Review of

The Chemistry of Fireworks

Michael S. Russell

Royal Society of Chemistry, 2000
ISBN 0-85404-598-8

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At first glance, this 117-page paperback book[1] looks very promising. According to the publisher's description, the book "is aimed at students with 'A' level qualifications or equivalent. The style is concise and easy to understand, and the theory of fireworks is discussed in terms of well-known scientific concepts wherever possible. It will also be a useful source of reference for anyone studying pyrotechnics as applied to fireworks."[1a]

The author of the work, Michael S. Russell, is a research chemist with a background in military and marine pyrotechnics, and he has worked as a firework display operator. He should be well qualified to write on this subject.

A quick look at the organization of the book is encouraging. The scientific material is presented in discussions of the various types of fireworks, and this seems a good way to achieve a balance between theory and practice. The initial enthusiasm and high expectations, however, soon turns to disappointment. Although the book is titled *The Chemistry of Fireworks*, there is not much chemistry, and there are far too many errors and misleading statements. In a book of this type, there should be none. There is quite a bit of physics, but this too is often either misleading or wrong, and the discussion of fireworks is rather superficial. Few formulations are given, and some of those are out-dated and downright dangerous.

The book has 12 chapters plus a glossary, the latter being located right after the Table of Contents. Some of the entries in the Glossary do not correspond to this reviewer's understanding of the current usage of the terms. For example, "bombette" is defined as "a combination of candles and/or shells packed in a box and fired by interconnecting fuse".[1b] Perhaps this definition comes from what Weingart[2a] calls "bombette fountains:"—"an effective combination of candles and floral shells packed in a box." The glossary in the third edition of Lancaster's *Fireworks Principles and Practice*, however, says that "bombette" is "in essence a mini shell, usually found as a component of a roman candle, and less often as a component of a mine or even as a sub-component of a shell."[3a] Another entry defines a mine as a "firework that is fired from a mortar and which contains a single propellant charge and pyrotechnic units".[1c] This excludes those mines in which the case of the firework serves as the mortar. The statement that meal powder is "used for priming and making matches"[1c] could be misleading. Presumably Russell was thinking about quick match, but it is likely that a reader would think of safety matches. A rocket is defined as a "self-propelled firework with stick for stabilization of flight".[1d] Are rockets with fins,[2b] or rockets stabilized by spinning,[4] any the less rockets for being without sticks? A notable aspect of the glossary is the number of entries associated with the British explosives regulations. The legislative control of fireworks is an important issue for those in the trade, but is it an appropriate subject for a book that is supposed to be about the *chemistry* of fireworks?

The first chapter, "Historical Introduction", is almost completely focussed on Black Powder. There are speculations about possible ways in which ancient Chinese alchemists might have discovered the fire-enhancing properties of saltpetre. Reading Russell's description of the alchemists' experiences with "their brew of honey, sulfur and saltpetre",[1d] one cannot help but wonder "How could he know *that*?" Presumably Russell's assertions are based on some work of historical research, but what, and by whom? This is an example of a very great shortcoming of this book: there are no references. There is a bibliography, but that is no substitute for references. It is most surprising, and regrettable, that the publishers did not insist that references be provided, particularly as they claim that the book will be "a useful source of reference for

anyone studying pyrotechnics as applied to fireworks."[1a]

The first chapter also includes a discussion of the pyrotechnic contributions of Roger Bacon, whose recipe for Black Powder is given as six parts by weight of saltpetre, five of "young willow (charcoal)" and five of sulfur. This recipe, along with the picture of Bacon on the same page,[1e] appears to have been taken from T. L. Davis' book *The Chemistry of Powder and Explosives*.[5a] Bacon's supposed recipe for gunpowder has been discussed in detail by Michael Swisher.[6] The recipe evidently originated in H. W. L. Hime's solution of an anagram, LVRV VOPO VIR CAN VTRIET attributed to Bacon, but for which "no manuscript authority now exists, nor do we know what ever did".[6a] According to Swisher, Hime gives Bacon's formula as *seven* parts of saltpetre, five of young hazlewood (charcoal) and five of sulfur. Swisher mentions that Davis "corrects" the formula to 6:5:5—a correction that does nothing to improve a formula already deficient in potassium nitrate. Davis' translation of the passage that includes the anagram[5b] is repeated word for word in this book,[1e] complete with the mistranslation of "corvli" as "willow" instead of "hazel". In his introductory remarks on the details of Black Powder manufacture, Russell states that a "loose" mixture of the three ingredients of Black Powder is "almost impossible to light", and "if ignition does occur, the burning is fitful and prone to extinguishment."[1f] Many a schoolboy knows better.

Another section in this chapter deals with "Further Uses of Black Powder". Here again the lack of references is frustrating. It would have been interesting to read more about the use of smoke from a potassium nitrate charcoal mix as a fire-extinguishing agent, an application that derives, we are told, from "the way in which the potassium salt in the smoke interferes with the combustion chemistry of a fire".[1g] Although it is supposed to provide a historical introduction to the chemistry of fireworks, this chapter offers instead a rather poor discussion of the development of Black Powder. Davis' outline[5c] of the development of pyrotechnic mixtures is vastly superior, despite having been written over half a century earlier.

The second chapter deals with the characteristics of Black Powder. There are brief discussions on the influence of pellet density and moisture content on burn time. The following sections, discussing the thermal decomposition of Black Powder and its ignition, introduce the Arrhenius equation,

$$k = A\mathrm{e}^{-E/RT}$$

where k is the rate constant of the reaction, A the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

This equation is almost immediately confused with one of similar form that deals with the time to ignition, rather than the reaction rate constant. This equation is presented in the book as equation (2.10):

$$t = A\mathrm{e}^{-E/RT}$$

"where t is the time to ignition (i.e., ignition delay) at a temperature T in degrees absolute, and the other parameters are as described for equation (2.9)". Equation (2.9) is the Arrhenius equation. An increase in the rate constant k is associated with a decrease in the time to ignition, so the negative sign of the exponent in the Arrhenius equation must be changed to positive if the equation is to describe the time to ignition. Additionally, the constant of proportionality will be different in each equation. Neither of these changes has been made. One might perhaps attribute this to a printer's error, had not the incorrect sign been used in both the exponential and logarithmic versions of the equation, and had the author not stated that the "other parameters" were the same in both equations.[1h] The associated graphs (Figures 2.5 and 2.6) are correct and inconsistent with the equation.

A section on the thermal analysis of Black Powder includes exceedingly terse descriptions of thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).[1i] The definitions of the latter two techniques appear to have suffered from the omission of some words. It seems as if the definition of DTA should have read "(a method) in which the temperature difference between a substance and a reference material *is measured as a function of temperature whilst the substances* are subjected to a controlled temperature program". The italicised words appear in

Russell's definition of TG but have been omitted in the definitions of DTA and DSC.

A discussion on the heat of reaction[1j] introduces the enthalpy change, but without any discussion of the sign convention that makes the enthalpy change *negative* when a reaction produces heat. This convention can be confusing to those new to the subject and would have been worth mentioning. The discussion of the calculation of the heat of reaction at a particular temperature is incorrect. The effect of the change in enthalpy of the products is discussed, but that of the change in enthalpy of the reactants is not. Both have to be taken into account. In the example given, a straight line is plotted between two calculated points. This assumes that the relationship is linear—an assumption that requires at least some justification.

The chapter on rockets is particularly bad. The statement that Black Powder is classed as a composite propellant is followed immediately by a definition of a composite propellant as one "where the fuel and oxidiser are intimately mixed". This is all very well, but the term "composite propellant" is usually used to mean one in which particles of solid oxidiser and powdered fuel are held together by a polymeric binder.[7a] Black Powder would not normally be classed as a composite propellant, though it would be according to Russell's definition. A book intended to introduce students to a subject should not introduce new definitions of terms that already have a specific technical usage.

The discussion of the science of rockets is hopelessly confusing. Equations are defined with some parameters specified in metric units (e.g., millimeters per second) and others in the same equation use non-metric units (e.g., pounds per square inch).[1k] An impressive-looking equation[1l] turns out to be nothing more than an attempt to show the calculation of the slope of a straight line—and it is wrong. Perhaps it is a misprint, but it is wrong all the same.

Having indicated an intention to show how to estimate the pressure inside an operating rocket motor, Russell digresses to make some remarks about the operation of a firework rocket. He writes, "In fact, the gunpowder charge is pressed with a spike so that there is a deep "cone" at the ignition end, this serving to increase the surface area of the propellant to perhaps 100 times that of the nozzle. As the propellant is consumed, its area diminishes and the gas flow or 'thrust' reduces".[1m] The statement that the area of the burning surface decreases as the propellant is consumed is exactly the opposite of what happens in the early stages of the combustion of rockets having a long conical cavity. After this confusing digression, Russell returns to his treatment of the pressure in a rocket motor, and he produces equations

$$K = A_p/A_N$$
$$= C \cdot p^{1-n}$$

that relate the chamber pressure p to the propellant area A_p and the nozzle area A_N, with C and n being constants. He writes that the equation

$$K = A_p/A_N$$

"can be compared with the burning rate equation (i.e., his equation (3.2): $R_B = 3.38p^{0.325}$ where R_B is the burning rate) by taking note of the fact that 'n' [or 0.325 in equation (3.2)] … becomes '$1-n$' [or 0.625] in the area ratio equation". This is an unsatisfactory explanation, to say the least. Inclusion of a proper derivation of the relationship[8a] would have taken little space and would have been well worthwhile. An example is then given of how the equations can be used to work out the pressure-time profile for a rocket, after the required constants have been determined by empirical measurement. The results are set out in Table 3.1.[1n] After an increment of 2 mm of propellant has been consumed, the area of the propellant is shown to have decreased from 50 to 40 cm^2. This is obviously impossible for a rocket burning from a central cavity.

A section on rocket design and manufacture gives some rather questionable pieces of information. For example, the reader is given the impression that the choke is formed after the propellant has been loaded and is told that a "pressing of clay" is applied on top of a flash-powder charge to close the head of the case of a thunderflash rocket.[1o]

The section headed "RECENT DEVELOPMENTS"[1p] could well have been omitted. Russell follows the bad example of Weingart[2c] by discussing V2 rockets, a topic that really has no place in a book on fireworks. We are told that

the Russians use military-type propellants in "rockets to reach astonishing heights in firework displays above the tall buildings in Moscow". It would have been interesting to know the source of this information, if only to find out how the Russians handle the problem of spent rockets falling into the city. Examples are given[1q] of "ingredients used for composite propellants". Some of the materials listed are not so used, having been found to be unsuitable. For example, Sutton[7b] writes "Nitronium perchlorate is objectionably hygroscopic, is relatively incompatible with available binders, and detonates easily. A decade of effort was made to overcome these problems… but it was to no avail". Furthermore, writes Sutton,[7c] "boron… has not proven to be a practical fuel". Russell, despite being a professional chemist, evidently believes boron to be a metal.[1q] It is regrettable that space has been given to this irrelevant and inaccurate material when there is no mention of some of the propellants based on whistle (see references 9 and 10) and strobe (see references 11 and 12) compositions that have been used in firework rockets in recent decades.

The next chapter covers mines and shells. Russell should have found no shortage of detailed information on the construction of shells. (See references 2d, 3b, 12, and 13.) Despite this, the information he gives is vague, misleading or inaccurate. For example, "the shell case can be made from paper, wood or similar material reinforced, with string". Then, a multi-break shell is said to break first at the maximum altitude, with successive breaks "afterwards while the shell is falling back to earth". Also, what are we to make of the statement that "Plastic…offers the advantage of unit construction whereby the lifting charge may also be contained inside the plastic case"?[1r] The introductory remarks give little confidence in the more technical sections that follow.

It is questionable whether a discussion of shell ballistics is really appropriate in a book on the chemistry of fireworks. The equation[1s] for the linear burn rate of Black Powder is different from that presented in the previous chapter.[1k] Much of the material presented in this chapter (even the numerical examples) have evidently been taken, without acknowledgement, from Dr. Shimizu.[15] The equation for the time of flight of a shell[1t] has been copied incorrectly[15a] and has been worked through to give a different answer (5.2 s) from that presented by Dr. Shimizu (6.4 s). It is odd that Russell did not notice this discrepancy. It is odd, too, that he indicates[1t] that the units of the acceleration due to gravity are dm s^{-2}, and then uses its value in m s^{-2}

A section on the efficiency of the transfer of energy between the burning powder[1u] and the shell reveals that Russell is under the impression that kinetic energy is not $\frac{1}{2} mV^2$, (where m is the mass and V the velocity), but rather $\frac{1}{2} mV^2/g$, where g is the acceleration due to gravity. Incidentally, he calls the acceleration due to gravity "the gravitational constant", a term that normally refers to the constant G in Newton's equation $F = Gm_1m_2/d^2$ where F is the gravitational force between two bodies of masses (m_1 and m_2) and d is the distance between them. Naturally enough, the use of an incorrect equation for the kinetic energy yields a wrong answer for the efficiency. Its small value (4.5%) is explained away by the observations that "the shell is never a good fit in the bore of the mortar, there are no gas-tight seals around the shell, and that the shell is never perfectly spherical (or cylindrical)".[1v] It is a pity that instead of trying to rationalize the answer, Russell did not check his original equation. A simple dimensional analysis, as taught in high school physics, would have alerted him that something was wrong.

The next chapter deals with fountains. Here again, Russell's idiosyncratic terminology is evident. He seems to think that "fountains" and "waterfalls" are equivalent. While waterfall effects can be achieved with fountains (see reference 2e), more usually waterfalls are made with fireworks having quite a different construction from that of a fountain.[3c16] The typical waterfall unit has a thin case designed to burn away as the composition is consumed—the opposite of what is required for a fountain. This chapter also is used to introduce atomic theory and quantum theory. Russell makes the interesting point that the colors of sparks are dependent on the type (i.e., chemical nature) of the material as well as on the temperature.[1x] Once again it is frustrating to be presented with

snippets of interesting information without any references to the original work.

A diagram of a 38 mm fountain [1y] shows a composition that contains only potassium nitrate, sulfur, charcoal, meal gunpowder and coated iron. However, the discussion of the same diagram refers to antimony trisulfide, fine aluminium, barium nitrate and dextrin. In the following paragraph, we are told "charcoal is used in excess because the decomposition of the extra charcoal is endothermic, the overall effect being to lower the exothermicity of the fountain composition and so reduce the burning rate." Furthermore, "at STP, for every gram of KNO_3 that decomposes, 0.39 litres of gaseous products are produced, whereas for every gram of charcoal that decomposes, 1.3 litres of gaseous products are produced (at STP)". What possible sense can be made of all this?

The next chapter begins with a very odd statement: "There are two main types of firework: wire sparklers…and tubed sparklers."[1z] Presumably Russell did not intend to write this—on the other hand, perhaps he really is exceptionally keen on sparklers. He discusses the production of a "silver sparkler" but gives as its composition one that he correctly indicates would produce only orange-red and gold sparks.[1aa] In describing the manufacture of tubed sparklers, he refers twice to the process of putting the powder into the tubes as the powder being "sifted in".[1aa] To "sift" means "to pass through a sieve". If the powder is "sifted in", that presumably means that a sieve is held over the top of the case and the powder passed through the sieve into the case. Is that really how these fireworks are filled?

The chapter on "bangers" begins with the incorrect statement that the terms "banger" and "squib" are equivalent.[1ab] The traditional British "squib"[17] was a different firework from the "banger" described in this chapter, though it, too, concluded its performance with a bang. Russell tells us that bangers were filled by the explosive charge being "sifted in".[1ab] Lancaster[3d] devotes a whole chapter to mixing and charging, but fails to mention this method of getting powder into cases.

The chapter on Roman Candles includes a remark about "the projectiles reaching greater heights with every shot".[1ac] Candle makers take care to avoid this happening, but it seems that what was once seen as a shortcoming is now regarded as an interesting effect. The manufacture of Roman Candles is outlined, and here again we are told that the delay composition is "sifted in". Once again, Russell presents one composition in a diagram and discusses another in the text.[1ad] The diagram shows a rather old-fashioned composition for a green star: barium chlorate, potassium chlorate, acaroid resin, charcoal and dextrin. Such a star would be regarded these days as too sensitive to shock and friction, as Russell himself explains in the next section.[1ae] In the text, however, we are told about a different composition: "a green star could contain barium nitrate, potassium chlorate and aluminium together with binders", and an analogous composition, with strontium nitrate and strontium carbonate replacing the barium nitrate, is suggested for a red star. Compositions combining a nitrate, a chlorate and aluminium have been called "death mixes"[18,19] because of the possibility of their spontaneous ignition in the presence of moisture. Given the large range of published compositions for red and green stars, it is most unfortunate that Russell has chosen to present these out-dated and potentially dangerous examples.

The section on the chemistry of the green star[1ae] starts off with a muddle. Chemical equations are presented showing the formation of singly ionised barium monochloride, $BaCl^+$. Yet, as Russell correctly indicates, the main species responsible for the green colour of barium flames is BaCl, the neutral barium monochloride molecule. The formation of $BaCl^+$ would not favour the production of green light.

The discussion of the chemistry of the red star[1af] makes the interesting point that the presence of chlorine promotes the volatilisation of $SrCl_2$, which subsequently dissociates to form SrCl. Oddly enough, Russell lists SrOH as the main species responsible for the red colour in Sr flames. This is true for laboratory flames coloured with strontium salts,[20] but is unlikely to be so for chlorine-rich pyrotechnic flames.

Rather crudely drawn diagrams are presented to illustrate the spectra of green[1af] and red[1ag] stars. These spectra could be confusing, because

the wavelength range extends well into the invisible near-infrared region of the spectrum. As a consequence, the main feature in the spectrum of the green star is a huge peak in the near infrared.

The next chapter discusses gerbs and wheels. One would have expected to find gerbs included in the chapter on fountains. According to Lancaster's glossary, the distinguishing feature of a gerb is its having a choke, whereas fountains may or may not be choked. In this book, the gerb is evidently distinguished from a fountain on the basis of a gerb having propulsive properties.[1ah]

The discussion of wheels introduces the term "Catherine Wheel", which Russell uses for any firework wheel.[1ai] This is consistent with the definition in Lancaster's glossary.[3e] It is noteworthy that in Alan St. Hill Brock's day the use of "Catherine Wheel" was evidently restricted to the firework that consists of a long, thin case coiled in a spiral around a central disc.[21a] This firework has very little in common with wheels that are driven by gerbs or drivers, and it deserves a name of its own. According to Brock, the French call it *Pastille*. Brock wrote "at one time, the latter name (i.e., Catherine Wheel) was also applied to the larger, compound wheels seen in displays".[21a] It seems that the once-specific English term has reverted to its former non-specific usage, and naturally this leads to confusion. The section in Russell's book on the construction of wheels[1ai] begins with a description of the manufacture of "Catherine wheels (pin wheels)", which are clearly "pastilles". We are then told, "Catherine wheels with diameters up to 50 cm are readily available". In this reviewer's experience wheels of this size are not constructed in the way Russell describes but are built with a number of drivers fixed to the wheel's rim.

Chapter 10, titled "Special Effects", does not deal as one might perhaps expect with fireworks in the motion picture industry but with a collection of topics including quick match, plastic fuse, lances, set pieces, flash and noise effects, whistles, smoke puffs, coloured smokes and electrical firing. It would be tedious to go through all these in detail, but a few remarks should be made. In the discussion of quick match we are presented with a third version[1aj] of the equation for the burn rate of Black Powder. The constants are different again from those in the previous two,[1k,1s] but we still find the units of one parameter being taken from the metric system and those of the other from the British.

In this book the term "quickmatch" refers to what the Americans call "black match"[2f] and what the British[21c] used to call "raw match:" cotton wick impregnated with gunpowder, prepared by treating the cotton wick with a paste of gunpowder and starch, gum or dextrin. This burns relatively slowly unless it is enclosed by a loosely fitting paper tube or "pipe". Raw match so enclosed was once called "quickmatch"[21b,2g] or "piped match",[3f] terms that were consistent with both the performance and the construction. According to Lancaster's glossary,[3g] however, "quickmatch" and "raw match" are now synonymous. This is another example of British firework terminology having lost some of its precision since the time of Brock.

In the discussion of piped match it is assumed that the increase in burn rate happens because "the paper pipe serves to trap some of the evolved gases and so increases the ambient pressure, thereby significantly increasing the rate of burning." A calculation of the expected increase, with the very generous assumption of an ambient pressure of 100 psi, produces a "theoretical burning time" of 28 seconds per metre. Russell admits that the actual burn rate is at least 100 times greater than this, and states "secondary effects play an important role".[1ak] The primary reason for the increased burn rate of piped match is that the "pipe" confines the flame, providing a "fire path" that forces hot gases and sparks along the surface of the enclosed match.[22,23]

The section on lances returns to the subject of coloured flames with a short discussion of the production of blue. The green colour of copper-containing flames in the absence of chlorine is erroneously attributed to "free copper atoms",[1al] when it is actually produced by CuOH.[24] Curiously, the green bands of CuOH are mentioned in passing later in this section.

A section on flash and noise effects contains a discussion of inorganic oxidizers. Some of the statements made are rather strange: "In practice, copper salts are not commonly used because of the difficulty involved in their ignition".[1am] It could be argued that this is a very economical way of summarizing the shortcomings of the copper salts of oxidizing anions. The statement could, less charitably, be described as vague and confusing. A table of inorganic oxidants[1an] includes ammonium dichromate, despite its available oxygen content being correctly given as zero.

The brief chapter on safety includes the statement "in any free country the inhabitants have the choice between purchasing and lighting their own fireworks, or leaving it to the professionals".[1ao] One can only agree. By this standard many citizens of the USA, and most citizens of Australia, do not live in a free country. In the final chapter on British fireworks legislation Russell notes the banning of the sale to the general public of bangers, fireworks containing bangers, aerial shells and maroons, and shells or maroons preloaded into mortars. Britain, too, seems well on the way to losing its status as "a free country" in this regard.

The bibliography at the end of the book is remarkable for its omission of the two works most relevant to the book's subject: Conkling's *Chemistry of Pyrotechnics*[25] and the Kosankes' and Jennings-White's *Lecture Notes for Pyrotechnic Chemistry*.[26] It would be interesting to know why these, and Shidlovskiy's classic textbook,[27] were left out while Brauer's book,[28] which is of very little relevance, was included.

In summary, this book fails to meet the expectations raised by the publisher's description. A book intended for the guidance of students should be accurate and consistent, and it should provide references to the literature. This book does not meet these very basic requirements. It would be disappointing enough to find so many shortcomings in a self-published work; one certainly does not expect to find them in a book published by the Royal Society of Chemistry. In publishing the book in its present state the RSC has grossly neglected its obligations to its readers and to the book's author.

With careful revision and the inclusion of appropriate references, this book could become a useful introduction to the chemistry of fireworks. Meanwhile, readers seeking instruction in this subject should look elsewhere.[25, 26]

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