any other detailed information, but it is possible that some of the findings may have to be amended when more results for normal shells become available.

Discussion

Fulcanelli[6] and literature from Westech[7] suggest that linear relationships can link M_2 with M_1. This would require that the ratio of M_2/M_1 is constant, which is not the case for the shells listed in Table 1 and was not found by Contestabile[2] or on examination of Shimizu's data.[1]

Similarly, the dependence of height attained on the ratio of propelled mass ($M_1 - M_2$) to propelling mass (M_2) for shells from two independent sources[1,5] indicates that different relationships can apply.

Shimizu[1] has reported different dependences on M_2 of the height attained by 120 and 150 mm shells, and, although the basis for these observations was not clear, it was felt that an important factor could be that not all the energy produced by the lift charge is used to drive the shell from the mortar. It is possible that the observed differences could relate to the relative magnitude of the losses incurred in propelling gases from the mortar tube.[1]

The quantity of lift charge used in a shell is related to its mass and size[8] for ballistic reasons and also because the magnitude of the effects from larger shells creates an additional requirement for them to function at progressively greater altitudes. The height attained by shells, if optimum fuse burning times apply and no other considerations predominate, would therefore be expected to be related to the energy input at launch. Figure 1 shows that if launch noise measured at 25 m is used as a rough measure of

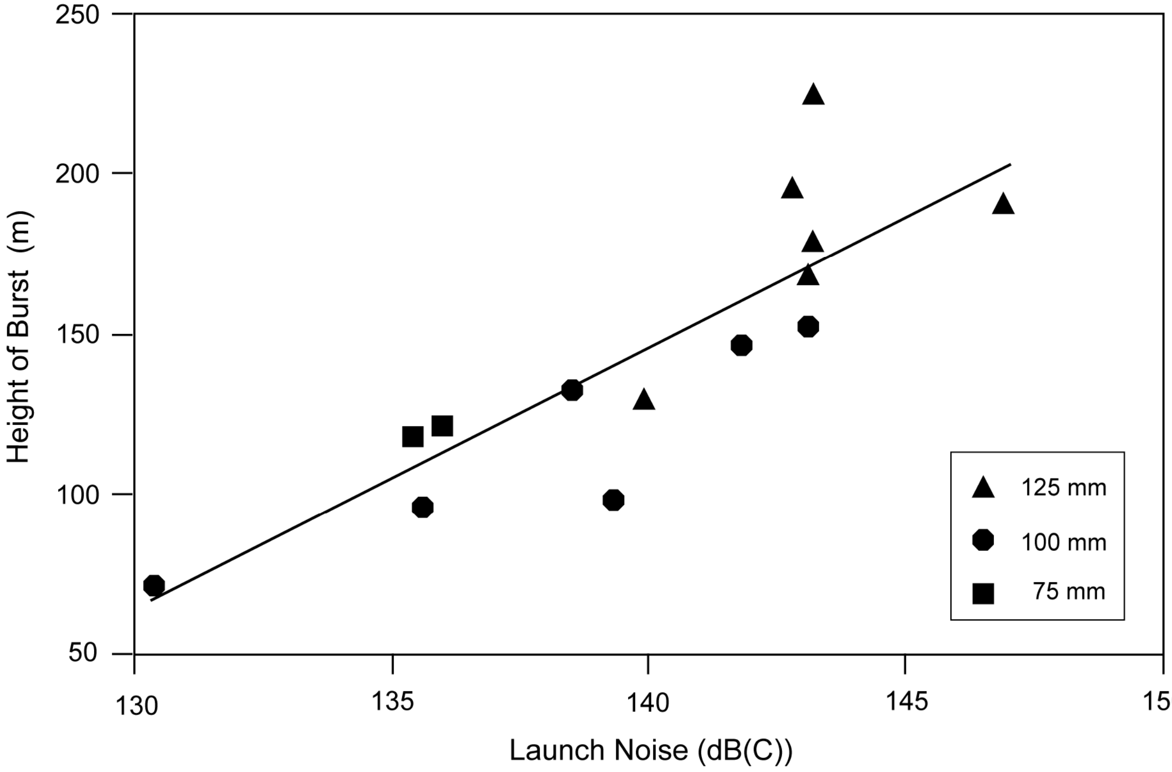

Figure 1. The dependence of height of burst on launch noise for shells with diameters 75 – 125 mm.

energy input to the shell, then a relationship of this type holds for those shells of 75, 100 and 125 mm diameter in Table 1 for which launch sound pressure level measurements are available.[5]

However, the limited data in Table 1 indicate that the height of burst decreases with M_2 for each size of shell, as was reported by Shimizu[1] for 150 mm shells containing more than 60 g of lift charge. This may reflect the different design approaches of the manufacturers of specific fireworks since a number of groupings are discernible (e.g., white shells are characterized by high M_2 and low heights of burst for each shell size).

It is possible to examine these results in a wider context by comparison with additional published work. Figure 2 summarises Shimizu's data, including some work with large diameter shells (ref. 1, Table 35). Although different modes of construction may have been employed for the shells and a number of other variables could be important in influencing performance, the general trend indicates an increase in burst height with M_2 up to a height of about 400 m, when considerations relating to visibility by the audience may start to predominate as a design issue. The form of Figure 2 is in agreement with that reported by Shimizu[1] (for 150 mm diameter shells) and by Contestabile[2] (for 140 mm diameter shells with M_1 = 1361 g); in both studies the height attained by the shells was seen to decrease at high values of M_2.

Shimizu has also examined the dependence of the height attained by shells on their mass, and attempted to obtain an indication of the optimum shell mass to give a maximum height. From the published results[1] for 120 mm shells, it is apparent that in order to attain a maximum height, the mass of the shell must be greater than 550 g. For 150 mm shells, Shimizu concludes that a maximum height of about 280 m would be obtained with shells having a mass of 1.2 kg.

The heights reached by those aerial fireworks in Table 1 for which the gross mass was known were plotted on the same graph as results from the literature, primarily those published by Shimizu. The resulting dependence, Figure 3, indicates that, even with some variation in the per-

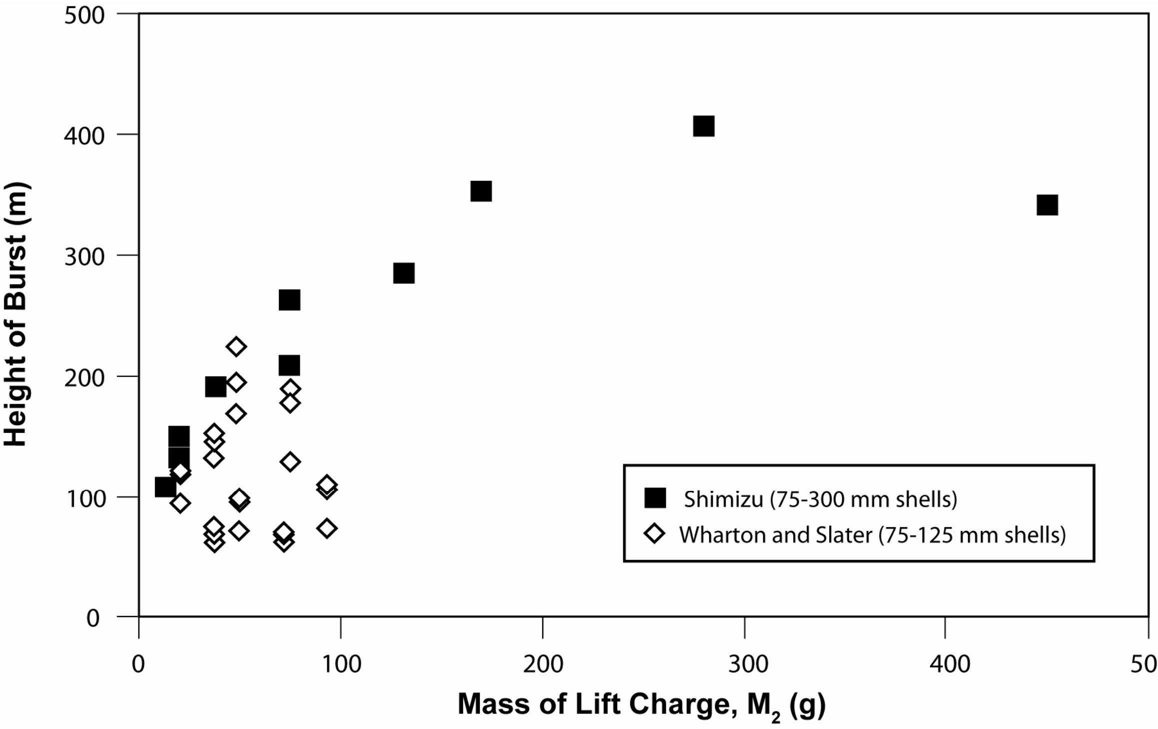

Figure 2. The relationship between height of burst and the mass of lift charge for a range of shell sizes.

formance of individual shells of a particular type, height increases with M_1 and an optimum height of about 400 m is reached as M_1 approaches 5 kg. Although the range of shell masses in the study by Contestabile and coworkers[2] was limited, data calculated for the heights of the (mainly dummy) shells were found to be evenly distributed about the line summarising the general form of the dependence in Figure 3. As a result of sample variability, Figure 3 contains insufficient data to substantiate previous proposals[1,2] that for each shell size there is a certain mass that will give a maximum height.

Details of the determination of shell burst heights from acoustic measurements have been presented in the literature[9] and work has recently been published[10] reporting the application of an electronic method.[11] The results for the mean height obtained using this technique are plotted with Shimizu's data and the mean values from reference 5 in Figure 4.

It has previously been reported[11] that shells burst at heights of 100 feet per inch of shell diameter, and this relationship was subsequently modified by Kosanke, Schwertley and Kosanke[10] to incorporate a 150 feet correction factor for shells having diameters of less than 12 inches (305 mm).

Published data indicate substantial variations in the performance of shells of the same type, e.g., in 8 trials with 255 mm shells[10] the highest burst height was 422 m and the lowest 206 m, and different modes of construction between shell types will also exert an influence. Nevertheless, Figure 4 suggests that there is a strong correlation between mean burst height and shell size. The dependence shown passes through the origin and yields the approximate relationship of 1.4 m of height per mm of shell diameter.

The general relationship in Figure 4 for spherical shells may also apply to cylindrical shells since a height of 105 m has been reported by Kosanke and Kosanke for a 100 mm cylindrical shell.[12]

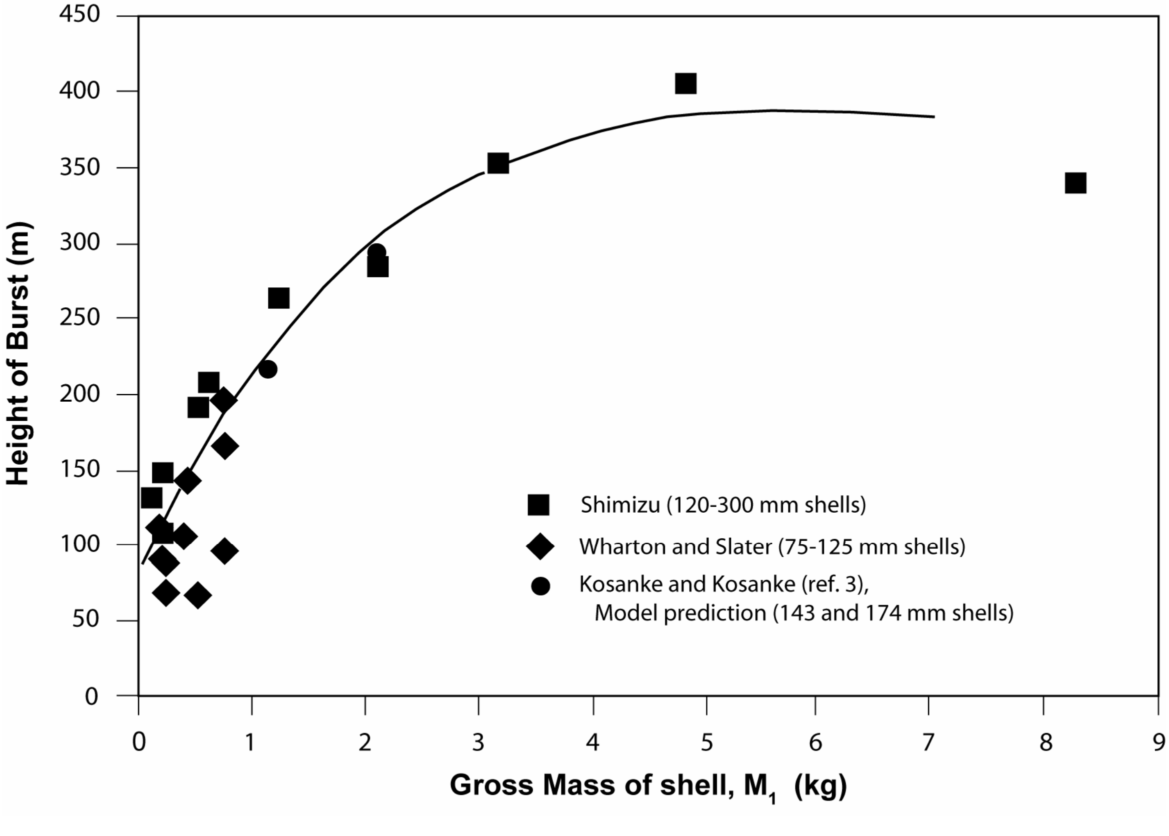

Figure 3. The dependence of height of burst on shell mass.

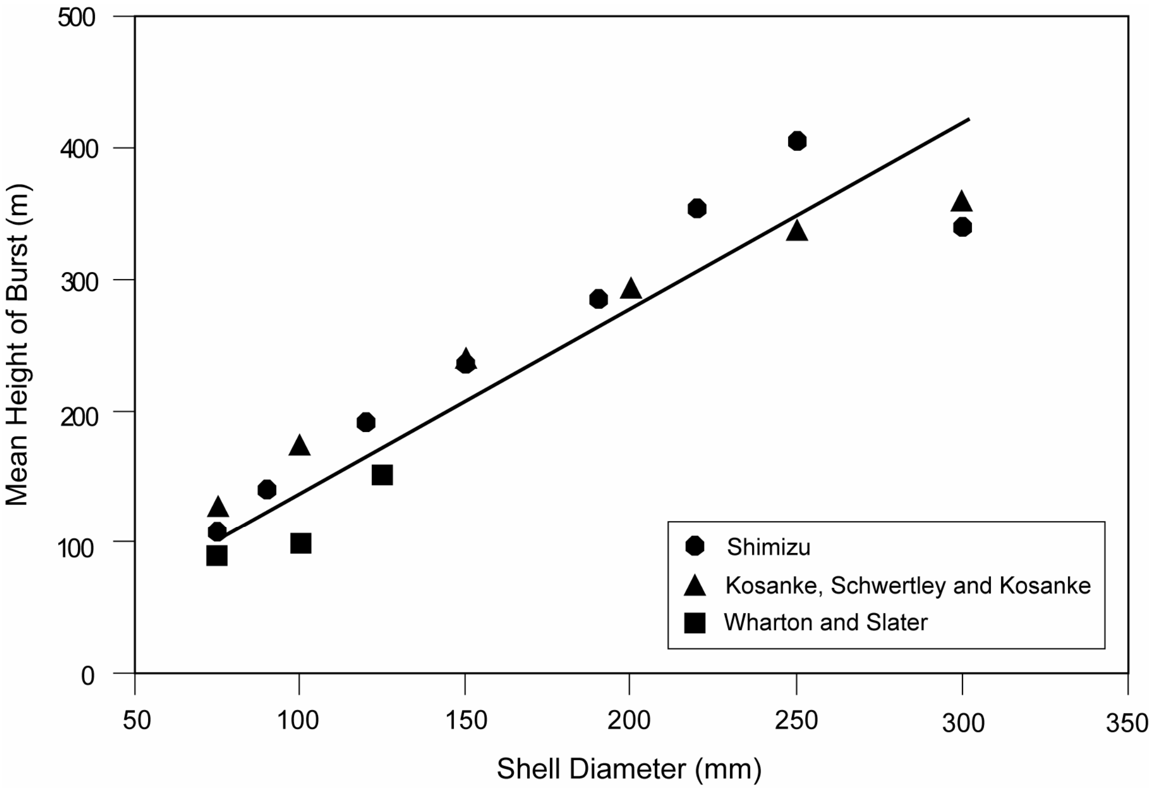

Figure 4. The dependence of the mean height of burst of shells on diameter.

Conclusion

Even though many variables (e.g., mode of construction, fuse burning time, mortar diameter) can affect the performance of firework shells, examination of literature data for the heights attained has indicated that common empirical relationships may link the height of burst with the shell diameter and the gross mass for a range of spherical shells.

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[Submitted February, 1995]

Observations on the Behaviour of Seamed Steel Mortar Tubes

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ABSTRACT

This paper reports results taken from a wider investigation of the effect of various parameters on the fragmentation behaviour of steel firework mortar tubes. During simulated misfire experimental information was obtained relating to the role of the weld in determining rupture behaviour in seamed steel mortar tubes. The results have helped to resolve different opinions on the hazard posed by fragmentation of welded and seamless mortar tubes.

Keywords: mortar, fireworks, steel tube, seamed tube

Introduction

Accidents involving misfires in mortar tubes have been reported for over 100 years.[1] Generally, the shell fails to leave the mortar prior to the burst charge operating, and potentially lethal fragments are projected over a large area when the mortar tube shatters.

After an accident in 1988, at the Glasgow Garden Festival as a result of which a firework operator lost a leg,[2] the UK Health and Safety Executive examined the extent of current knowledge relating to the safe use of mortar tubes. Little published material was available at that time and therefore a programme of research was initiated to provide information on the fragmentation characteristics of different mortars tube types and the effectiveness of mitigation measures such as mortar tube burial and sandbagging. The need for such work was reinforced by subsequent accidents in Japan[2] during 1989 and two reports of prematurely exploding shells from the USA[3] in 1994. It is envisaged that safety-related information of this type could form an important input to the development of Guidance for firework display operators.

A recent survey of factors relating to the use of mortars at firework displays[4] provided information on the types of shells and mortar tubes commonly used in the UK. This enabled an experimental programme to be designed to investigate the fragmentation behaviour of a range of steel tubes when various types of firework shells were exploded in them.

It has been previously reported[2] that there are conflicting views in the literature on the suitability of seamless steel tubes for use as firework mortar tubes. The NFPA code[5] states that either seamed or seamless tubes are suitable, while Shimizu[6] suggests that seamless mortar tubes are unsafe because when they burst the fragments radiate in all directions. Shimizu recommends the use of welded tubes because he feels that they will fail preferentially at the weld and therefore the fragment danger area can be predicted. The Canada Centre for Mineral and Energy Technology (CANMET) has recently carried out a wide ranging study of firework mortar materials,[7] which included sheet steel spot-welded tubes. Their work considers the fragmentation of mortar tubes but does not discuss the position of tube failure in relation to the tube seam. A comparison of seamed and seamless tubes was therefore carried out as part of our wider study in order to resolve the differences between the published advice.

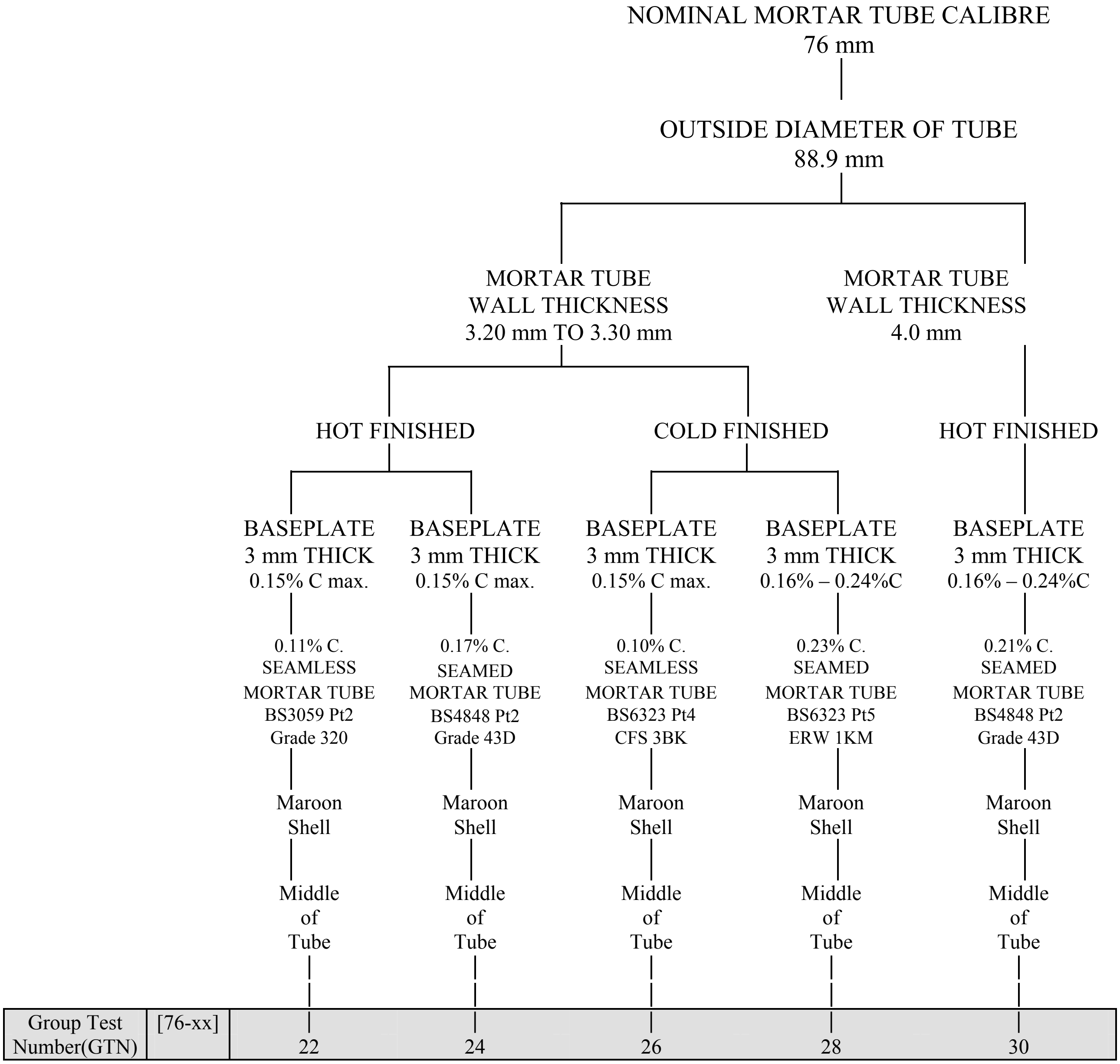
Experimental

Details of the mortar tubes used to provide data for this paper are given in Figures 1a and 1b. The variables shown in the Figures (percent carbon, wall thickness, type of finish, etc.) were chosen for the detailed study. A discussion of the reasons for their selection will be given in the full paper.[8]

The weld along the seamed tubes was formed using an electric resistance welding method. Baseplates for the 76 mm and 152 mm calibre tubes were 3 mm and 6 mm thick, respectively, and were fitted inside the tube wall and continuously welded into place using a Metal Inert Gas (MIG) welding technique.

Maroon shells for 76 mm and 152 mm calibre tubes and cylindrical multibreak shells for 152 mm calibre tubes were used because previous work[4] had identified that these types of shell were considered to pose the greatest fragmentation hazard.

Each group of tests in the full study was allocated a Group Test Number (GTN), these have



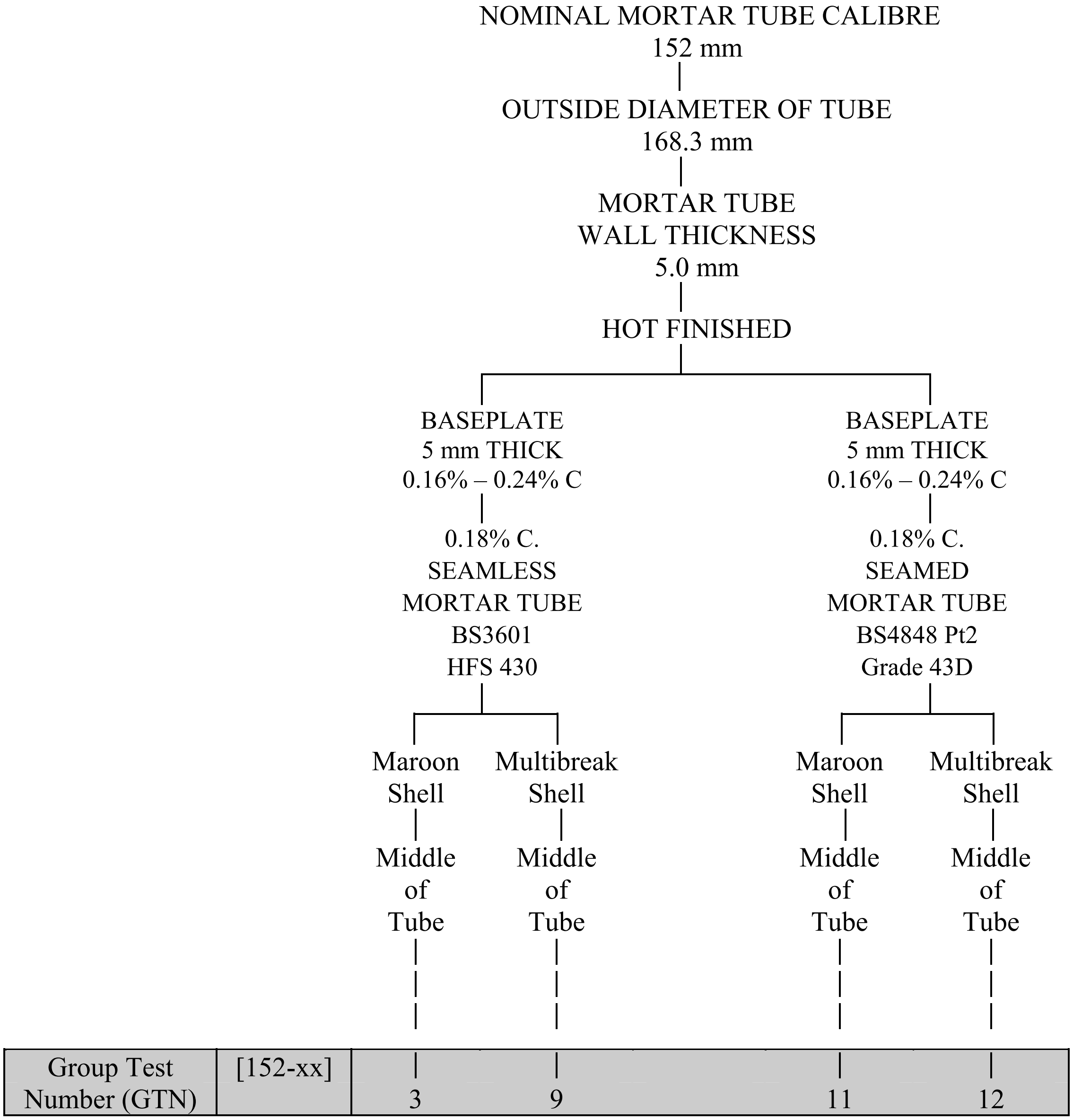
Mortar tube 600 mm long [exceeds NFPA min. of 21" (533 mm)]

Figure 1a. Firing programme for seamed and seamless mortar tubes.

been retained in this paper and are included in Figures 1a and 1b. A minimum of three tests was carried out on all the Group Test Numbers shown.

Experiments were carried out in a Blast Cell, 4 m square and 3.6 m high, which had a polyethylene sheet pinned over the thick wooden wall lining. Tests were done with the mortars positioned in the centre of the Blast Cell and seamed tubes placed so that the seam faced in the same direction each time.

During the course of the full study,[8] it was demonstrated that the lift charge made no measurable difference to the number of fragments produced in steel mortar tubes. Therefore, shells were fired with their lift charges removed. This allowed the shells to be suspended from insulated copper wire slings so that the half height of the shell was aligned with the half height of the mortar tube. The wire was taped to the shell, hooked over the top of the mortar tube and taped into position. Wire 0.56 mm in diameter was used for all except the 152 mm calibre mul-



Mortar tubes 1000 mm long [exceeds NFPA min. of 37" (940 mm)]

Figure 1b. Firing programme for seamed and seamless mortar tubes.

tibreak shells which, because of their larger mass, required wire of 1.25 mm diameter.

Tubes of 152 mm calibre were free standing, whereas the 76 mm calibre tubes were supported by inserting the tube base into a sheet of expanded polystyrene 50 mm thick and 450 mm square. It was considered that the constraint of the support would be insufficient to affect the fragmentation of the tube.

For each group of tests the x, y and z co-ordinates were recorded for fragments embedded in the wooden Cell lining, and for 'witness marks' made on the polyethylene sheet by deflected projectiles. A 'witness mark' was defined as a mark or cut on the plastic sheeting caused by a projectile that had not embedded into the wooden Cell lining at that point. The x, y co-ordinates described the plane of the floor, and the z co-ordinate the vertical displacement. Specific information about the trajectory of a particular fragment could not be inferred from the witness mark data but it was considered useful as a separate measure of the overall distribution of projectiles when a mortar tube burst. The distribution of fragments and witness marks on each wall of the Cell was examined in order to determine whether the fragments/witness marks had any directional characteristics.

Results

All the 76 mm calibre seamed and seamless mortar tubes that were tested ruptured when using maroon shells, while the tests with 152 mm seamed tubes showed that some tubes ruptured and others were only deformed. Table 1 indicates that some tubes failed along the welded seam while others did not. A total of nine 76 mm calibre seamed tubes were examined and it was found that four failed away from the seam. In the seven tests carried out on seamed 152 mm calibre tubes only two tubes ruptured, one along the seam and the other away from the seam (see Table 1).

No fragments were found embedded in the wooden Cell lining after any of the tests. The mean number of witness marks produced by 76 mm calibre, 3.25 mm wall thickness, seamed and seamless tubes was 6.5 and 12.5, respectively, while the equivalent value for the seamed 4 mm wall thickness tube was 6.0. In all tests the witness marks appeared to be randomly distributed on the walls of the Cell.

Table 1. Failure Details for Seamed Tubes.

Test Number	Group Test Number (GTN)	Calibre (mm)	Wall Thickness (mm)	Shell Type	Ruptured Along the Seam? (Y/N)
94/09/20/MA/04 94/09/20/MA/05 94/09/20/MA/06	76-24	76	3.25	Maroon	Y Y Y
94/09/29/MA/04 94/09/29/MA/05 94/09/29/MA/06	76-28	76	3.25	Maroon	Y N N
94/09/29/MA/07 94/09/29/MA/08 94/09/29/MA/09	76-30	76	4	Maroon	Y N N
94/10/06/MA/01 94/10/10/MA/01 94/10/10/MA/02	152-11	152	5	Maroon	Y Did not rupture Did not rupture
94/12/05/MU/10 94/12/05/MU/11 94/12/12/MU/01 94/10/20/MU/03	152-12	152	5	Cylindrical multibreak	Did not rupture Did not rupture Did not rupture N

Discussion

There is clear evidence from the study to indicate that the mode of failure of seamed tubes is not always consistent. Four of the nine 76 mm calibre tubes that failed had split away from the weld, while one out of two of the 152 mm calibre tubes that failed split away from the weld. The random distribution of the witness marks from the tests suggests that failure of seamed tubes does not occur preferentially at any one position on the tube. This work indicates that the technical basis from which safety procedures require specific positioning of the mortar seam may need to be examined in detail.

Some explanation of the above observations can be made by considering the purpose for which the tubes were originally manufactured. In the UK, mortar tubes are commonly made from commercially available steel tube used for general engineering purposes, where reproducible strength is required throughout the tube's length and circumference. Accordingly, when seamed tube is made, the manufacturers produce welded seams of comparable strength to the steel in the main body of the tube. This means that the seamed tubes should perform as well as the equivalent seamless tube and that the position at which the rupture originates cannot be predicted with any degree of certainty.

As the sheet steel tubes used in the CANMET study[7] were spot welded, the weld could be the weakest point in the tube, which would therefore be expected to fail at the seam. With tubes of this type it is possible that fragment trajectories may be predicted, but further work would be necessary to confirm this.

The mean number of witness marks observed for seamed tubes was approximately half that recorded for seamless tubes. This suggests that the number of projectiles produced from seamed tubes is less than that of equivalent seamless tubes, which may be a significant factor when considering the safety of such tubes. However, the number of witness marks does not directly measure the number of tube fragments produced because projectiles can be produced from the shell as well as the tube, and ricochets may also occur. In view of this and the small sample population, no firm conclusion can be drawn from these data until more extensive studies are undertaken.

Conclusions

This paper has considered the failure mode of firework mortar tubes fabricated from commercially available mild steel seamed and seamless tube. The work indicates that the trajectory of projectiles from a rupturing mortar cannot be predicted for either type of tube tested and that, in the light of these findings, safety procedures that assume a preferential direction for the fragmentation of seamed tubes may need to be examined.

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[Submitted February, 1995]

An Introduction to PROPEP,
A Propellant Evaluation Program for Personal Computers

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ABSTRACT

Propellant evaluation programs are used to estimate the performance of rocket propellants, to compare the performance of different propellants, and to evaluate the effects of formulation changes. While the program output may not be exact, it compares well with experimental results. Their major weakness lies in the accuracy and completeness of the underlying thermochemical database used for calculations. These programs are potentially useful for the evaluation of non-rocket chemical equilibrium. This article provides a guide to installing, testing and using ***PROPEP****, a propellant evaluation program available in the public domain. Some basic knowledge of computer terminology, chemistry, etc. is required.*

Keywords: chemical equilibrium, PEP, propellant, rocket, thermodynamics, evaluation

Introduction

PEP is an acronym for Propellant Evaluation Program. **MICROPEP** and **PROPEP** are Personal Computer (IBM PC or compatible) versions of **PEP** and **NEWPEP**, which were written at the Naval Weapons Center, China Lake, CA. **MICROPEP** was the original program released by Larry Williams and John Cunningham of Martin Marietta. **MICROPEP** had several quirks and preferred to run on a "clean" system. **PROPEP** reduced or eliminated **MICROPEP**'s problems and added improvements. Both programs were developed by employees of Martin Marietta and made available for public use. There is no support and there are no warranties for these programs. Anyone using **PROPEP** must form their own opinion concerning its suitability and accuracy for their application.

There are other programs written to perform thermodynamic calculations on propellant and explosive formulations, including **NASA/Lewis**, **BLAKE**, **TIGER**, etc. However, **PROPEP** has several advantages. It is available in the public domain, and it runs on PC's with a math coprocessor. The source code and data files are included on the distribution disks; so they can be studied or modified. The program is simple to use and produces usable data. Last, but not least, **PROPEP** is "free."

PROPEP also has drawbacks. Understanding and using its capabilities and output may not be as easy as users would like. It sometimes "bombs" out or gives "bad" results, for example, with a mixture of zinc and sulfur. This is because the thermochemical data for the possible reaction products (in all possible physical states) are not included in **PROPEP**'s **JANNAF.DAF** file. This file contains thermochemical data (from several sources) for program use. If the **PROPEP** output has question marks or error messages, the results may be incorrect. Also, if necessary reaction product information is not available, **PROPEP** will produce incorrect results. Much like humans, the program makes the best estimates it can, based on its knowledge base. Users must form their own opinion about the accuracy of output for their applications. **PROPEP** dislikes small quantities (less than 0.5%) of any ingredient. It attempts to do what it is told to do, rather than what might be wanted. The other **PEP** programs share many, if not all, of these drawbacks. All programs of this type must make simplifying assumptions. Sutton[1] presents a good introduction to the basic methods used for thermodynamic calculations, and he explains some of these assumptions.

PROPEP can also be used to improve one's understanding of propellant combustion. For example, **PROPEP** can be used to compare propellants and to evaluate the effects of formulation changes. Using **PROPEP,** initial evaluations of propellants can be made without physically preparing and testing each formulation. This can save time, work, material, and expense. **PROPEP** calculates density, temperatures, molecular weights, reaction product information, exhaust velocity, specific impulse, specific heat values, etc. It does not, however, provide burn rate versus pressure information; the author is unaware of a program with this capability.

System Information

MICROPEP would not run on the author's PC with a 286 central processing unit (CPU) until a math coprocessor was installed. A math coprocessor is also needed to run **PROPEP**. The suggested minimum configuration is a PC with a 286 CPU and a math coprocessor. A PC with a 486 CPU (and a math coprocessor) is much faster; a Pentium CPU should be even better.

Program Information

PROPEP originally was distributed on two 5.25" 1.2M floppy disks but will fit on a single 3.5" 1.44M disk.

Disk 1 contained the following files:

READ.ME – preliminary information,

PROPEP.TXT – brief instructions for using the program,

PROPEP.EXE – the executable program,

PEPCODED.DAF – the ingredient file,

JANNAF.DAF – reaction product information used by the program,

SETUP.PEP – file telling the program where to find the files it needs,

INPUT.DAT – a sample input file, and

SAMPLE.CHK – output file for sample input file.

Disk 2 contained:

PROPEP.FOR – FORTRAN source code for the main program,

JANCREAT.FOR – FORTRAN source code used to create **JANNAF.DAF**, and

JANINPUT.DAT – input information needed for **JANCREAT.FOR**.

Installation and Test

As always, make backup copies of program disk(s) and store original disk(s) in a safe place. Unless the user is a programmer with access to a FORTRAN compiler, the files listed as being on Disk 2 are not needed.

The author recommends installation of **PROPEP** on a PC's hard drive. Prior to installation, a directory for the **PROPEP** files must be created. **PEP** is the suggested directory name. Any name can be used, but the user will need to modify the **SETUP.PEP** file for any directory name other than **PEP**. The setup file uses **PEP** as the directory name with the program installed on the C drive. Copy all files, listed on Disk 1, to the **PEP** directory. Make backup copies of the files **INPUT.DAT**, **PEPCODED.DAF**, and **SETUP.PEP**. by using the same filenames, but using the extension of "**.BAC**" for the backup copies. **PROPEP** is sensitive to field lengths, etc. Thus, if mistakes are made during changes to files, it is convenient to have backup files available. After changes have been made and the program works correctly, update the backup files for future use.

EDIT is an **ASCII** editor provided in **MS-DOS** versions 5 and 6. It can be used to make changes to **SETUP.PEP**. These changes are needed before **PROPEP** can be run (changes are explained below). Other **ASCII** editors may be used but make sure **PROPEP** can read their output by testing with the sample files.

Print the following files for future reference:

READ.ME – one page,
PROPEP.TXT – about five pages,
INPUT.DAT – one page,
SAMPLE.CHK – one page, and
SETUP.PEP – one page.

The author also printed out **PEPCODED.DAF** (about 34 pages). Some users may find it easier to scan a written copy than to use the monitor screen, while others may prefer to use their editor's search function to find ingredients. Print at least the first page of **PEPCODED.DAF** as this page has information on the format for the ingredient information. **PEPCODED.DAF** contains 1092 lines. The information provided in **PEPCODED.DAF** and this article should function as a program manual.

Edit the **SETUP.PEP** file to tell **PROPEP** where to find the files it needs (An example follows.). If **PROPEP** will be operated from the PC's hard disk or from a single high density (**HD**) floppy disk, Line 1 should contain "**HD**." Line 2 contains the full path to the file – **PEPCODED.DAF**. Line 3 is not used by **PROPEP**, but must have something in it anyway. (See below.) Line 4 is the full path to the reaction product file. Line 5 is the location of the default output file. If these files were placed in a directory other than **PEP**, change these lines to reflect the directory used. The file, **SETUP.PEP**, should now look like the following if **PROPEP** is executed from the **PEP** directory on the **C**: drive:

- **HD**
- **C:\PEP\PEPCODED.DAF**
- **C:\PEP\NOTUSED**
- **C:\PEP\JANNAF.DAT**
- **C:\PEP\PROPEP.OUT**

When satisfied with **SETUP.PEP**, save it and exit the editor.

As a test, run the sample data provided in **INPUT.DAT**. First, change to the **PEP** directory; then type "**PROPEP,**" and press Enter. Introductory information about the program is displayed along with the message "**CARRIAGE RETURN TO CONTINUE**." After the carriage return (Enter key) is pressed, information is displayed about the ingredients being considered. The case being run and the starting time are also displayed. When the calculations are complete, "**EXECUTION TERMINATED: 0**" appears on the screen, and the DOS prompt is displayed. Print the **SAMPLE.OUT** file and compare it with a printout of the **SAMPLE.CHK** file. (See Figure 1 for an example of typical **PROPEP** results.) If they are identical, other evaluations may be run. A very minor bug in the program is that there are four unneeded spaces after "**CHAMBER RESULTS FOLLOW**" and "**EXHAUST RESULTS FOLLOW**" in the output file. If desired, these spaces can be edited out before printing. The sample run is a single set of calculations using liquid oxygen and hydrogen in a rocket engine. The engine operates at a chamber pressure of 1000 psia (6.89 MPa) and exhausts to a pressure of 14.7 psia (101 kPa). ("psia" is absolute pressure in pounds per square inch.)

PROPEP – Application and Demonstration

Much research has been done on black powder in the last twenty years. One suggestion from this research[2,3] was to substitute phenolphthalein for charcoal. The goal of this substitution was the production of a "good" black powder with less lot-to-lot variation than conventional Black Powder. This is because phenolphthalein is a well characterized material, while charcoal has many uncontrollable variables in its composition. How do the **PROPEP** results for a black powder made with charcoal compare with results for a black powder made with phenolphthalein?

Charcoal and phenolphthalein are not contained in the ingredient file, **PEPCODED.DAF**, However, the information is available.[2–4] One formulation for charcoal is $C_{322}H_{184}NO_{37}$ [Roseville B[2]]. Its heat of formation is approximately –595 cal/g, and a typical density is about 0.0542 lb/in^3 (1.50×10^3 kg/m^3). The chemical formula for phenolphthalein is $C_{20}H_{14}O_4$. Its heat of formation is approximately –431 cal/g, and its density is 0.0461 lb/in^3 (1.28×10^3 kg/m^3).

Ingredients can be placed in the **INPUT.DAT** file as user defined ingredients; however, if they are added to **PEPCODED.DAF**, they will be available for future use. Use an **ASCII** editor to add charcoal and phenolphthalein to the end of **PEPCODED.DAF** as lines 1093 and 1094. Each item on a line must be aligned with the item above it. All numeric fields are right justified and all letter fields are left justified. Use only capital letters in **PEPCODED ENTRIES**. Be sure to place the "**]**" at the end of each line.

For the first part of the demonstration, edit the **INPUT.DAT** file to run black powder made with charcoal. This example uses 74% potassium nitrate, 10.4% sulfur, and 15.6% charcoal (a standard black powder composition.[5] The first line in **INPUT.DAT** is the name of the output file. Type:

"BLKPWDRC.OUT"

Line 1 has only one field with a length of up to 12 characters. This allows the use of a standard filename structure (up to an eight character filename, a period ".", and a three character extension). The second line describes the file and will be printed at the top of each output page. For the second line type: "Charcoal BP". The second line contains one field that can be up to 17 characters long. Three items are entered on Line 3: the number of the **PEPCODED.DAF** ingredients used, the number of user defined ingredients (zero if all ingredients are in the ingredient file – **PEPCODED.DAF**), and the number of cases to be run (one case for each chamber pressure and/or formulation). In this example, results will be calculated for two chamber pressures, 29.4 and 1000 psia (203 kPa and 6.89 MPa). Each field in Line 3 is five characters long, thus for Line 3 type:

"~~bbbb~~3~~bbbb~~0~~bbbb~~2"

(where, ~~b~~ is used to indicate a blank space). Remember, spacing is critical. Line 4 is used for calculating density I_{SP} and is also used with control option 3 in Line 7. From the **MICROPEP** instructions, *"For the evaluation of non-rocket chemical equilibrium of any type, propellant screening, tactical missiles, first stage rockets a value of 1 should be input. If performance of upper stages is the topic of analysis, appropriate values are 0.7 for second stage, and 0.2 for third stage. This requires use of control option three."* Control options are set in Line 7. For Line 4 type: "1." Line 4 contains a single field with a length of up to 12 characters. Line 5 is the initial temperature of the ingredients, in Kelvin, and can be used to study temperature conditioning effects. Type: "298." [This is 25 °C (77 °F).] Line 5 has one field that may be 12 characters long. Line 6 contains the *"Quadratic coefficients for solid specific heat. Used with temperature difference to adjust the system enthalpy for heating and cooling. (defaults to 0.3 cal/gm K)."* The previous quote is from **PROPEP.TXT**. Line 6 has three fields, each 12 characters long. For Line 6 type:

".3~~bbbbbbbbbb~~0.0~~bbbbbbbbb~~0.0"

Line 7 has eight fields, each one character long. These fields function as switches to select control options. "0" is used for off and "1" for on. The options are (again, quoting from the **PROPEP.TXT** file):

1) *Delete exit calculations*
2) *Include ionic species in calculations*
3) *Include boost velocities and nozzle design data*
4) *Input pressures in atmospheres instead of PSI*
5) *Increase numerical precision of species list*
6) *Output a list of all combustion species considered*
7) *Fix temperature*
8) *Debug options*

For Line 7 type: "00000000". Line 8 holds the line numbers for the ingredients from the **PEPCODED.DAF** file. For Line 8 type:

"~~bb~~821~~bb~~898~~b~~1093".

These are the line numbers for potassium nitrate, sulfur, and charcoal, respectively. Line 8 contains up to 10 fields, each five characters long. Line 9 (repeated once for each case to be run) contains selected chamber pressure, selected exhaust pressure, and the weight percentage of each ingredient. Use the same order of ingredients as in Line 8. Weights may be used instead of percentages, if preferred. Each repetition of Line 9 can have up to 12 fields, each with 12 characters. For Lines 9 and 10 type:

~~bbbbbbbb~~29.4~~bbbbbb~~14.70~~bbbbbbb~~74.00~~bbbbbbb~~10.40~~bbbbbbb~~15.60

~~bbbbbb~~1000.0~~bbbbbbb~~14.70~~bbbbbbb~~74.00~~bbbbbbb~~10.40~~bbbbbbb~~15.60

After editing, the file should look like:

```
BLKPWDRC.OUT
Charcoal BP
    3    0    2
1.
298.
.3          0.0         0.0
00000000
  821  898 1093
  29.4      14.70       74.00       10.40       15.60
1000.0      14.70       74.00       10.40       15.60
```

All of **PROPEP**'s functions are not being used, thus the above line numbers are not the same as those given in **PROPEP.TXT**. Lines 8 and 10 were not used, so Line 8 corresponds with **PROPEP.TXT**'s Line 9 and Line 9 corresponds with Line 11. Note that for the first case, a chamber pressure of 29.4 psia (203 kPa) is used. **PROPEP** does not operate reliably with pressures lower than this, although it sometimes provides results. The second case will be run at 1000 psia (6.89 MPa), which is a standard pressure for comparison of propellants. (Note that more information about the input file configuration and use is available in the **PROPEP.TXT** file.) Save the new **INPUT.DAT** file and exit the editor; then type "**PROPEP**" and press the Enter key to run the charcoal evaluations. When the program run is finished, print the results, which are contained in the file

BLKPWDRC.OUT.

To continue this demonstration, again edit **INPUT.DAT** and change Line 1 to:

"BLCKPWDRP.OUT".

Change Line 2 to "Phenolphthalein BP" In Line 8, change "1093" to "1094". Save the file **INPUT.DAT** and exit the editor. Type "**PROPEP**" and press the Enter key to run. When the program is finished, print the **BLKPWDRP.OUT** file. Sample printouts for the higher pressure runs follow as Figures 1 and 2.

Based on these calculated results, phenolphthalein looks like a good substitute for charcoal in black powder. The sample cases have similar chamber temperatures, specific heat ratios, characteristic exhaust velocities, densities, etc. In fact, phenolphthalein might be better than charcoal if the black powder is to be used as a rocket propellant. However, this is only part of the story. Real life testing must also be performed to prove that the substitute black powder will work in the desired application. If the results had varied widely, we probably wouldn't want to actually try using phenolphthalein in a black powder substitute. Thus **PROPEP** can be used as a tool to help minimize experimentation with "real" mixes. It can help optimize a formulation in a much shorter time.

Thus far, phenolphthalein has been determined to be a good candidate to replace charcoal in a black powder substitute. The next step could be to vary the composition to help decide whether or not to use the standard black powder percentages. To do this, edit the **INPUT.DAT** file again. This time, change Line 1 to "PHENOLBP.OUT". Notice the use of output file names that indicate something about their content. Change the last field in Line 3 from "2" to "3". The percentage of potassium nitrate will be held constant and the percentages of sulfur and phenolphthalein will be varied. To do this, make changes as shown below:

```
PHENOLBP.OUT
Phenolphthalein BP
    3    0    3
1.
298.
.3          0            0
00000000
  821  898 1094
1000.00     14.70       74.00       10.40       15.60
1000.00     14.70       74.00       13.00       13.00
1000.00     14.70       74.00       15.60       10.40
```

Save **INPUT.DAT** and run **PROPEP** again. After the run, print the file, **PHENOLBP.OUT**. Examine the values for C* (characteristic exhaust velocity — a good indication of propellant efficiency). Note that either change lowered C* below its original (or Case 1) value. Accordingly, if the substitute black powder is to be used in a rocket motor, the "standard" composition appears best. However, it may still be advantageous to try other chemical ratios. In addition, the experimenter may wish to raise or lower the chamber temperature for some applications. Formulations may be altered to increase or decrease the amounts of a given reaction product to enhance a desired effect; and densities may be adjusted by varying the composition. **PROPEP** can be used to quickly help determine the "best" tradeoff.

This gives some idea of **PROPEP**'s capabilities. As mentioned earlier, **PROPEP** does not provide burn rate information. If burn rate information is available from another source or from testing, it can be combined with **PROPEP**'s output information for preliminary rocket motor design.

Some key relationships used in rocket motor design[6,7] are:

$$r = a \cdot P_c^n$$

$$Kn = b \cdot P_c^{1-n}$$

$$P_c = c \cdot Kn^{(1/1-n)}$$

$$Kn = (P_c \cdot g) / (r \cdot \rho \cdot C^*)$$

In these equations:

r	is burn rate (in/s in the English system),
a	is the burn rate coefficient,
P_c	is chamber pressure (psia), and
n	is the burn rate exponent. (It is also the slope of a log-log plot of burn rate and chamber pressure.)
Kn	is burning surface area divided by nozzle throat area (both in same units).
b	is the Kn coefficient
c	is the pressure coefficient,
g	is gravitational constant (32.17 ft/sec^2),
ρ	is propellant density (lb/in^3), and
C^*	is characteristic exhaust velocity (ft/sec).

For conversion to SI Units:

1 in/sec = 25.4 mm/s
1 psi = 6.89 kPa
1 lb/in^3 = 2.77x10^4 kg/m^3
1 ft/s^2 = 0.305 m/s^2
1 ft/s = 0.305 m/s

```
Charcoal BP       Run using June 1988 Version of PEP,
 Case  2 of  2      7 Apr 1995 at  6:41:33.94 pm

  CODE                                   WEIGHT    D-H  DENS      COMPOSITION
   821 POTASSIUM NITRATE                 74.000  -1167  0.07670    1N   3O   1K
   898 SULFUR                            10.400      0  0.07470    1S
  1093 Charcoal                          15.600   -595  0.05420  322C 184H  37O   1N
THE PROPELLANT DENSITY IS 0.07185 LB/CU-IN OR  1.9887 GM/CC
THE TOTAL PROPELLANT WEIGHT IS  100.0000 GRAMS
NUMBER OF GRAM ATOMS OF EACH ELEMENT PRESENT IN INGREDIENTS
   0.616095 H     1.078166 C     0.735239 N     2.319561 O
   0.324331 S     0.731891 K
****************************CHAMBER RESULTS FOLLOW    *****************************
 T(K)  T(F)  P(ATM)   P(PSI) ENTHALPY  ENTROPY   CP/CV     GAS   RT/V
1917. 2991.   68.02  1000.00   -95.64   134.63  1.1118  1.631   41.702
SPECIFIC HEAT (MOLAR) OF GAS AND TOTAL=   11.324   16.325
NUMBER MOLS GAS AND CONDENSED=   1.6312   0.3440
  0.51358 CO2        0.36759 N2         0.34650 CO         0.23798 H2O
  0.21417 K2CO3*     0.12978 K2S*       0.05251 S3         0.04008 KHO
  0.03774 H2         0.01174 H2S        0.00984 SO2        0.00405 S2
 3.84E-03 CSO       3.34E-03 K         7.37E-04 HS        7.02E-04 SO
 3.69E-04 S4        1.91E-04 S2O       1.42E-04 K2SO4     1.17E-04 K2H2O2
 2.72E-05 H         1.79E-05 S         1.58E-05 KH        1.49E-05 HO
 6.78E-06 CS2       4.40E-06 NH3       4.14E-06 KCN       1.64E-06 K2
 1.40E-06 NO
THE MOLECULAR WEIGHT OF THE MIXTURE IS   50.628
****************************EXHAUST RESULTS FOLLOW    *****************************
 T(K)  T(F)  P(ATM)   P(PSI) ENTHALPY  ENTROPY   CP/CV     GAS   RT/V
1289. 1861.    1.00    14.70  -117.40   134.63  1.1178  1.633    0.612
SPECIFIC HEAT (MOLAR) OF GAS AND TOTAL=   10.959   15.419
NUMBER MOLS GAS AND CONDENSED=   1.6332   0.3642
  0.67260 CO2        0.36759 N2         0.24617 H2O        0.24480 CO
  0.20465 K2S*       0.15950 K2CO3*     0.05219 H2         0.03650 S3
 8.01E-03 H2S       3.25E-03 KHO       1.21E-03 CSO       3.02E-04 K
 2.63E-04 S2        1.64E-04 SO2       4.57E-05 S4        2.30E-05 HS
 3.98E-06 K2H2O2    3.25E-06 SO        2.49E-06 K2SO4     1.25E-06 S2O
THE MOLECULAR WEIGHT OF THE MIXTURE IS   50.066
**********PERFORMANCE:  FROZEN ON FIRST LINE, SHIFTING ON SECOND LINE**********
IMPULSE   IS EX      T*       P*      C*     ISP*  OPT-EX  D-ISP      A*M   EX-T
  136.2  1.1138   1814.   39.58  2648.6           10.66  270.9  0.08234  1245.
  137.6  1.0977   1825.   39.80  2672.8   101.6   10.83  273.7  0.08309  1289.
```

Figure 1. Sample output from standard black powder run at 1000 psia (6.89 MPa).

```
Phenolpthalein BP Run using June 1988 Version of PEP,
 Case  2 of  2     27 Mar 1995 at  7:13: 1.67 pm

  CODE                                   WEIGHT    D-H  DENS      COMPOSITION
   821 POTASSIUM NITRATE                 74.000  -1167  0.07670    1N   3O   1K
   898 SULFUR                            10.400      0  0.07470    1S
  1094 Phenolpthalein                    15.600   -431  0.04610   20C  14H   4O

THE PROPELLANT DENSITY IS 0.06933 LB/CU-IN OR  1.9190 GM/CC
THE TOTAL PROPELLANT WEIGHT IS  100.0000 GRAMS

NUMBER OF GRAM ATOMS OF EACH ELEMENT PRESENT IN INGREDIENTS
   0.686076 H     0.980109 C     0.731891 N     2.391694 O
   0.324331 S     0.731891 K

****************************CHAMBER RESULTS FOLLOW    ****************************
 T(K)  T(F)  P(ATM)   P(PSI) ENTHALPY  ENTROPY   CP/CV     GAS   RT/V
2052. 3235.   68.02  1000.00   -93.08   137.96  1.1190  1.685   40.367

SPECIFIC HEAT (MOLAR) OF GAS AND TOTAL=   11.464   15.768
NUMBER MOLS GAS AND CONDENSED=   1.6852   0.3115
  0.50939 CO2        0.36591 N2         0.34364 CO         0.24997 H2O
  0.12417 K2CO3*     0.12393 K2S*       0.09710 KHO        0.06333 K2SO4*
  0.03553 H2         0.02925 S3         0.02410 SO2        0.01004 K
 8.04E-03 H2S       4.69E-03 S2        2.84E-03 CSO       1.90E-03 SO
 1.04E-03 HS        5.86E-04 K2SO4     3.24E-04 S2O       3.03E-04 K2H2O2
 1.73E-04 S4        6.84E-05 H         5.39E-05 HO        5.26E-05 KH
 4.82E-05 S         1.09E-05 K2        6.53E-06 NO        5.82E-06 KCN
 4.54E-06 KO        3.72E-06 CS2       3.09E-06 NH3       1.71E-06 NS

THE MOLECULAR WEIGHT OF THE MIXTURE IS   50.085
****************************EXHAUST RESULTS FOLLOW    ****************************
 T(K)  T(F)  P(ATM)   P(PSI) ENTHALPY  ENTROPY   CP/CV     GAS   RT/V
1417. 2092.    1.00    14.70  -117.16   137.96  1.1217  1.654    0.605

SPECIFIC HEAT (MOLAR) OF GAS AND TOTAL=   11.188   15.099
NUMBER MOLS GAS AND CONDENSED=   1.6536   0.3526
  0.68984 CO2        0.36592 N2         0.28567 H2O        0.22898 CO
  0.21977 K2S*       0.07216 K2SO4*     0.06066 K2CO3*     0.04237 H2
  0.02337 KHO        0.00887 S3         0.00323 H2S        0.00307 K
 1.15E-03 SO2       5.72E-04 CSO       3.02E-04 S2        7.56E-05 K2SO4
 4.15E-05 HS        4.00E-05 K2H2O2    2.48E-05 SO        7.24E-06 S4
 3.55E-06 S2O       1.63E-06 H

THE MOLECULAR WEIGHT OF THE MIXTURE IS   49.845
**********PERFORMANCE:  FROZEN ON FIRST LINE, SHIFTING ON SECOND LINE**********

IMPULSE   IS EX      T*      P*      C*    ISP*  OPT-EX  D-ISP      A*M   EX-T
  142.5  1.1213   1935.   39.47  2778.4          10.48   273.4  0.08638  1300.
  144.8  1.0982   1954.   39.80  2811.0   106.9  10.90   277.8  0.08739  1417.
```

Figure 2. Sample output from phenolphthalein black powder run at 1000 psia (6.89 MPa).

The **PROPEP.TXT** file provides more information on interpretation of **PROPEP**'s output. Warning: in the output file, specific impulse (I_{SP}) is labeled as "**IMPULSE**" below the "**PERFORMANCE: FROZEN ON FIRST LINE, SHIFTING ON SECOND LINE**". If instructions refer to I_{SP} with no *'s or other modifiers, they mean the **IMPULSE** value. Sutton[1] is an excellent source of information on rocket propulsion topics. The sixth edition has improved and expanded coverage.

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Introductory Chemistry for Pyrotechnists, Part 1: Atoms, Molecules, and Their Interactions

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ABSTRACT

This is the first in a series of tutorials that introduce the concepts of chemistry to practicing pyrotechnists. It begins with the fundamental ideas of atoms and molecules. The reactions of these entities, together with their symbols, their nomenclature, their stoichiometry, and their energetics, are then described with pyrotechnic examples.

Keywords: chemistry, atomic theory, chemical formulas, chemical equations, stoichiometry, energetics, nomenclature

Introduction

If you're building fireworks without a rudimentary understanding of chemistry, you're hindering yourself. You may well be able to fabricate numerous and wonderful pyrotechnic devices. You might have read books, watched videos, and taken courses on all aspects of fireworks construction. You may even have served apprenticeships with the masters of pyrotechnics. But with little chemistry, by and large, all you know is *how* to do it. If you ever wanted to improve a formulation or to create a novel and original effect—and what pyrotechnist hasn't?—you'd have to go beyond the scope of your reference works and outside the experience of your mentors. And lacking chemical insight, you could only do that by accident, by hunch, or by trial and error. Any such approach would be hazardous at least and tedious at best.

On the other hand, if you understood a surprisingly small number of fundamental chemical concepts, you'd know *why* many fireworks phenomena work as they do. You'd possess the background to channel your creative efforts in safer, more efficient directions. And you'd have the credentials to exonerate yourself with your mother, who always told you, "Never touch that stuff unless you know exactly what you are doing!"

So, why haven't you studied more chemistry? It's probably because you've never found a chemist who would talk to you on your level. You're a fireworks person. Your IQ has the normal three digits, not four, not two. You don't want to be snowed or patronized. And you're practical. You don't want a treatise on the whole breadth of chemical science. You just want to know and understand what applies to pyrotechnics. If that's the kind of introductory chemistry you've been seeking, then this series of articles is for you.

Chemical Thinking

Interestingly, to begin thinking chemically, you don't need to get all formal and scientific. Instead, you simply have to use your imagination.

It's easy to visualize something that's within your own experience. For example, take a sheet of aluminum foil. Tear off a corner. Examine the removed scrap. Isn't it still aluminum? Of course. The tearing action hasn't changed it into some new substance. With a razor blade, pare off a minute flake. That shaving, too, is still aluminum. You can envision all this.

What's great about imagination is that you can also venture out beyond your experience. In your mind's eye, go on creating ever–smaller fragments of the aluminum foil. You can picture yourself viewing and manipulating those pieces at whatever sub-microscopic level you wish, can't you? What would you get if you kept doing this forever? Would each of the new flecks continue to be aluminum? Chemists would say, "No, they wouldn't!" According to them, the process would lead to some tiniest–possible particle of aluminum, which, if subdivided further, would become something different.

Actually that idea isn't as far-fetched as it first sounds. Liken the aluminum foil to a big sheet of postage stamps. As long as you tear off pieces along the perforations, you are just creating smaller sheets of stamps. But when you come to the smallest–possible "sheet"—a single stamp—you can't go any further; if you tear *it* up, it no longer works for postage.

To chemists, any sample of aluminum is a huge number of minuscule particles which are all essentially identical to each other. Each chemist has in mind something analogous to a skyscraping stack of acre-sized postage-stamp sheets that has shrunk to the dimensions of the sample. Can you see the same preposterous spectacle in your own imagination? If so, you are thinking chemically.

Atoms

The primary, "postage–stamp" particle of aluminum is called an aluminum *atom*. An atom is the smallest unit of an element that retains its properties. You have never experienced any one of these on an individual basis because they are so incredibly minute. Take, for example, one of the tiniest bits of aluminum that you *have* encountered: a lone 5-micron minigrain of German dark aluminum. This speck, though barely visible, contains a whopping quadrillion aluminum atoms (10^{15} or 1,000,000,000,000,000 atoms, give or take a few hundred trillion)! Your personal computer, at top speed (100 MHz), would take nearly four months to count them. But if you can conceive of aluminum atoms as single entities, then you have begun to grasp the most fundamental chemical concept.

This concept, the atomic theory, says that *every* element, not just aluminum, is composed of atoms. Just as postage stamps vary in size and denomination, so do the atoms of other elements like sulfur, carbon, or magnesium. All atoms of a particular element are alike, but they differ from the atoms of any other element. Imagine the frantic behavior of the aluminum atoms in a salute mix as it explodes. If you ignite separate samples of the same flash powder, the new aluminum atoms are going to behave identically, right? But if you replace the aluminum with, say, zinc, you know that something different is going to happen. That's because zinc atoms are not the same as aluminum atoms, and, on ignition, they are going to do their own frantic thing.

There are just over a hundred different elements, and, thus, there are only that many different kinds of atoms. Each element (and atom) has a name and a chemical symbol. And each is characterized by its own unique behavior. Those most commonly found in pyrotechnics are listed in Table 1.

Table 1. Elements Commonly Used in Pyrotechnics.

Name	Symbol	Typical Valence State*	Atomic Weight
Aluminum	Al	+3	26.98
Antimony	Sb	+3	121.75
Arsenic	As	+3	74.92
Barium	Ba	+2	137.33
Bromine	Br	–1	79.90
Calcium	Ca	+2	40.08
Carbon	C	+4	12.01
Chlorine	Cl	–1	35.45
Chromium	Cr	+3	52.00
Copper	Cu	+2	63.55
Hydrogen	H	+1	1.01
Iodine	I	–1	126.90
Iron	Fe	+3	55.85
Lead	Pb	+4	207.2
Lithium	Li	+1	6.94
Magnesium	Mg	+2	24.30
Manganese	Mn	+2	54.94
Mercury	Hg	+2	200.59
Nitrogen	N	–3	14.01
Oxygen	O	–2	16.00
Phosphorus	P	–3	30.97
Potassium	K	+1	39.10
Silicon	Si	+4	28.09
Sodium	Na	+1	22.99
Strontium	Sr	+2	87.62
Sulfur	S	–2	32.06
Titanium	Ti	+4	47.90
Zinc	Zn	+2	65.38

* Most elements have other valence states, but these are the ones most likely to be found.

Molecules

It's the interaction of atoms that causes pyrotechnic effects. But the interaction has to be *chemical*.

Take, for example, the classic model-rocket fuel, zinc and sulfur. When the two elements are mixed, they both retain their properties. They interact only on a physical basis. If you vibrated the loose mixture, the heavier zinc dust would sink to the bottom, and the lighter sulfur powder would float to the top. You'd see a yellow layer separate from the grayish mass, and you'd verify that the two elements had kept their characteristic colors. If you added acid, the zinc would produce bubbles of hydrogen gas, just as if it were alone. If you heated the mixture, the sulfur would melt into a smelly, brown syrup at about 120 °C, as if no zinc were around. Right to the end of the countdown, neither element would lose its identity no matter how intimately the two were intermingled in the casing. (This is a desirable attribute for a well-behaved rocket.)

But on ignition, the fireworks happen. The elements interact chemically, and something new takes their place. Instead of yellow or gray substances, you now have an abundance of white ashes—not off-white, not pale yellowish-gray, but bridal-gown *white*. Its color is so deep and intense that the residue was once used widely as an artist's pigment. Further, if you tested it, no part of the ash would form bubbles with the strongest of acids nor would any of it melt even at temperatures of many hundreds of degrees. It is nothing at all like the zinc or the sulfur you started with. Yet, remarkably, chemical analysis would show that the new material contained both. The white product is not a new kind of mixture of elemental zinc and elemental sulfur, rather it is a *compound* of the two. A compound is a substance composed of two or more elements that are united chemically in fixed proportions.

Now imagine how this process takes place on the atomic level. Like the individual bits of German dark aluminum, the tiny specks of zinc dust in the mixture are each collections of billions upon billions of atoms. So are each of the pieces of sulfur powder. Even at the tiniest mesh sizes and with the most intimate of mixing, these conglomerations of atoms can come in contact with each other only at a few places on their surfaces. (See Figure 1, Top.)

And, at room temperature, there is little likelihood that many zinc and sulfur atoms can get together. The rocket fuel simply lies dormant in its casing. But when the fuse is lit, fire comes to the mixture. The sulfur nearest to the fuse melts and oozes around the solid zinc. (See Figure 1, Bottom.) Now there is much more physical contact between much more energetic zinc and sulfur atoms. And chemistry happens. Zinc and sulfur atoms begin to pair off and bind together. The result of each union is a *molecule* with, in this case, two atoms tightly connected with a chemical bond. Furthermore, each molecule finds itself with less chemical potential energy (energy in storage) than the unbound atoms from which it was formed. The excess potential energy takes kinetic form as heat and light, and a chemical reaction has taken place. The energy quickly spreads throughout the mixture, initiat-

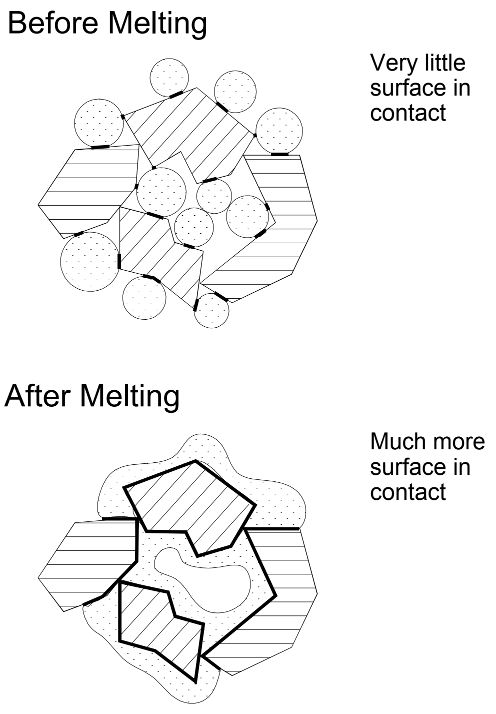

Figure 1. An illustration of the greatly increased contact with the melting of one component of a mixture.

ing more combinings of zinc and sulfur, releasing more chemical potential energy, and producing more heat and light. In a flash (literally), nearly all the zinc and sulfur atoms are united into molecules, and the rocket flies. This little description is the springboard into a number of chemical concepts that need elaboration. Among them are the symbolic representation of molecules, the naming of molecules, the symbolic representation of chemical reactions, the proportions in which substances react, and energy considerations. The balance of this article is devoted to their explanations.

Formulas

As the rocket fuel is burned, one atom of zinc, Zn, combines with one atom of sulfur, S. The *formula* of the resulting compound is written as ZnS, a combination of the elements' symbols. Other simple compounds, such as table salt, which is made from the elements sodium, Na, and chlorine, Cl, are written similarly, NaCl. But most compounds are not straightforward, one-to-one combinations. Water and carbon dioxide are surely the most familiar of these. The formula for a water molecule, having two hydrogen atoms and one oxygen atom, is, of course, H_2O. Carbon dioxide, having one carbon and two oxygens, is CO_2. In general, a chemical formula shows the symbol for each element in the compound followed by a subscript indicating how many atoms of that element are in the molecule. The absence of a subscript is understood to mean 1. Thus a molecule of antimony trisulfide, Sb_2S_3, is a combination of two antimony atoms and three sulfur atoms.

Why is water H_2O and not HO_2 or just HO? Each element has a typical combining capacity or *valence state*. This is either a positive or negative integer, and it represents the bonding behavior of its atoms. Table 1 lists the most likely valence state for each element. The handy thing about an element's valence state is that it tells you the subscript on the *other* element in a compound.

Here's how you use it. First, note that two elements combine only when they have valence states of opposite sign. Second, simply criss-cross the valence states to get the subscripts in the formula. Find in the Table 1, for example, that hydrogen is +1 and oxygen is –2. Once you notice that the signs are opposite, you don't need them any longer. Criss-crossing just the numbers, you would get H_2O_1. But don't show any subscripts that are 1; instead write the well-known formula as H_2O. [Can you see why HO_2 or HO won't work? Verify, by this method, that antimony trisulfide should indeed be Sb_2S_3.] There is one other wrinkle in this process that needs to be ironed out. Try carbon (+4) and oxygen (–2). The result, C_2O_4, is not the formula of carbon dioxide. So the third rule is this: whenever both subscripts can be divided by the same number, do it. Thus, divide the 2 and the 4 by two to get the correct formula, CO_2. [That is how you would predict the formula, ZnS, right? Try it.]

This criss-cross trick is designed for compounds that contain only two different elements. If there are three or more elements, things become messy. However, certain combinations of atoms, called functional groups, often stay together as units in multi-element compounds. They can be treated as above. Table 2 is a listing of common functional groups in pyrotechnic and explosive compositions. Criss-crossing their valence states works just as if they were

Table 2. Common Functional Groups.

Name	*Formula*	*Valence State*
Ammonium	NH_4	+1
Azide	N_3	–1
Benzoate	$C_7H_5O_2$	–1
Bicarbonate	HCO_3	–1
Carbonate	CO_3	–2
Chlorate	ClO_3	–1
Dichromate	Cr_2O_7	–2
Fulminate	CNO	–1
Nitrate	NO_3	–1
Oxalate	C_2O_4	–2
Perchlorate	ClO_4	–1
Peroxide	O_2	–2
Picrate	$C_6H_2N_3O_7$	–1
Salicylate	$C_7H_5O_3$	–1
Sulfate	SO_4	–2
Styphnate	$C_6HN_3O_8$	–2

single elements. For example, barium chlorate, a possible ingredient for green stars, would be $Ba_1(ClO_3)_2$ or just $Ba(ClO_3)_2$. Note that the parentheses are necessary here; without them—$BaClO_{32}$—you'd be giving the silly impression that the molecule contained thirty-two oxygen atoms. Ammonium nitrate, part of the Oklahoma City explosive, would come out $(NH_4)_1(NO_3)_1$, or NH_4NO_3. Parentheses are not needed whenever the subscript is 1. [What would be the formulas of potassium dichromate and ammonium oxalate? Who would have believed that, after reading these few pages, you would be jotting down such jargon as $K_2Cr_2O_7$ and $(NH_4)_2C_2O_4$?]

Names of Compounds

Chemists have thick manuals itemizing the current set of rules for giving any compound a unique and systematic name. But you don't have to know the gory details in order to make sense of most names. Generally a compound has a two-word name. The first word is the name of the element (or functional group) with the positive valence state. The second word names the one with the negative valence state. Sometimes various official prefixes (e.g., di- and tri-), suffixes (e.g., -ide), and/or roman numerals (e.g., IV) are thrown in to avoid ambiguity, but grasping their exact purpose won't add much to your understanding at this point. The only additional information you may need is the ability to recognize a few common leftovers from an out-dated system (e.g., cuprous and cupric refer to copper; ferrous and ferric mean iron). Otherwise, look up in a technical dictionary any names you can't translate (e.g., orpiment and Paris green).

Chemical Equations

You've just been reading whole paragraphs that describe the reaction between zinc and sulfur to give zinc sulfide. Much of that description could be summarized symbolically by a *chemical equation*:

$$Zn + S \rightarrow ZnS$$

Here the plus sign is read as "and," and the arrow is read as "reacts to give or to yield." The elements in the original mix, which disappear in the course of the reaction, are called *reactants*. That which appears in their place is called the *product(s)*.

Most reactions are not this simple. Take, for example, the burning of potassium chlorate with lampblack carbon to give potassium chloride and carbon dioxide. Written in shorthand form, it becomes

$$KClO_3 + C \rightarrow KCl + CO_2$$

The three oxygen atoms, originally attached to the chlorine atom of the potassium chlorate, leave, and two of them connect themselves to the carbon atom. Somewhere in the process, if you believe this notation, an oxygen atom gets lost. That just can't happen in chemistry. Molecules can fall apart, and molecules can form. But every atom that you start with in the reactants has to be there in the products. That's a law of nature. Therefore, the notation must be mistaken. What's needed here is a *balanced* chemical equation, one that follows this conservation-of-atoms law:

$$2\ KClO_3 + 3\ C \rightarrow 2\ KCl + 3\ CO_2$$

Now, both in the reactants and in the products, there are two potassium atoms, two chlorine atoms, six oxygen atoms, and three carbon atoms. These fundamental ingredients are conserved; they have only redistributed themselves into different molecules.

Examples of balanced chemical equations include the thermite reaction,

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$$

the decomposition of nitroglycerin (an understatement if there ever was one),

$$4\ C_3H_5N_3O_9 \rightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

and one of the reactions in the space shuttle's solid rocket boosters

$$6\ NH_4ClO_4 + 10\ Al \rightarrow 3\ N_2 + 9\ H_2O + 6\ HCl + 5\ Al_2O_3$$

This last equation, though balanced, is too simplistic a representation of the overall launch-vehicle reaction. (This is because of other materials, such as binders, mixed with the ammonium perchlorate and aluminum.) The reaction in the shuttle's main engines, however, is considerably less complex:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Stoichiometry

With a balanced equation as a description of a chemical reaction, you are able to *count* precisely the number of atoms of each element involved. In fireworks formulations, however, you *weigh* the substances. *Stoichiometry* (a word whose Greek roots mean the measurement of components) is the conversion between these two processes.

In the model-rocket fuel, one atom of zinc reacts with one atom of sulfur. To formulate the fuel properly, then, you want to mix equal numbers of atoms. That does *not* mean mixing equal weights of each. Zinc atoms do not weigh the same as sulfur atoms. (Remember the postage stamps of different sizes and denominations?) What you need are the parts by weight that contain the same number of atoms. This is given by each element's *atomic weight*. If the atomic weight is expressed in grams, the amount of the element is called a *mole*. According to Table 1, the atomic weights of zinc and sulfur are 65.4 and 32.1, respectively. Thus, you would mix 65.4 parts zinc and 32.1 parts sulfur, by weight—approximately 2 grams or ounces or pounds of zinc to every 1 of sulfur—to make the rocket fuel. If you are interested in percentages, which means you want all the parts by weight to add up to 100, you have to do some calculations. The weight of zinc, divided by the total weight of all components, times 100%, gives you the number you want,

$$\frac{65.4}{(65.4+32.1)} \times 100\% = 67.1\%$$

Similarly, you can obtain 32.9% for sulfur.

For reactants that are compounds instead of just elements, you need a way to find the parts by weight that give equal numbers of molecules. You want the compound's *formula weight*, or the sum of the atomic weights of each atom in the molecule. For potassium nitrate, KNO_3, the formula weight is the sum of 1(39.1), for the one potassium atom, plus 1(14.0), for the single nitrogen atom, plus 3(16.0), for the three oxygen atoms, giving a total of 101.1. Similarly, for barium perchlorate, $Ba(ClO_4)_2$, the formula weight is

$$1(137.3) + 2[1(35.5) + 4(16.0)] = 336.3$$

Put all this together for the first step in the Senko-Hanabi reaction of black powder.

$$2\,KNO_3 + 3\,C + S \rightarrow K_2S + 3\,CO_2 + N_2$$

What proportions of each reactant should be mixed according to this equation? Will it come out to be the classic 75-15-10 proportions? For 2 molecules of KNO_3, the parts by weight are 2(101.1) = 202.2; for 3 atoms of carbon, they are 3(12.0) = 36.0; and for one atom of sulfur, they are 1(32.1) = 32.1. So, in parts by weight, the ratio of the mixture should be 202.2 to 36.0 to 32.1. The total weight is the sum of these, or 270.3, and the percentages come out to be 74.8% potassium nitrate to 13.3% carbon to 11.9% sulfur. These aren't quite equal to the venerable black powder proportions; the mixture is slightly sulfur-rich. Apparently this helps promote the beautiful branching sparks of the Senko-Hanabi effect.

The challenge of the stoichiometric approach to pyrotechnic formulation is to obtain a plausible chemical equation. There's no problem identifying what reactants are involved, but it may be difficult to discern what some or all of the products should be. Studies have shown, for example, that when black powder burns, it does not produce just the three products shown above. Rather it yields dozens of products. It happens that these three are the most abundant of the products, but a more complete equation may imply slightly different proportions of the reactants. Nevertheless, a balanced equation, whether you discover it in a reference text or you create it as best you can alone, is still a better first approximation to the ideal composition than any random conglomeration.

Energy in Pyrotechnics

The whole point of formulating pyrotechnic mixtures is to produce kinetic energy, especially in the form of sound and light. Since such energy cannot be created out of nothingness (that's another law of nature), it has to be extracted from the chemical potential energy already existing in molecules.

The nitrate and perchlorate compounds commonly found in pyrotechnic compositions are examples of substances that contain large stores of chemical potential energy. The ash and gas that result from their ignition are compounds of considerably lower potential energy. The difference is released as the kinetic energy of the pyrotechnic effect: sparks, flame, and/or noise.

In order to get the reaction going, however, the ingredients must be supplied with an amount of initiating or *activation energy*. That's because the reactant atoms and molecules have to be propelled against one another with enough force to break some of the existing chemical bonds. Only as a result of such collisions can the new chemical bonds of the product molecules be formed. For example, in the chlorate-lampblack reaction above, the oxygen atoms first have to be torn away from the chlorine atoms in potassium chlorate—that is, activation energy must be provided—before they can combine with the carbon atoms. But the resulting carbon dioxide molecules have so much less chemical potential energy than the reactant molecules that all the invested activation energy and considerably more gets returned as kinetic energy.

You can visualize this on the diagram in Figure 2. As the pictured reaction, a generalized pyrotechnic process, progresses from left to right, it first has to climb an energy hump (the activation energy). Once over the top, however, it coasts back down to its original level, recovering the energy it has just expended. Then it continues to drop to the energy level of the products, releasing the heat (or other kinetic energy) of reaction.

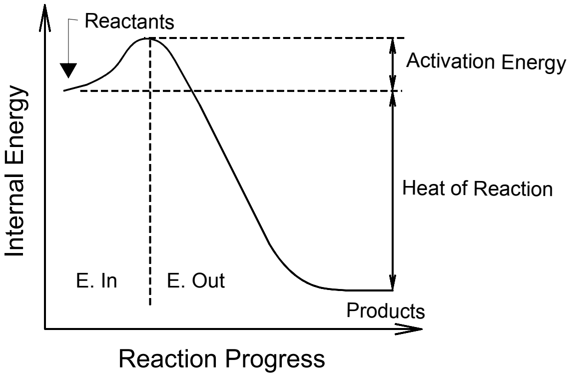

Figure 2. An illustration of activation energy and heat of reaction for a chemical reaction.

The activation energy hump acts as a barrier to reaction. And because different compositions have different-sized activation energy restraints, they differ in their ease of ignition. Some of the humps are small, making the reaction mixture sensitive to accidental ignition. Chlorate-sulfur mixtures and nitroglycerin are examples of energetic materials with dangerously low activation energy barriers. Relatively tiny amounts of initial energy, from static electricity, minor impact, or slight friction, for instance, can be enough to set them off. Other formulations, like thermite mixtures, have inconveniently high activation energy barriers and are difficult to ignite. Good pyrotechnic compositions, like black powder, have "Goldilocks" activation energies: not too high, not too low, but just right.

The Foundation of It All

Being able to imagine how atoms, molecules, and energy interact puts you well on the way to understanding the full chemistry of fireworks. What remains for future parts of this series are just deeper examinations of these fundamental principles.

Concussion Mortar Internal Pressure, Recoil and Overpressure as Functions of Powder Mass

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ABSTRACT

A concussion mortar can be defined as a device used to produce a noise and jarring shock for dramatic effect at events such as stage productions. It consists of a thick-walled tube, closed at one end to form a combustion chamber (barrel). A type of pyrotechnic flash powder is loaded into the combustion chamber and fired with an electric match. Although concussion mortars are used quite frequently, for the most part, detailed measurements of their manner of functioning have not been reported in the literature. In the present study, internal mortar pressure, recoil force and overpressure (air blast) were measured as functions of concussion powder load. It was determined that a full load (1.0 ounce or 28 g) of a strontium nitrate and magnesium concussion powder produced peak internal pressures averaging approximately 3100 psi (21 MPa). It was also observed that the width of the pressure peak ranged from approximately 7 ms for light loads, down to less than 2 ms for heavy loads. The recoil produced for a full load averaged approximately 5.9 lbf·s (26 N·s). The peak overpressure for a full load, at a point 5 feet from and 3 feet above the mortar (1.52 m and 0.91 m, respectively), averaged approximately 1.5 psi (10 kPa). In addition, there were a number of unexpected observations, which have not been fully explained at the time of this writing.

Keywords: concussion mortar, overpressure, recoil force, internal pressure, flash powder

Introduction

The present study is an extension of an earlier work by one of the authors,[1] and was undertaken to better characterize and understand the functioning of concussion mortars. (Concussion mortars are used to produce a loud noise and jarring shock for dramatic effect at events such as stage productions.) A more thorough study of concussion mortars is appropriate because safety may be enhanced through a more complete understanding of their operating characteristics.

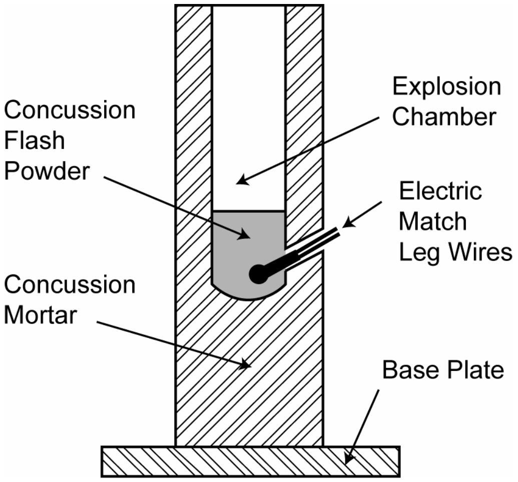

Figure 1. An illustration of the construction and setup of a concussion mortar.

Typically, a concussion mortar consists of a thick steel bar, which is welded to a heavy steel base plate. The steel bar contains a combustion

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chamber (barrel), produced by drilling a hole (on axis) into one end. For the concussion mortar used in this study, the steel bar was 2 inches (5 cm) in diameter with a 1 inch (2.5 cm) hole machined to a depth of 4.5 inches (11.5 cm). The construction of a concussion mortar is illustrated in Figure 1, which also shows its loading with a charge of powder and an electric match. Because of the partial confinement, upon firing the electric match, the concussion powder burns explosively (see Figure 2). The high pressure created in the combustion chamber causes those gases and hot particles to be forced rapidly upward and out of the concussion mortar. This produces a downward reaction force, the recoil of the mortar. As the gases exit the mortar, they expand as a shock wave that is heard and felt by the audience. With a fuel rich concussion flash powder, such as the one used in this study, there will be additional burning of the exiting material (gases, and liquid and solid particles) as they mix with oxygen from the air.

In this study, internal mortar pressure, recoil force, and overpressure as functions of powder load were investigated. Internal mortar pressure is of interest to assure there is an adequate safety margin in the strength of the combustion chamber. Mortar recoil force is of interest to assure that the placement of concussion mortars can be such that their recoil will not damage other equipment. Overpressure (air blast) is of interest to assure that the placement of concussion mortars is such that permanent auditory damage will not occur to individuals. (Note that the present study only provides limited overpressure data, and that additional studies are anticipated by the authors.)

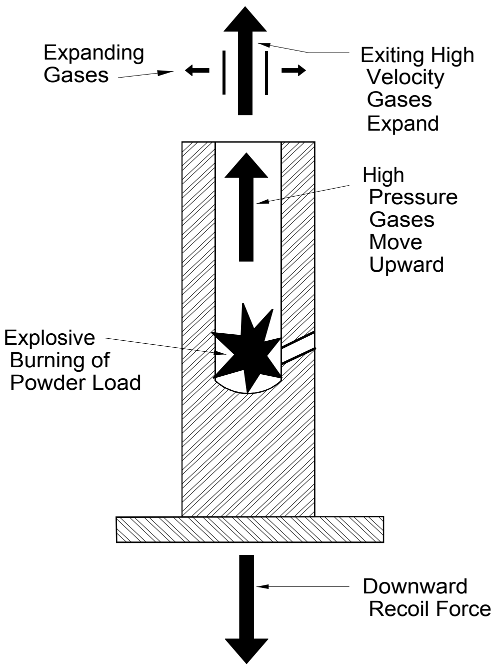

Figure 2. An illustration of the firing of a concussion mortar.

Experimental Method

A concussion mortar was modified as illustrated in Figure 3. A hole was drilled into the bottom of the combustion chamber. This allowed the installation of a pressure transducer, which was used to measure the internal pressures produced upon firing the mortar. During use, the channel connecting the pressure transducer and combustion chamber was filled with silicon grease. This allowed the measurement of pressure in the chamber while excluding concussion powder and combustion residues. In addition, a hinge assembly was attached to one end of the base plate of the mortar, and the mortar was positioned such that the bore of the combustion chamber was located directly over a force transducer.

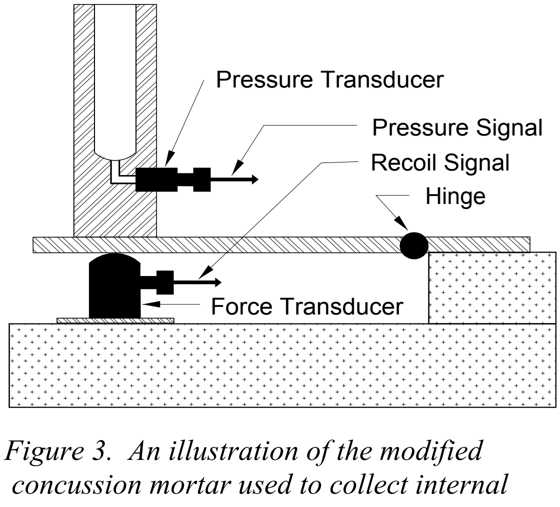

Figure 3. An illustration of the modified concussion mortar used to collect internal mortar pressure and recoil force data.

The pressure transducer was a quartz piezoelectric gauge with a 0 to 75,000 psi (0 to 520 MPa) range, manufactured by Kistler Instrument Corp. (Model 617C). The Kistler gauge produces a current output signal, which was converted to a voltage signal using a PCB Piezotronics voltage amplifier (Model 401A03). The force transducer also was a quartz gauge, with a 0 to 5000 lbf (0 to 22 kN) range, manufactured by PCB Piezotronics (Model 208A05).

Overpressure (air blast) measurements were made with the equipment setup as illustrated in Figure 4. Measurements were made using a free-field blast pressure probe aimed at the muzzle of the concussion mortar from a point 5 feet (1.52 m) distant and 3 feet (0.91 m) above the mortar. The pressure transducer has a ceramic sensing element with a pressure range of 0 to 50 psi (0 to 340 kPa) and was manufactured by PCB Piezotronics (Model 137A12). This particular type of pressure transducer is somewhat temperature sensitive. The concussion powder used was quite metal fuel rich, and a significant thermal pulse was generated upon firing. To eliminate the effect of this thermal pulse on the pressure measurements, the pressure transducer was covered with a thin film of silicon grease; then a 0.001 inch (0.025 mm) thick film of aluminized mylar was used to tightly cover the grease.

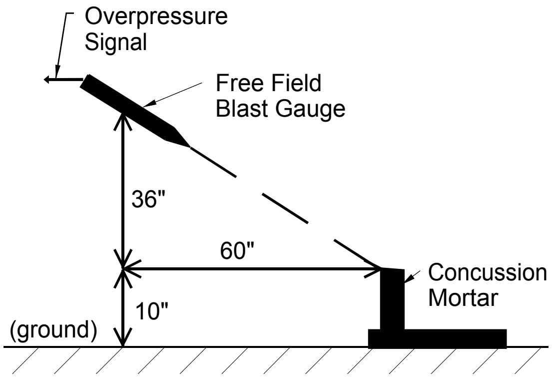

Figure 4. An illustration of the physical setup used to collect concussion mortar overpressure data.(For conversion to SI units, 1 inch = 25.4 mm.)

In each case, the power source and amplifier for the gauges was manufactured by PCB Piezotronics (Model 480D09). The results were recorded and temporarily stored using a digital oscilloscope. Permanent storage and plotting of the data was accomplished through the use of a personal computer.

The pyrotechnic powder used in the measurements was Luna Tech's Pyropak Concussion Flash Powder. It was supplied as a 2-component (binary) system in packaging of 1.0 ounce (28 g) units. This is a fuel rich combination of strontium nitrate and magnesium. The mixed powder was weighed and loaded loosely into the top of the concussion mortar. The powder was ignited using a Pyropak "ZD" type electric match, which was inserted through a small hole at the base of the combustion chamber of the mortar (shown enlarged in Figure 1). An attempt was made to be consistent in the placement of the electric match; this was accomplished each time by inserting the match as far as possible and then withdrawing it about 1/8 inch (3 mm) to raise it slightly off the bottom of the combustion chamber.

Between each mortar firing, the bore of the mortar was cleaned (and to some extent cooled). This was accomplished using compressed air and a large test-tube brush. This was done for consistency in the results as well as for safety. Large numbers of measurements were being made, often with only a few minutes between mortar firings. On several occasions, even several minutes after a firing, incandescent particles were blown from the mortar upon cleaning. This could have caused a premature ignition of the concussion powder while loading, had the mortar not been well-cleaned before hand.

Concussion Mortar Internal Pressure

Significantly different internal pressure profiles (pressure versus time) were obtained for light and heavy powder loads. Figure 5 presents somewhat typical pressure profiles for light (<12 g) and heavy (>12 g) powder loads. It was common for light loads to exhibit broad and periodic pressure peaks, while heavy loads essentially always produced single, fairly narrow peaks. There was also considerable variation between pressure profiles from shot to shot even for the same powder load. This was especially true for intermediate concussion powder loads (8 to 14 g), when either broad multiplets

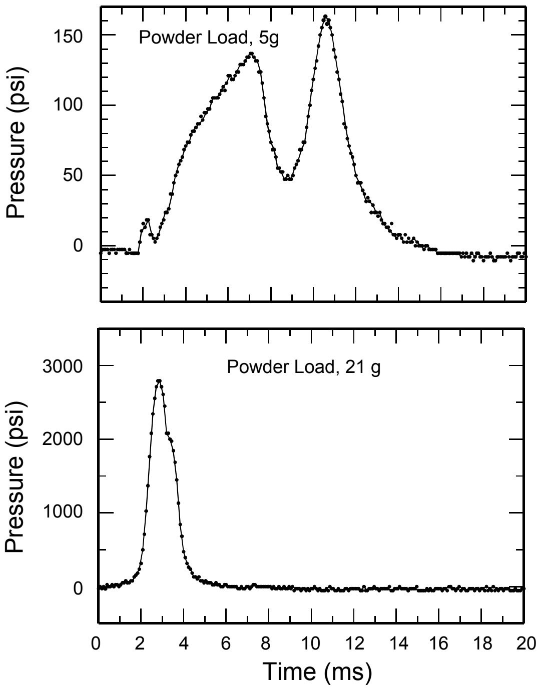

Figure 5. A comparison of typical concussion mortar internal pressure profiles for light and heavy powder load masses.
(For conversion to SI units, 1 psi = 6.89 kPa.)

or more narrow single peaks occurred intermittently, see Figure 6. The full set of internal mortar pressure data is presented in Table 1.

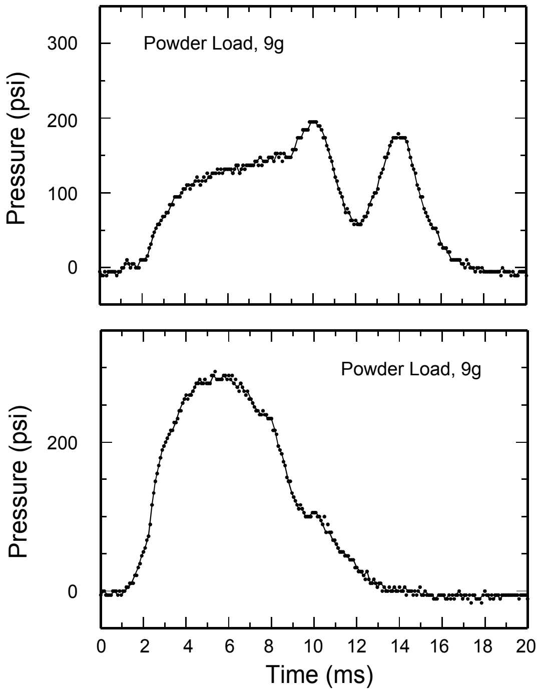

Figure 6. A comparison of two internal pressure profiles for the same powder load mass.
(For conversion to SI units, 1 psi = 6.89 kPa.)

Table 1. Internal Concussion Mortar Pressure Data.

Load (g)	Peak Pressure (psi)	Peak Width (ms)	Pressure Impulse (psi·s)
2	41	6.7	0.22
2	46	6.3	0.22
3	95	5.9	0.48
4	131	8.3	0.63
5	163	7.2	0.91
6	189	5.2	1.16
7	211	7.8	1.32
7	184	7.3	1.31
8	268	5.7	1.70
8	226	6.6	1.44
9	194	11.4	1.70
9	295	6.2	1.91
10	395	5.2	2.08
11	353	6.2	2.19
11	874	2.4	2.42
12	1050	2.0	2.72
12.5	647	4.1	2.82
13	1190	2.3	3.07
13	1540	1.6	2.93
14	1450	1.8	3.12
14	1580	1.7	3.01
14	1470	1.8	3.13
14	1710	1.6	3.03
14	1290	2.2	3.14
14	1180	2.1	2.72
14	1890	1.4	3.14
14	1630	1.5	2.55
14	1660	1.4	2.59
16	2210	1.3	2.32
17	2260	1.6	3.70
18	1890	1.6	3.12
19	2470	1.5	3.57
20	2390	1.8	4.02

Load (g)	Peak Pressure (psi)	Peak Width (ms)	Pressure Impulse (psi · s)
21	2050	1.8	3.92
21	1820	1.8	3.30
21	2050	2.0	4.27
21	2790	1.4	3.79
21	1970	2.0	4.18
21	2710	1.9	5.28
21	1970	1.3	2.68
22	1870	1.6	2.97
23	2580	1.6	4.43
24	2890	1.7	4.14
25	2500	1.5	3.77
26	2870	1.8	4.65
27	2890	1.9	5.23
28	2870	2.1	5.74
28	2710	1.9	4.86
28	3160	2.1	6.13
28	3680	2.1	5.05
28	3420	1.8	6.06
28	2710	1.8	4.88
28	3470	1.8	6.12
28	2710	1.9	5.34
28	2930	1.8	5.43

(For conversion to SI units, 1 psi = 6.89 kPa.)

Included in Table 1 is peak width information expressed as full-width-at-half-maximum (FWHM) of the pressure peaks. This was chosen as the indicator of peak width, because of the difficulty and subjectiveness of establishing precisely where peaks begin and end. Figure 7 is a graph of FWHM for pressure peaks as a function of concussion powder load mass. Note the transition from broad to narrow pressure peaks which occurs around 12 g loads.

Peak internal mortar pressure as a function of powder load is presented as a graph in Figure 8. Because of the varying width of the peaks, time integrated data was generated as a better estimator of the total energy released per firing, see Figure 9.

In one set of measurements, internal mortar pressures were taken with a second pressure transducer installed in the side of the mortar, 1.5 inches (3.8 cm) below the muzzle. In these tests, significantly lower pressures were recorded for the upper location. These results are presented in Table 2.

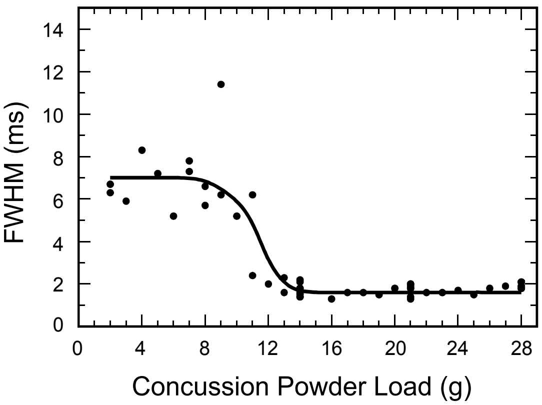

Figure 7. A graph of full-width-at-half-maximum (FWHM) for internal pressure peaks as a function of concussion powder load mass.

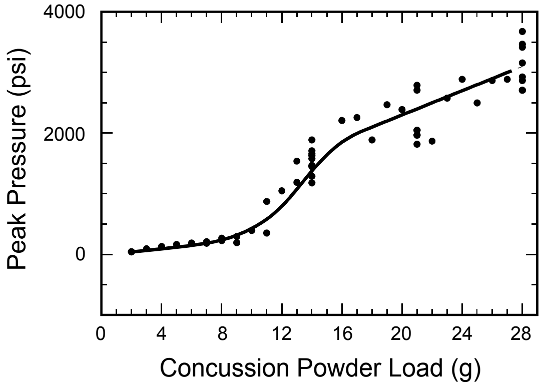

Figure 8. A graph of peak internal pressure as a function of concussion powder load mass.
(For conversion to SI units, 1 psi = 6.89 kPa.)

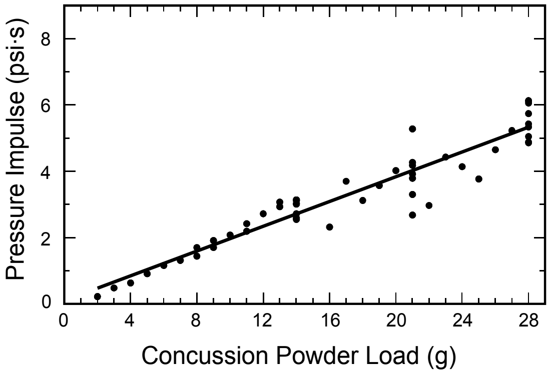

Figure 9. A graph of time integrated internal pressure (Pressure Impulse) as a function of concussion powder load mass.
(For conversion to SI units, 1 psi·s = 6.89 kPa·s.)

Table 2. Comparative Internal Pressure Data.

Load (g)	Peak Pressure Bottom (psi)	Peak Pressure Top/Side (psi)	Pressure Ratio
14	1710	950	0.56
14	1290	720	0.56
14	1180	820	0.69

(For conversion to SI units, 1 psi = 6.89 kPa.)

Concussion Mortar Recoil

For each concussion mortar firing, the recoil force profile has the same approximate shape as the internal pressure profile; for an example, see Figure 10. When there is only a single peak in one, there is always a single peak in the other. When there are multiple peaks in one, there are multiple peaks in the other, as well, and the relative spacing and amplitudes are similar. However, there seems to be a systematic shift in the timing of the peaks, with the recoil force peaks falling progressively farther behind the internal pressure peaks. In Figure 10 note that the first peaks ("1") occur at essentially the same time; there is nearly a 1 ms shift between the second peaks ("2"); and there is approximately a 2 ms shift in the timing of the third peaks ("3"). Similar time shifting of the peaks occurred whenever there were clearly defined multiple peaks. Similarly, when only single peaks were produced, every time the pressure peak preceded the recoil peak by about 0.5 ms.

The full set of recoil force measurements is presented in Table 3. The width of recoil force profiles varied much like they did for internal pressure. However, there was an additional factor that affects the widths of the recoil force peaks; that is the nature of the surface upon which the concussion mortar was placed. When the surface is very firm and hard, such as a concrete slab, the recoil force peaks are relatively narrow. When the mortar is placed on a more yielding surface, such as the ground or on thick carpet, wider peaks are produced. To illustrate this, consider the recoil force data reported in Table 3 for full powder loads (1.0 ounce or 28 g). The first four measurements (28–a) were made with the concussion mortar placed firmly on a concrete slab, the next five measurements (28–b) were made with the mortar on the ground, and the last three measurements (28–c) were made with the mortar placed on thick carpet. A summary of these results is given in Table 4. Note that there is a substantial increase in average peak width (46% and 260% when on the ground and carpet, respectively), accompanied by a significant decrease in peak force (27% and 66%, respectively). Note however, that the impulse (time integrated recoil force) is much less affected (5% and 22% reductions, respectively).

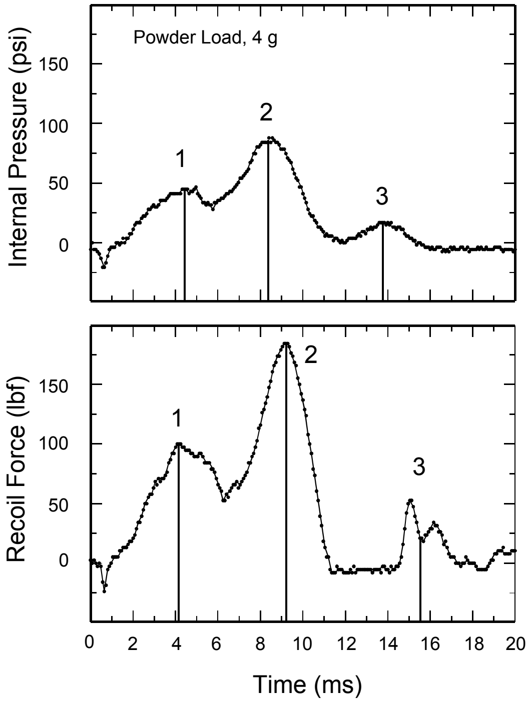

Figure 10. A comparison of an internal pressure profile and the recoil force profile for the same concussion mortar firing.
(For conversion to SI Units, 1 psi = 6.89 kPa, and 1 lbf = 4.45 N.)

During the course of taking the recoil force data in this study, the location of the equipment and the nature of the supporting surface had to be changed several times because of operational constraints. Accordingly, it is felt that only the impulse data (rather than the peak force results) is sufficiently consistent to be relied upon, see Figure 11.

Table 3. Concussion Mortar Recoil Force Data.

Load (g)	Force (lbf)	Peak Width (ms)	Impulse (lbf·s)
2	52	7.7	0.27
2	56	6.9	0.26
3	91	6.3	0.46
4	131	6.0	0.61
5	150	8.6	0.90
6	175	4.4	1.10
7	211	7.4	1.26
8	269	6.9	1.48
8	277	5.2	1.50
9	213	12.5	1.58
9	303	6.0	1.69
10	366	5.7	1.92
11	299	6.7	2.06
12	1090	2.2	2.48
12.5	538	4.1	2.39
13	1400	1.8	2.68
14	1980	1.4	3.07
14	2110	1.3	3.10
14	1940	1.4	3.04
14	1910	1.4	3.01
14	1910	1.4	3.05
16	2540	1.3	3.68
17	2840	1.3	3.96
18	2370	1.4	3.44
19	3010	1.4	4.32
20	3210	1.3	4.44
21	2970	1.3	4.03
21	2490	1.3	3.44
21	2920	1.4	4.19
21	3100	1.6	4.93
21	3070	1.6	4.88
21	2470	1.7	4.52
21	3140	1.6	5.23
21	2360	1.6	3.92
22	3850	1.1	4.76
23	4190	1.2	5.27
24	4410	1.1	5.15
25	3960	1.2	5.02
26	4600	1.1	5.65
27	4710	1.1	5.65
28–a	4640	1.2	5.92
28–a	4450	1.2	5.66
28–a	5050	1.1	6.22
28–a	5500	1.1	6.50
28–b	4110	1.6	6.43
28–b	3140	1.8	5.23
28–b	4070	1.6	6.46
28–b	2950	1.8	5.06
28–b	3550	1.6	5.62
28–c	1380	4.3	4.49
28–c	2170	3.8	5.28
28–c	1350	4.2	4.43

(For conversion to SI units, 1 lbf = 4.45 N.)

Table 3 Notes:

a– Mortar on concrete.
b– Mortar on ground.
c– Mortar on carpet.

Table 4. Results of Changing the Support Surface for the Concussion Mortar Fired with 28 g (1.0 ounce) Loads.

Parameter	Concrete	Ground	Carpet
Peak Pressure	4910 psi	3560 psi	1630 psi
FWHM	1.15 ms	1.68 ms	4.10 ms
Impulse	6.08 psi·s	5.76 psi·s	4.73 psi·s

(For Conversion to SI Units, 1 psi = 6.89 kPa.)

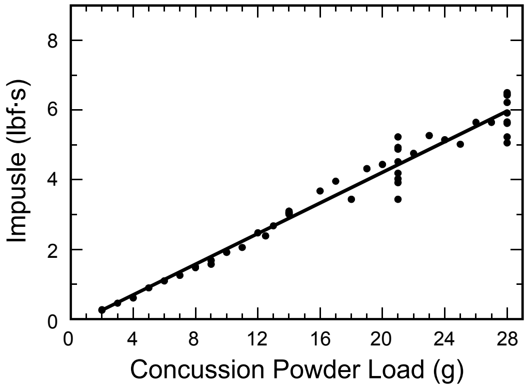

Figure 11. A graph of time integrated mortar recoil force (Impulse) as a function of concussion powder load mass.
(For conversion to SI units, 1 lbf = 4.45 N.)

Concussion Mortar Overpressure

Overpressure (air blast) profiles for the explosion of individual charges have the standard shape illustrated in Figure 12–bottom. Except for the heavy powder loads, the pressure profiles observed in this study do not have this shape, see Figure 13.

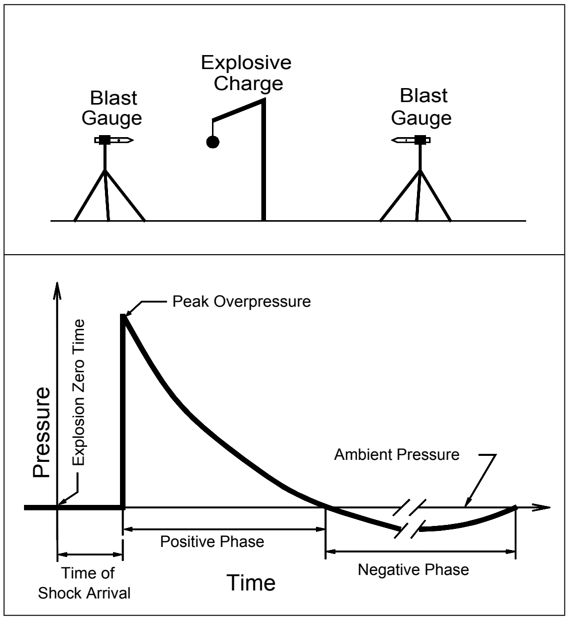

Figure 12. An illustration of a typical setup and overpressure profile from an explosive charge.

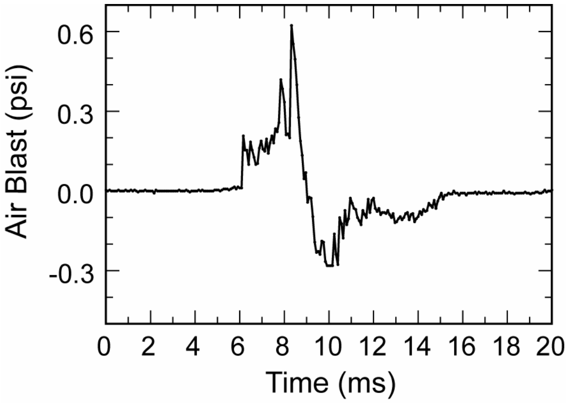

Figure 13. A concussion mortar overpressure profile.
(For Conversion to SI Units, 1 psi = 6.89 kPa.)

In addition, for light powder loads (<12 g), there tends to be random oscillatory fluctuations in the overpressure profile, see Figure 14. From the many other measurements made during this and previous studies, it is certain that the fluctuations are not the result of instrument or electrical noise. Further, these random oscillations essentially disappear for heavy powder loads (>20 g). The combination of peak narrowing and the reduction of the oscillatory fluctuations for heavier powder loads, results in pressure profiles that appear much like those of explosions, see Figure 15.

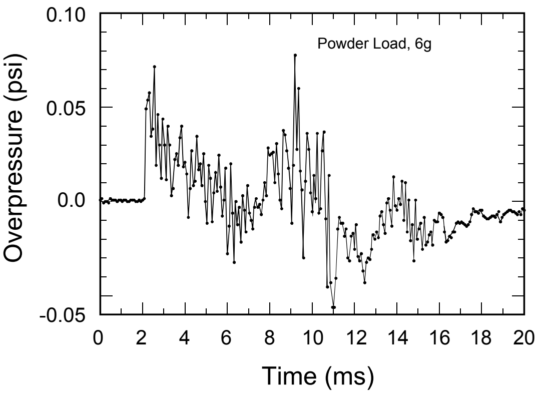

Figure 14. An example of an overpressure profile for a light powder load
(For Conversion to SI Units, 1 psi = 6.89 kPa.)

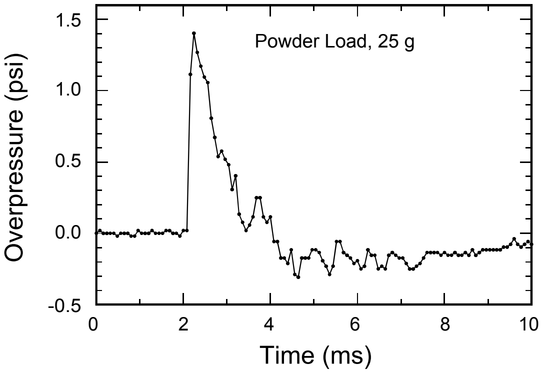

Figure 15. An example of an overpressure profile for a heavy powder load.
(For Conversion to SI Units, 1 psi = 6.89 kPa.)

The full set of results is presented in Table 5. Because of the presence of significant random oscillatory fluctuations in many of the profiles, the rapid rise of many others, and because it is the duration of the positive phase of the blast wave that is of interest, it was felt that attempts to determine the FWHM would be difficult and of little value. Accordingly, for each profile, an estimate of the duration of the positive phase was made. However, in some cases it was first necessary to mentally smooth the profiles to be able to pick the end point of the positive phase. Figure 16 is a graphical presentation of overpressure impulse as a function of concussion powder load mass.

Table 5. Concussion Mortar Overpressure Data.

Load (g)	Peak Pressure (psi)	Positive Phase (ms)	Pressure Impulse (psi·ms)
2	0.015	5.8	0.033
2	0.036	9.0	0.059
2	0.033	9.2	0.053
3	0.092	2.0	0.075
4	0.075	5.1	0.11
5	0.056	6.3	0.092
6	0.078	8.7	0.11
6	0.075	9.6	0.11
6	0.087	5.1	0.13
7	0.073	10.0	0.10
8	0.11	4.7	0.16
8	0.096	5.4	0.12
9	0.20	3.4	0.17
10	0.20	4.2	0.30
11	0.23	4.0	0.26
12	0.13	4.6	0.20
12	0.30	4.2	0.46
12	0.13	5.4	0.22
13	0.54	2.2	0.50
14	0.57	2.6	0.59
15	0.75	1.9	0.60
16	0.58	2.9	0.66
16	0.62	3.0	0.63
17	1.12	1.8	0.67
18	0.92	1.6	0.63
19	1.06	1.8	0.74
20	1.17	2.5	0.86
20	0.83	2.3	0.80
21	1.21	1.7	0.94
22	1.13	1.6	0.80
23	1.32	2.1	0.94
24	1.00	1.6	0.86
25	1.40	2.0	0.96
26	1.38	2.4	0.92
27	1.34	2.0	0.96
28	1.40	2.1	0.96
28	1.38	2.1	0.92
28	1.60	2.2	1.00
28	1.63	1.2	0.92
28	1.62	2.0	1.12

(For Conversion to SI Units, 1 psi = 6.89 kPa.)

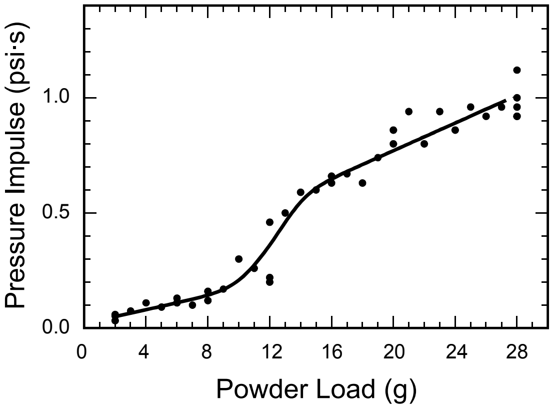

Figure 16. A graph of pressure impulse as a function of powder load mass.
(For Conversion to SI Units, 1 psi = 6.89 kPa.)

Discussion

Much of what was observed in these measurements may have been predicted. For example, over the range of concussion powder loads, internal mortar pressure increases with load mass. That is to say, it would be expected that internal mortar pressure would be greater for a 6 g load than for a 3 g load. However, this study was particularly interesting for the authors because a number of unexpected observations (for which the authors presently do not have satisfactory explanations). For example, it would not have been predicted that the internal mortar pressure profiles would narrow rather precipitously over a small range of loads (see Figure 7). Indeed, the data is fairly consistent with there being two essentially constant profile widths, one about 7 ms and one about 2 ms, with a fairly rapid transition between the two, occurring at powder loads of about 11 g. More unexpected was the observation that the wide internal mortar pressure profiles often consisted of a number of individual peaks (see Figures 5 and 6). Presumably this is an indication of some type of gross instability in the burning of light powder loads, but what would cause such instability? The times between these peaks are much longer than can be explained by some type of pressure reflection, along the length of the mortar, acting to cause pressure induced variations in burn rate. What is observed almost seems like multiple explosions overlapping in time; but would that even be possible, and if so, what is the mechanism that produces such a series of explosions within the concussion mortar?

One reason for this study was to determine the safety margin in the strength of concussion mortars. One method that has been used for centuries to verify that the strength of a device like a cannon provides an adequate safety margin, is to fire the device when intentionally overloaded with powder (a so-called "proof firing"). Note that even successful proof firings can damage and dangerously weaken the device being tested. Further, proof firings do not give quantitative information on the pressures being developed internally and thus cannot quantify the pressure safety margin. Accordingly, internal pressure measurements were made as part of this study. Using Luna Tech's Concussion Flash Powder, it appears that the internal mortar pressure for a maximum 28 g (1.0 ounce) load does not exceed 4000 psi (28 MPa) at the bottom of the combustion chamber and less near the muzzle of the mortar. It is important to note that the use of other, more violently burning, flash powders would certainly produce much higher internal mortar pressures! Accordingly, the following discussion concerning the adequacy of the strength of the concussion mortar used in this study only applies to its use with Luna Tech's Concussion Flash Powder.

To calculate the strength safety margin for a concussion mortar, it is necessary to first determine its burst strength. For one way to do this, consider the following. Concussion mortars are generally made using a mild, cold-rolled steel (such as SAE 1018), the yield strength of which is rated[2] at 40,000 psi ($2.8x10^8$ N/m^2). Clavarino's equation[3] can be used to estimate the maximum burst strength of a thick walled cylindrical pressure vessel with closed ends (the bottom of a concussion mortar's combustion chamber). Similarly, Birnie's equation[3] can be used for the calculation at the open end of the concussion mortar. When these calculations are performed, using the yield strength as the safe strength of the steel, the result is a maximum burst strength of a little over 20,000 psi (1.4 MPa). Accordingly, there is a pressure safety margin of at least a factor of five for the concussion mortar in this study using Luna Tech's Concussion Flash Powder. (It is important to note that the authors are not mechanical engineers. Accordingly, some degree of caution is appropriate regarding the information in this paragraph.)

The recoil forces measured in this study during the firing of a concussion mortar with a full load of powder are in good agreement with the earlier study,[1] especially considering the significantly different methods employed. In the earlier work, when using Luna Tech's Concussion Flash Powder, it was observed that the recoil, produced upon firing the mortar in a downward direction, was sufficient to raise a 25 pound (11.4 kg) mortar, 8 inches (0.20 m) into the air. This corresponds to an initial upward velocity of 6.6 feet/s (2.0 m/s). When using the impulse measured in this study for the concussion mortar fired on a concrete slab, an initial upward velocity of 7.9 feet/s (2.4 m/s) would be produced for the same mortar mass. This value is only 20% higher than the earlier result.

The recoil forces recorded in this study (as high as 5500 lbf), probably appear to some readers as being quite high. However, it is important to remember that these high forces are being applied for less than 2/1000 of a second. This is the same impulse and similar force that could be produced by dropping a 25 pound (11.4 kg) object from a height of one foot (0.3 m). Further, should it be deemed necessary, the peak recoil force can be significantly reduced (e.g., by 66%) by simply placing the concussion mortar on a soft surface such as carpeting (see Table 4). Note that it is not peak force, but impulse that is a measure of a recoiling concussion mortar to cause damage. However, the use of carpet under the mortar is also energy absorbing, as indicated by the 22% reduction in impulse.

The shape of the overpressure profile, under some conditions of these measurements, is not the same as those from explosions (see Figures 12, 13, and 14). As a result, the scaling equations used to predict blast pressures at various distances from an explosion may not be reliable. Accordingly, a more complete discussion of the expected effects of concussion mortar firing on human hearing will be delayed until more complete data has been assembled. However, some comments can be made regarding sound levels at the distance used in this study, 5.8 feet (1.8 m). For the full recommended powder load (1.0 ounce or 28 g) of Luna Tech's Concussion Flash Powder, the maximum measured pressure was approximately 1.6 psi (11 kPa). It is reported that upon exposure to a blast pressure of 15 psi approximately half the population will suffer rupture of the ear drum (tympanic membrane); at 3.2 psi approximately 1% will experience rupture of their ear drums.[4] Further, the threshold for ear drum rupture is reported[4] to be in the range of 2 to 4 psi.

Ruptured ear drums are not the only concern relating to noise induced hearing loss, there can also be temporary and permanent loss in hearing acuity (referred to as baseline shifts). Various researchers have set different criteria for what degree of hearing loss is acceptable, under specific circumstances. However, by one set of criteria, an exposure to a single impulsive sound event of less than 162 dB "will not produce an excessive risk of hearing loss".[5] Further, for exposure to 100 impulsive noise events (explosive sounds) per day, the acceptable sound level is approximately 140 dB.[5] At the distance used in this study, a sound level of 160 and 140 dB should be observed for loads exceeding approximately 12 and 2 grams, respectively.

Graphing internal mortar pressure and recoil force as impulse and pressure impulse produced straight lines, thus effectively eliminating the effect of varying peak width. However, when this was done for overpressure, there is a somewhat obvious break in the curve at about 12 g loading mass (see Figure 16). In effect, powder loads greater than 12 g are disproportionately more effective at producing overpressure (air blast) than are loads less than 12 g. It might be possible that this is the result of some type of increased efficiency in the explosive burning of the concussion powder inside the mortar. However, if that were the case, a similar break would also have to be present in the impulse curve for internal pressure, and no such break occurs (see Figure 9). A more likely explanation is that the added blast is being produced outside the mortar. Recall that the concussion flash powder used in these measurements is quite fuel rich (approximately 1.5 times the stoichiometric amount of magnesium). Most of this excess must surely burn as it mixes with oxygen from the air. If the mixing is thorough and fast, that burning can be violent enough to contribute to the production of overpressure.

Acknowledgments

The authors gratefully acknowledge Bob Greenburg, John Bergman, Scot Anderson, Ed Brown, Tom Foster and Steve Wilson, who assisted with some aspect of this work. In addition, the technical and editorial input of Mark Grubelich is especially appreciated.

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Prediction of Flame Temperatures, Part 1: Low Temperature Reactions

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ABSTRACT

A method based on heat of reaction and heat capacity at constant pressure (ΔH_r and C_P) was devised for the prediction of flame temperatures for simple "low temperature" pyrotechnic reactions containing either potassium chlorate, potassium perchlorate, potassium nitrate, or ammonium perchlorate ($KClO_3$, $KClO_4$, KNO_3, or NH_4ClO_4) as the oxidant, and a mixture of shellac and sodium oxalate ($Na_2C_2O_4$) as fuels. The method has an average error of ±41° for 15 reactions covering a 700° temperature range around 2200 K, with essentially no systematic error. Good predictions were obtained on calculations based on the published decomposition schemes of $KClO_3$, $KClO_4$, and KNO_3, but the prediction of the flame temperatures of NH_4ClO_4 mixtures required a different decomposition scheme than those published in the pyrotechnic literature.

Keywords: flame temperature, heat capacity, thermodynamics, heat of reaction

Introduction

Much of pyrotechnics involves the study of flames. A flame can be defined as "the hot luminous mass of gas or vapor near a burning mass," Since a flame is "hot," one of the questions that can arise is "how hot is the flame?" The answer to this question has many far-reaching ramifications because many phenomena depend on temperature: the luminosity of black body objects, the excitation of atomic and molecular species, the presence or decomposition of molecular species which emit colored light (e.g., barium monochloride) or black body radiation (e.g., magnesium oxide).

However, the measurement of flame temperatures is not an easy task. Normal thermometers are out of the question, and even a platinum resistance thermometer cannot be used, since the flame temperatures generally exceed the melting point of platinum. Flame brightness does not equal temperature, so luminosity cannot be used. Shimizu has published a number of flame temperature studies using the sodium–D line reversal method. This method depends on the fact that a cloud of sodium atoms will disproportionately absorb the light emitted by a cloud of relatively hotter sodium atoms, while they will not absorb the light emitted by a cloud of relatively cooler sodium atoms. The flame is seeded with sodium atoms, and a variable temperature source (typically a tungsten filament), which is also seeded with sodium atoms, is viewed through the flame. The temperature of the filament is raised, and the intensity of the sodium line is compared to the black body radiation background. When the sodium line becomes less bright than the background (the sodium in the flame is absorbing the filament-generated sodium radiation compared to the filament background), then the filament temperature is greater than the flame temperature. The temperature of the D–line reversal is the temperature of the flame. This technique is beyond the capabilities of most pyrotechnic experimenters.

Thus, the purpose of this study was to devise a theoretical method which will enable any experimenter to estimate flame temperatures, using commonly available personal computers. This paper discusses the prediction of the flame temperature of some relatively simple mixtures. Future papers will examine more complex mixtures, the interactions between temperature and luminosity, and the fate of molecular species.

Method

Not all chemical reactions give off (or absorb) the same heat for the same weight of reactants. For example, a thermite mixture based on 75% iron(III) oxide (Fe_2O_3) and 25% aluminum (Al) gives off 0.93 kcal/gram, while a similar mixture consisting of 74% chromium oxide (Cr_2O_3) and 26% Al gives off only 0.60 kcal/gram.[1a] Since this liberated heat warms the products of a pyrotechnic reaction, then it follows that a more exothermic reaction should generally give a hotter flame temperature. Thus, it is necessary to calculate the amount of heat released by a given reaction (heat of reaction, ΔH_r). Fortunately, ΔH_r is relatively easy to compute[2] by determining the nature of the starting materials and the products. Then one assumes that all of the starting materials are rendered into their individual atomic components, and the amount of heat needed to do that is calculated. Then the amount of heat released when those atoms are combined to give the products is calculated. The difference of these two numbers gives ΔH_r. This can be done by reference to tables of the Heats of Formation (ΔH_f) for each compound.[3,4] Stable products have negative heats of formation (e.g., potassium nitrate, –118.2 kcal/mol), and unstable products would have positive heats of formation (e.g., ozone, 34.1 kcal/mol). Heat is required to break apart a molecule such as potassium nitrate (KNO_3), so it would require the input of 118.2 kcal for each mole (101.1 g). Most reactions do not actually occur by being broken into single atoms and then recombining to give the products — the actual step by step process is much more complex and involves numerous polyatomic intermediates. However, the thermodynamic property of the change of heat (ΔH_r) is independent of the actual reaction steps, but depends only on the starting materials and final products. Thus this imaginary process can be used to calculate ΔH_r.

Once ΔH_r is known, a correlation between ΔH_r and flame temperature (T) could be investigated. This was done for 38 reactions with flame temperatures that were published by Shimizu.[5,6] The results are shown in Figure 1. The heat of reaction was calculated per 100 grams since molar quantities cannot be used for mixtures of many different molecules of different molecular weights. It can be seen that there is a definite trend to the correlation, but the correlation is not good (correlation coefficient, R^2 = 0.482). There are some particularly disturbing features of this graph. For example, reactions with ΔH_r = –100 kcal/100 g ±10% show flame temperatures ranging from 2100 to 3800 K, and reactions that show a flame temperature of about 2800 K come from reactions with ΔH_r ranging from –125 to –300 kcal/100 g. Examination of the points furthest from the line showed that some exhibited the well known temperature lowering effect of organic additives to a magnesium fuel; that is the reactions with a high ΔH_r (~–300 kcal/100 g) but low flame temperatures (~2800 K) contained both magnesium and an organic fuel. However, some "simple" reactions, such as 50:50 mixtures of either barium nitrate or potassium perchlorate ($Ba(NO_3)_2$ or $KClO_4$) and magnesium (Mg) also showed surprising behavior. The two had similar flame temperatures (~3800 K), but their ΔH_r differed by almost 200 kcal/100 g. Thus, this simplistic method was deemed to be nearly useless.

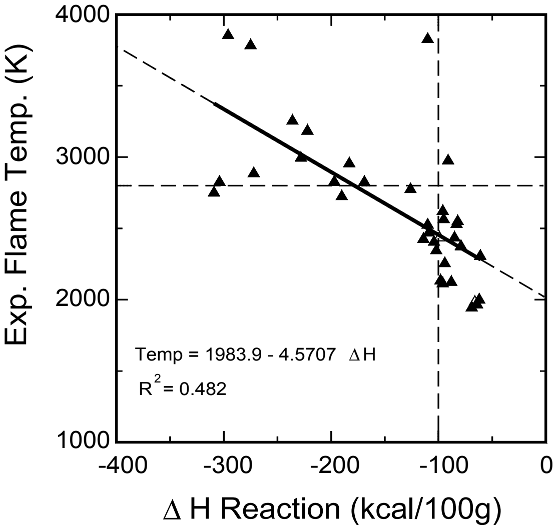

Figure 1. Attempted correlation of ΔH_r with flame temperature.

One of the major problems with this method was due to the fact that the temperature of any body is not only determined by the amount of heat absorbed by that body (ΔH_r), but also by the heat capacity (C_P) of that body. In this discussion, the term "body" can mean a complex mixture of solids, liquids, or gases. The heat ca-

Table 1. The Values for C_P (cal/mole deg) Used in this Study.

Temp (K)	KCl	K_2CO_3	CO_2	H_2O	O_2	Na_2O	C	H_2	N_2	HCl	Cl_2
300	12.26	20.50	8.89	8.03	7.02	17.45	2.05	6.89	6.69	6.96	8.12
500	13.08	22.50	10.67	8.41	7.43	19.43	3.49	6.99	7.07	7.00	8.62
700	13.86	24.23	11.84	8.95	7.88	21.40	4.44	7.03	7.35	7.16	8.82
900	15.03	26.16	12.66	9.54	8.21	23.38	4.97	7.15	7.67	7.42	8.92
1100	17.2	28.09	13.24	10.15	8.44	25.35	5.30	7.30	7.94	7.69	8.98
1300	17.59	30.02	13.65	10.72	8.60	27.00	5.52	7.49	8.16	7.93	9.03
1500	17.59	31.97	13.95	11.23	8.74	27.03	5.66	7.72	8.33	8.14	9.07
1700	17.59	33.91	14.17	11.67	8.86	27.06	5.76	7.92	8.46	8.31	9.10
1900	9.29	35.87	14.35	12.05	8.97	27.07	5.83	8.11	8.56	8.44	9.13
2100	9.33	36.80	14.49	12.37	9.08	27.10	5.99	8.28	8.64	8.56	9.17
2300	9.37	36.80	14.60	12.63	9.19	27.11	5.94	8.43	8.70	8.66	9.20
2500	9.41	36.80	14.69	12.86	9.30	15.01	5.97	8.58	8.76	8.74	9.24
2700	9.45		14.77	13.06	9.40	15.01	6.01	8.70	8.80	8.81	9.29
2900	9.52		14.84	13.23	9.50	15.01	6.04	8.81	8.84	8.87	9.36
3100	9.56		14.84	13.37	9.60	15.01	6.07	8.91	8.87	8.92	9.40
3300	9.60		14.95	13.50	9.68	15.24	6.10	9.01	8.90	8.97	9.46
3500	9.64		15.00	13.62	9.72		6.13	9.11	8.94	9.04	9.52
3700	9.68		15.05	13.72	9.84		6.16	9.20	8.95	9.09	9.57
3900	9.72		15.09	13.81	9.90		6.20	9.29	8.98	9.11	9.62
4100	9.72		15.14	13.89	9.96		6.23	9.38	9.00	9.13	9.66

pacity of different bodies is not the same. It takes more heat to warm 1 mole of CO_2 by 1 °C than it takes to warm 1 mole of N_2 (8.87 *versus* 6.96 calories/degree mole). That is because heat is related to motion, and the molecules of carbon dioxide (CO_2) are substantially heavier than the molecules of nitrogen (N_2). Compare two hypothetical reactions which each yield –10.0 kcal. If one reaction gives 1 mole of CO_2 as a product, then the rise in temperature of the gas will be 10/0.0087 = 1140°. A similar reaction that yields 1 mole of N_2 will experience a rise in temperature of 10.0/0.0069 = 1440°. Thus, one of the things that will have to be taken into account is the molar quantities and heat capacity of the gaseous and solid products produced in any pyrotechnic reaction.

In addition, the heat capacity of a material is not constant with changing temperature. As a body becomes hotter it generally takes more heat to warm that body by a given temperature difference. For example, it takes 8.87 calories to warm 1 mole of CO_2 by 1 °C at room temperature, but at pyrotechnic temperatures (2500 K) it requires 14.69 calories for the same effect. Thus, to accurately calculate the temperatures of pyrotechnic flames, the changing values of C_P must also be accounted for. The values of C_P used in this study are listed in Table 1. Most of these values were taken from the JANAF tables.[3] Others were obtained using the formulas for calculating C_P given in the *CRC Handbook*.[4] In addition to C_P, the phase transition temperatures, heats of transition, or changes in molecular structure are given[3,4] in Table 2. Where a molecule breaks into two fragments (e.g., $Na_2O \rightarrow NaO^{\cdot} + Na^{\cdot}$) the value for C_P is taken as the sum of the heat capacities for the fragments.

Table 2. Phase Transitions, Heats of Transition, or Changes in Molecular Structure.

Change	Temp. (K)	Heat (kcal/mol)
$KCl_{(s)} \rightarrow KCl_{(l)}$	1044	+6.28
$KCl_{(l)} \rightarrow KCl_{(g)}$	1700	+28.7
$K_2CO_{3(s)} \rightarrow K_2CO_{3(l)}$	1170	+7.80
$K_2CO_{3(l)} \rightarrow K_2O + CO_2$	2100	+106
$Na_2O_{(s)} \rightarrow Na_2O_{(l)}$	1193	+10
$Na_2O_{(l)} \rightarrow NaO_{(g)} + Na_{(g)}$	2250	+108
$Cl_{2(g)} \rightarrow 2Cl^{\bullet}_{(g)}$	2100	+30

The process used to calculate the final flame temperature is as follows: First the ΔH_r is calculated using tables that give ΔH_f for the starting materials and products at 298 K (room temperature). The heat which is liberated by the reaction is then assumed to warm the reaction products to their final temperature. This is done by a process of stepwise calculation. All the products (except water, discussed below) start in their standard states (solid, liquid, gas) with an initial temperature of 298 K. Then, given their molar quantities, and heat capacities and any phase transitions, the amount of energy required to raise the temperature by a given amount is calculated. This study used a step size of 200 K, which was chosen as a compromise between accuracy and the tedium of entering long tables of numbers into the spread sheets. The amount of heat required is subtracted from the amount of heat that was available, and the process is repeated until the final step requires all of the available heat (or more). Interpolation between the final two steps gives a good estimation of the actual temperature.

Surprisingly all of the phase transitions *except* that of the vaporization of water had to be taken into account. If the loss of heat due to heat of vaporization (ΔH_{vap}) of water ($H_2O_{(l)} \rightarrow H_2O_{(g)}$) was included in the stepwise temperature calculations, all of the flame temperatures were predicted to be too low by an amount corresponding to $\Delta H_{vap}(H_2O)$. This probably reflects the fact that the reaction actually doesn't occur at 298 K, but at an elevated temperature above the boiling point of water. Warming a fuel to a temperature above 373 K (100 °C) requires less heat input than warming and boiling the same amount of water. Liquid water contains a network of strong hydrogen bonds, and the boiling of water requires a large amount of heat to break these hydrogen bonds. Since these hydrogen bonds do not exist in a fuel, no heat is needed to break such hydrogen bonds when raising the temperature of a fuel past 373 K. If the fuel then burns above this temperature, the product water formed will already be in a gaseous state. The fact that other transitions such as the melting of potassium chloride ($KCl_{(s)} \rightarrow KCl_{(l)}$) had to be taken into account may reflect the fact that the crystal forces holding potassium chlorate ($KClO_3$) together are roughly the same as those holding KCl together, so the same answer is obtained no matter if we calculate ΔH_{vap} for $KClO_3$ or for KCl. Thus, the calculations still work in spite of the simplifying assumption that the heat of reaction warms a KCl product rather than $KClO_3$ starting material.

This method contains several other simplifications. For example, molecules such as $KClO_3$ do not begin to give off oxygen, and fuels such as shellac do not begin to burn, until they have been warmed by several hundred degrees. However, the C_P of the starting materials is almost the same as the combined C_P of the products, so the effects of ignoring this effect are negligible.

This calculation can be simplified slightly by using heats of decomposition which give known products. For example, there is no need to calculate ΔH_f for the decomposition of potassium chlorate ($KClO_3 \rightarrow K^{\cdot} + Cl^{\cdot} + 3/2\ O_2$) and then recalculate the ΔH_f for potassium chloride ($K^{\cdot} + Cl^{\cdot} \rightarrow KCl$). Instead one may take the shortcut of adding the heat payback of forming KCl (–104.4 kcal/mol) to the heat cost of decomposing $KClO_3$ (–95.1 kcal/mol) to find that one actually obtains –10.6 kcal/mol when $KClO_3$ decomposes. This fact can be experimentally verified by placing a small amount of pure $KClO_3$ on an anvil and striking it with a hammer. It is possible to get the sample to decompose without a fuel. This is one reason $KClO_3$ is such a useful yet sensitive and potentially dangerous oxidizer. The ΔH_f and heat of decomposition (ΔH_{decomp}) values used for this study are listed in Table 3.[1,4,8]

A complication could also arise due to the fact that the ratios of the products of reactions can change depending on a number of factors. These factors are generally poorly controlled in a pyrotechnic environment. For example, a change in pressure can cause a shift in the equilibrium of a reaction. When black powder is burned in a gun, the products vary depending on the pressure. The sudden escape of the bullet causes a sudden adiabatic decrease in temperature and pressure, and the product ratio is a snapshot of the product mixture at the elevated pressures. Under conditions which afford comparatively low pressure one obtains predominantly potassium carbonate (K_2CO_3) and potassium sulfide (K_2S), while at higher proof load pressures one obtains[7] potassium sulfate (K_2SO_4) and potassium cyanide (KCN). However, flames gen-

Table 3. Heats of Decomposition and Heats of Formation Used in this Study.

Reaction	ΔH (kcal/mol)
$KClO_3 \rightarrow KCl + 3\ O$	–10.6
$KClO_4 \rightarrow KCl + 4\ O$	–0.68
$2\ KNO_3 \rightarrow K_2O + N_2 + 5\ O$	+75.5
$2\ NH_4ClO_4 \rightarrow N_2 + 3\ H_2O + 2HCl + 5\ O$	–107.9
$2\ NH_4ClO_4 \rightarrow 2.5\ Cl_2 + 2\ N_2O + 2.5\ NOCl + HClO_4$ $+ 1.5\ HCl + 18.75\ H_2O + 1.75\ N_2 + 12.75\ O$	–53.4
$N_2O \rightarrow N_2 + O$	–20
$2\ NOCl \rightarrow N_2 + O_2 + Cl_2$	–12.6
$HClO_4 \rightarrow HCl + 4\ O$	–12.3
Shellac $\rightarrow 16\ C + 32\ H + 5\ O$	+227
$Na_2C_2O_4 \rightarrow Na_2O + 2\ C + 3\ O$	+214
H_2O	–68.3
CO_2	–94.1
HCl	–22.0
N_2, O_2, H_2, C, Cl_2	0.0 (defined)

erally occur at near-atmospheric pressures, so the shift of equilibria is not generally a significant complication for this study.

However, the calculation of ΔH_r for black powder did reveal two significant problems, both related to the proper choice of the reaction products. The majority of pyrotechnic compositions are fuel rich. When shellac is burned in an oxygen deficient environment the amounts of CO_2 (producing –94.1 kcal/mol), carbon monoxide (CO) (–26.1 kcal/mol) and H_2O (–68.3 kcal/mol) formed may vary depending on conditions. There is no easy guideline to determine the ratios *apriori*. Thus one often has to calculate a range of ΔH_r based on the possible product ratios.

In this study three numbers were calculated using different methods: (**A**) The "most stable first" method, in which the reactants that gave the most stable products scavenged all of the oxygen first, followed by the second most stable, etc., until all of the oxygen was consumed. The assumption behind this method is that the product molecules and fragments are in dynamic equilibrium at the reaction temperature, and react to give a predominance of the most stable products. (**B**) The "balanced" method, in which all of the reactant molecules were consumed proportional to their concentrations in the reaction. (**C**) The "hydrogen first" method, in which the hydrogen was consumed first, then the carbon, etc. The basic assumption behind the hydrogen–first method is based on the fact that when a reactant molecule approaches an organic fuel molecule, the hydrogens are the most accessible atoms on the fuel. All three methods were used, and were then judged on their ability to predict the flame temperatures. One method was clearly superior, as shown below.

In addition, one has to be careful to consider possible "secondary" reactions. The accepted mode of decomposition[1b] for KNO_3 is to give potassium oxide (K_2O), N_2, and O_2. However, calculations for ΔH_r for black powder based on these products gave values that were from 22 to 35 kcal/100 g too low compared to the experimental measurement. However, the discrepancy was due to the fact that the experiments were performed in a sealed bomb immersed in a water bath, which held the initial products in close proximity. As the mixture released its heat to the bomb bath, this allowed the K_2O to combine with the CO_2 releasing additional heat. By adding in the ΔH_r contribution of the reaction of K_2O with CO_2 we were able to obtain a theoretical value of –62.8 kcal/100 g, as compared to the experimental value[1c] of –66 kcal/100 g.

Results

A detailed example of how one of these calculations was carried out is given here. The other calculations all followed this general method. The system chosen for the detailed expostulation is a mixture of 70% $KClO_3$, 20% shellac, and 10% sodium oxalate ($Na_2C_2O_4$).

First the molar ratios of the three components were calculated. A sample size of 100 grams was assumed for the ease of calculation. The molecular weights of $KClO_3$ and $Na_2C_2O_4$ were found by simple calculation, and the value for shellac ($C_{16}H_{32}O_5$, mw = 304) was taken from Conkling. Thus 70 grams of $KClO_3$ is 0.571 moles, 20 grams of shellac is 0.068 moles, and 10 grams of $Na_2C_2O_4$ is 0.075 moles. The ΔH_{decomp} for $KClO_3$ is –10.6 kcal/mol. Thus the decomposition of 0.571 moles yields –6.05 kcal of heat. The ΔH_{decomp} for shellac (227 kcal/mol) and for $Na_2C_2O_4$ (214 kcal/mol) were taken from *Langes Handbook of Chemistry.*[8] It was assumed that the products of decomposition for sodium oxalate would be Na_2O and 2 C and 3 O. Thus the value for ΔH_{decomp} for the two fuels was 31.3 kcal/mol (0.068 × 227 + 0.075 × 214).

The decomposition of 0.571 moles of $KClO_3$ would yield 1.71 moles of oxygen atoms (not O_2), and the decomposition of the fuels would yield 1.23 moles of carbon atoms, 2.16 moles of hydrogen atoms, and an additional 0.56 moles of oxygen atoms to afford a total of 2.27 moles of oxygen atoms. Since the total amount of oxygen needed to burn the carbon and hydrogen completely would be 3.54 moles (2 oxygens for each carbon, and 1 oxygen for each 2 hydrogens), this means that the mixture is fuel rich, and that the oxygen have-to-need ratio is 0.63. This is important for calculating the heat of combustion *via* the different methods.

Method **A** gives nearly complete combustion of the C to give 1.13 moles of CO_2. This would give –106.3 kcal/100 g. Since this would consume all of the oxygen, 0.10 moles of carbon and 1.08 moles of H_2 would be unreacted. No water would be formed. The total heat output from method **A** would be –81.1 kcal/100 g.

Method **B** balanced the amount of C and H consumed based on the percentage of available oxygen. Since there was only 63% of the needed oxygen, each reactant would afford only 63% of its potential product, and leave 37% behind as unconsumed reactant. Thus 0.6 × of CO_2, affording –72.8 kcal of heat. Only 0.63 × 1.08 moles of hydrogen would be burned, to afford 0.68 moles of H_2O and –46.3 kcal. The total is –93.9 kcal/100 g, which is more than that obtained from method **A**. This would leave 0.46 moles of carbon and 0.40 moles of H_2 unreacted.

Finally, method **C** assumes that all of the hydrogen burns first to afford 1.08 moles of H_2O affording –73.7 kcal/mol. The remaining 0.22 moles of oxygen would burn 0.11 moles of carbon to yield 0.11 moles of CO_2 releasing –10.3 kcal. The total amount of heat released in this fashion would be –58.85 kcal/100 g.

The values for ΔH_r and molar amounts for the products found by methods **A**, **B** and **C** were then placed in spread sheets. Table 4 shows the method **A** spread sheet for this reaction. The columns under each molecule label (KCl, CO_2, etc.) contain the heat capacities (C_P) for each product, as found in the JANAF tables.[3] The column to the right of each of these columns contain the moles of each molecule, and then the amount of heat required to raise that amount of product from the temperature of the previous row to the temperature of that row. So, for example, it requires 2.86 kcal to raise 1.13 moles of CO_2 from 900 K to 1100 K. Note that there are several discontinuities in the values for KCl and Na_2O which are underlined. These correspond to phase transitions or decompositions, where a product goes from a solid to a liquid phase, or from a liquid to a gas phase. These phase changes require two changes: First, the C_P for the two phases will be different. For example, the C_P of solid KCl ranges from 12.26 to 15.03 cal/mole, the C_P of liquid KCl narrowly ranges from 17.20 to 17.59 cal/mole, and the C_P

Table 4. Copy of the Spread Sheet for the Calculation of the Temperature of the Flame of a Mixture of 70% Potassium Chlorate, 20% Shellac, and 10% Sodium Oxalate. The Details of the Spread Sheet are Given in the Text.

Cmpd	KCl		CO_2		H_2O		Na_2O		C		H_2		
Moles		0.57		1.13		0		0.074		0.1		1.08	ΔH
Temp	C_p	ΔH	C_p	ΔH	C_p	ΔH	C_p	ΔH	C_p	ΔH	C_p	ΔH	Rem.:
300	12.26		8.89		8.03		17.45		2.05		6.89		
500	13.08	1.39	10.67	2.00	8.41	0.00	19.43	0.25	3.49	0.04	6.99	1.48	75.87
700	13.86	1.49	11.84	2.41	8.95	0.00	21.4	0.28	4.44	0.06	7.03	1.50	70.16
900	15.03	1.58	12.66	2.67	9.54	0.00	23.38	0.31	4.97	0.08	7.15	1.51	63.92
1100	17.2	5.29	13.24	2.86	10.15	0.00	25.35	1.08	5.3	0.09	7.3	1.54	53.04
1300	17.59	1.96	13.65	2.99	10.72	0.00	27.00	0.37	5.52	0.10	7.49	1.57	46.03
1500	17.59	2.00	13.95	3.08	11.23	0.00	27.03	0.39	5.66	0.11	7.72	1.61	38.81
1700	17.59	18.30	14.17	3.15	11.67	0.00	27.06	0.39	5.76	0.11	7.92	1.66	15.11
1900	9.29	1.05	14.35	3.20	12.05	0.00	27.07	0.39	5.83	0.11	8.11	1.71	8.628
2100	9.33	1.05	14.49	3.24	12.37	0.00	27.10	0.39	5.99	0.11	8.28	1.75	2.058
2300	9.37	1.06	14.6	3.27	12.63	0.00	27.11	0.39	5.94	0.11	8.43	1.78	–4.587
2500	9.41	1.06	14.69	3.29	12.86	0.00	15.01	8.98	5.97	0.11	8.58	1.82	–19.87
2700	9.45	1.07	14.77	3.31	13.06	0.00	15.01	0.22	6.01	0.11	8.7	1.85	–26.46
2900	9.49	1.07	14.84	3.33	13.23	0.00	15.01	0.22	6.04	0.12	8.81	1.87	–33.10
3100	9.52	1.08	14.84	3.35	13.37	0.00	15.01	0.22	6.07	0.12	8.91	1.90	–39.78

(Temp. is in Kelvin, C_p is in cal/mol deg, and ΔH is in cal.)

of gaseous KCl is 9.29 to 9.72 cal/mole. Secondly, melting or boiling requires additional heat as per Table 2. For example, it requires 28.7 kcal/mol to convert liquid KCl at 1700 K to gaseous KCl at the same temperature. These values are also available from the JANAF tables. Note that C_P is reported in calories while heats of phase changes are reported in kcal.

The last column sums up all of the heat penalties and calculates how much heat remains. At 2100 K there are still 2.06 kcal remaining from the reaction, but at 2300 K there is a deficit of 4.59 kcal. Linear interpolation between these two points gives an estimated flame temperature of 2160 K.

Figure 37 of Reference 5 gives flame temperature as a function of the composition of four mixtures of potassium chlorate and shellac, and of the distance along the flame. Figure 2 of this paper is taken from that figure, but has been modified to give temperatures in K. The agreement of the estimated temperature (2160 K) and the temperature one cm from the burning surface (2190 K) is very good. Note that the curve for 70% $KClO_3$ starts at about 2190 K, then rises to about 2260 K, and then declines. This can be explained in the following fashion: Since this is a fuel rich mixture, the flame contains substantial amounts of hydrogen and some carbon. As these reactants travel away from the source of the flame, oxygen from the surrounding air dif-

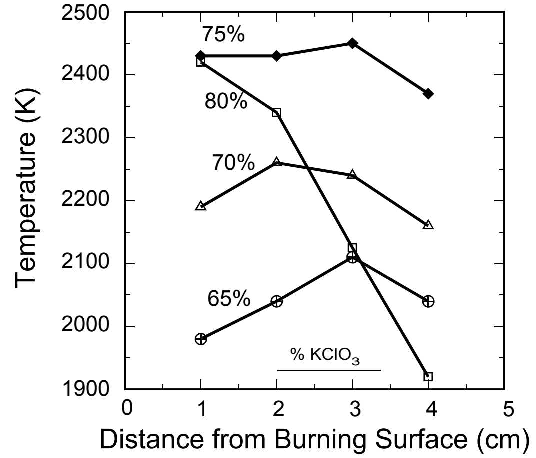

Figure 2. Flame temperature as a function of distance from the burning surface, for a mixture of n% potassium chlorate, 90–n% shellac, and 10% sodium oxalate (after Shimizu).

fuses into the flame and burns these highly reactive components. This releases additional heat without the "cost" of having to disassociate any oxidizers. Note that the 80% $KClO_3$ mixture is oxygen rich (17% extra oxygen), and shows a steady decline from its initial high temperature. This is probably due to the fact that the fuel is consumed by the oxidizer in the mixture and that no further reaction occurs away from the initial reaction. The 75% mixture is slightly fuel rich (17% oxygen poor), and so it shows a competition between cooling of the burnt products and warming by the burning of the remaining hydrogen by external oxygen. The flame temperature stays constant for 3 cm, and then begins to decline. Both the 70% and 65% mixtures are very oxygen deficient (37 and 49% respectively). These each show an initially low flame temperature which rises as external oxygen combines with the unburned fuels. This behavior is also seen in the shapes of the temperature versus distance curves for potassium perchlorate and ammonium perchlorate[6] (not reproduced here).

The flame temperatures predicted for the three methods are; **A**, 2161 K, **B**, 2431 K, and **C**, 1708 K. This trend was observed over all of the oxidizers studied. Method **A** consistently came closest, method **B** consistently gave an estimated temperature which was several hundred K too high, and method **C** always gave a temperature which was too low by several hundred K. Although all three methods were tried for each of the mixtures analyzed in this paper, only method **A** is reported.

The values for 15 reactions containing varying amounts of $KClO_3$, $KClO_4$, KNO_3 or NH_4ClO_4 with shellac (and with 10% $Na_2C_2O_4$ added for the line reversal method) are reported in Table 5 and shown in Figure 3. The small average error seems to indicate that there is no systematic error in the method. The absolute error is 2% (46°/2200 K), which is probably within the unreported errors in the experimental methods (for example, the combination of the weighing errors for the compositions tested and the errors in the temperature measurements may well be 2%).

Table 5. Estimated Flame Temperatures for Potassium Chlorate or Potassium Perchlorate, with Shellac and 10% Sodium Oxalate. Experimental Values are Taken from Shimizu.

Oxidizer	% Shellac	Est. Temp. (K)	Exp. Temp. (K)	Error (K)
80% $KClO_3$	10	2420	2430	–18
75% $KClO_3$	15	2460	2430	+28
70% $KClO_3$	20	2160	2190	–32
65% $KClO_3$	25	1960	1980	–22
80% $KClO_4$	10	2400	2370	+24
75% $KClO_4$	15	2450	2530	–88
70% $KClO_4$	20	2400	2400	–4
65% $KClO_4$	25	2160	2080	+75
75% KNO_3	15	1980	1950	+27
70% KNO_3	20	1940	1980	–43
65% KNO_3	25	1930	1840	+88
80% NH_4ClO_4	10	2470	2420	+48
75% NH_4ClO_4	15	2400	2470	–67
70% NH_4ClO_4	20	2300	2343	–41
65% NH_4ClO_4	25	2200	2110	+87

Average Error, absolute value:	46°
Average Error, signed:	+4.1°

Estimated Temperatures for ammonium perchlorate taken from Table 6.

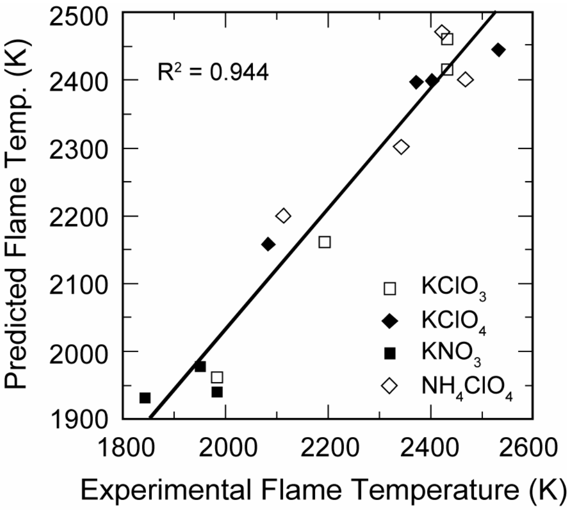

Figure 3. Predicted versus experimental flame temperatures for 15 different mixtures of oxidizer, shellac, and 10% sodium oxalate.

An additional complication arose while examining the system containing ammonium perchlorate (NH_4ClO_4) and shellac. An initial assumption had been made that the decomposition of the ammonium perchlorate followed the equation:

$$2\ NH_4ClO_4 \rightarrow N_2 + 3\ H_2O + 2\ HCl + 2.5\ O_2$$

This gives an exothermic decomposition, a high yield of oxygen and no solid products. One of the things keeping the temperature of the $KClO_3$ and $KClO_4$ reactions down was the rather high heats needed to melt and vaporize KCl. Since NH_4ClO_4 gives only gases, the thermal inertia of this reaction was low and the estimated temperatures were over 3000 K for all four ratios of NH_4ClO_4 to shellac. This did not agree with the experimental values, which ranged from 2113 to 2468 K.

Conkling[1d] says that over 350 °C the reaction for the decomposition of NH_4ClO_4 is

$$10\ NH_4ClO_4 \rightarrow 2.5\ Cl_2 + 2\ N_2O + 2.5\ NOCl +$$
$$HClO_4 + 18.75\ H_2O + 1.5\ HCl + 6.38\ O_2$$

The combination of the lower heat of decomposition and the reduced amount of oxygen available gave an overall ΔH_r which is too low. The effect of the low value of ΔH_r was exacerbated by the increased amount of water formed, since water has a high C_P on a per-gram basis. The estimated flame temperature for an 80% NH_4ClO_4/ shellac/ $Na_2C_2O_4$ flame based on this decomposition scheme was 2283 K, compared to the experimental value of 2423 K. The predicted temperatures were also too low for the reactions containing 75, 70, and 65 percent of NH_4ClO_4. Unfortunately, the original paper cited by Conkling was not available at our library, and so some assumptions about the reaction scheme above were made. It seems reasonable to assume that the perchloric acid ($HClO_4$) was formed *via* incomplete decomposition, since the re-formation of perchloric acid from a mixture of hot radicals of chlorine, hydrogen, and oxygen is entropically very unfavorable. It should be reasonable to assume that given a longer reaction time (or hotter temperature) that the perchloric acid ($HClO_4$) would not survive the reaction. In addition, it was felt that the N_2O and NOCl had probably formed either through the condensation of intermediate radicals ($NO^{\cdot}$ and $Cl^{\cdot}$) or as side product of the quenching of an incomplete reaction (e.g., N_2O).

Thus, it was suspected that some of the products shown in the equation above were either decomposing or failing to form. Since the value of ΔH_r is independent of the actual reaction pathway, the same result would be obtained if the products decompose, or simply fail to form from a high energy “stew” of intermediates. Thus, the spread sheet was modified to utilize the mixture of products based on the previous reaction scheme, and to modify them by “decomposing” the suspected product and calculating the amount of heat and oxygen (and hydrogen, etc.) liberated. The results for various assumptions are shown in Table 6.

Nitrous oxide (N_2O) is a good oxidizer and is used in model rocketry. It seems unlikely that N_2O would survive long in a fuel rich environment. N_2O is thermodynamically unstable and decomposition would yield both heat (–20

Table 6. Estimated Flame Temperatures for Various Mixtures of Ammonium Perchlorate, Shellac and Sodium Oxalate. The Columns Show What Temperatures Were Predicted When the Secondary Molecules Formed in the Decomposition Were Assumed to Decompose Further (or Equivalently, Were Never Made).

% NH_4ClO_4	Exp. Temp.	N_2O, NOCl Temp. (K)	$HClO_4$ Temp. (K)	$HClO_4$, N_2O Temp. (K)
80	2423	2330 (+48)	2430 (+3)	2470 (+48)
75	2468	2300 (–166)	2250 (–221)	2400 (–67)
70	2343	2210 (–135)	2160 (–188)	2300 (–41)
65	2113	2110 (–3)	2060 (–53)	2200 (+87)

(   ) = Difference with experimental temperature kcal/mol) and 1 mole of oxygen atoms for each mole of N_2O. When the assumption was made that the N_2O decomposed and the oxygen was utilized to oxidize some of the previously unburned carbon, then the ΔH_r went up, and the flame temperature was estimated to rise to 2378 K (exp. = 2423 K).

On the other hand, if it was assumed that the $HClO_4$ decomposes instead, then only –12.3 kcal/mol would be released upon decomposition, but a greater amount of oxygen would be evolved. This can be utilized to make both carbon dioxide and water which liberates a large amount of heat, and the predicted flame temp is raised to 2426 K. This predicted temperature is in amazingly good (and probably somewhat serendipitous) agreement with experiment. In fact, the best overall agreement between theory and experiment is obtained when it is assumed that *both* the N_2O and $HClO_4$ decompose (or are not formed in the first place). Although there are some reasonable agreements (the last column), it is obvious that more experimental and theoretical work needs to be done to accurately understand this oxidizer system.

Conclusion

The use of thermodynamics calculations promises to give the pyrotechnician a way to quickly and easily predict the temperature of pyrotechnic reactions. The method contains some dramatic assumptions such as the hypothesis that all of the carbon is oxidized before the hydrogen begins to be oxidized. These assumptions were made to put the method within the reach of a pyrotechnician who has access to a spreadsheet but who might lack the ability to run a more complicated simulation program. In spite of these simplifications the results are very accurate on mixtures of a single oxidant and a mixture of shellac and sodium oxalate. In addition, the method has given us several pointers to new directions of research with regard to the actual mode of decomposition of ammonium perchlorate. The next paper in this series will discuss more complex systems, such as those containing metallic fuels or mixed metal and organic fuel systems.

Acknowledgments

The author would like to thank Dr. Takeo Shimizu and Prof. Wesley Smith (of Ricks College) without whom this work would have been impossible. The author would also like to thank Bill Nelson, Mark Buda and the members of The Pyrotechnics Mailing List, and those few lonely souls on the Usenet group rec.pyrotechnics who discuss actual pyrotechnics.

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