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CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is felt to be important for the reader to be duly cautioned. Without the required training and experience no one should ever experiment with or use pyrotechnic materials. Also, the amount of information presented in this Journal is not a substitute for necessary training and experience.

A major effort has been undertaken to review all articles for correctness. However, it is possible that errors remain. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

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Organic Fuels: Composition and Formation Enthalpy
Part II — Resins, Charcoal, Pitch, Gilsonite, and Waxes

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ABSTRACT

The utilization of free energy minimization computer programs in areas of combustion research is likely to increase in the future. These programs require the specification of the reactant chemical formulas and their respective formation enthalpies as part of the input data set. Frequently, for common compounds, the values required are readily available in handbooks. Complex organic compounds or poorly characterized mixtures may not have the required data available in a directly usable form. This article evaluates a variety of organic fuels used in pyrotechnics from the perspective of establishing useful chemical formulas and formation enthalpies. Along the way, it is the author's intention to simplify the methods used, to illustrate how many disparate sources of information may be drawn upon to achieve the estimation of the required values, and to demonstrate that each of the methods used is itself relatively easy to perform or calculate.

Keywords: chemical composition, enthalpy of formation, higher heating value (HHV), Benson Group, free energy minimization, ultimate analysis, trace elements, acaroid resin, Xanthorrhoea, shellac, charcoal, pitch, gilsonite, bitumen, wax, paraffin, beeswax, naphthalene, anthracene, hexachlorobenzene, gallic acid, polyvinyl chloride, polyvinylidene chloride, hexamethylenetetramine, sodium benzoate, sodium salicylate, stearin

Introduction

A considerable variety of organic fuels are available for, and used in, pyrotechnic formulations. Choosing the right fuel for the intended application is made all the more difficult if the data required to make an informed decision is incomplete or unavailable. The primary focus of this article is to present chemical formulas and formation enthalpy estimates for common organic fuels that will be useful to the pyrotechnist and energetics chemist.

The author believes that, in the future, the use of *free energy minimization* software will find wider acceptance as an important tool for use in the combustion products analysis of pyrotechnic formulations. These programs allow the investigator to simulate, study, and optimize the combustion properties of a pyrotechnic formulation prior to actually handling the potential ingredients. This will certainly expedite the formulation development cycle and improve the end product.

These programs require, in part, that the chemical composition and formation enthalpies of the ingredients—the *reactants*—be specified as part of the input data set. The compositions of these fuels range from simple, pure compounds to complex mixtures that are poorly characterized. Many of the fuels have variable composition, and this may be due in part to the source location, climate, collection time of year, or species. In some cases, the chemical compositions are readily available in handbooks. The formation enthalpies, on the other hand, are rarely available, but may be estimated using a variety of methods.

The reference values listed in the following tables are expressed as either *higher heating value* (HHV), *formation enthalpy* ($\Delta_f H^o$), or *combustion enthalpy* ($\Delta_c H^o$). Units of kilojoule (kJ) or megajoule (MJ) per kilogram (kg) or mole are used for both. Formation enthalpies are for the solid phase unless otherwise indicated. The method used for estimating the $\Delta_f H^o$ is denoted by superscripted letters following the value:

H	HHV's
C	Combustion Enthalpy
B	Benson Group Additivity
PB	Partial Benson Group Additivity
E	Equation
F	Flame temperature and formulation

Each of these methods is described in "Six Methods for Estimating the Formation Enthalpy of Organic Compounds".[1] For convenience, the chemical formulas are generally represented using a common basis such that comparisons may be readily made between the different fuels. The author arbitrarily chose a C_6 formula basis because many fuels are derived from simple C_6-based molecules. CAS numbers are provided when available.

Part One[2] covered organic fuels based on wood, its direct derivatives, related carbohydrates, exudates, and rosin.

Part Two covers acaroid resin, shellac, the destructive distillation of wood: charcoal and pitch, Gilsonite, waxes, and a sampling of pure fuels and synthetic polymers.

Acaroid Resin

Acaroid resin (sometimes spelled *Accroides)* is derived from the Australian "grass tree" *Xanthorrhoea* (also known as *yacca*,[3] or *blackboy* due to the blackened trunks burned by bush fires[3–5]). The resin exudes from the plant and cements the bases of the dead leaves together and so forms the bulk of the trunk.[3,5,6] It is remarkable for its high phenolic content.[6] The fresh resin obtained is known as *Yacca gum*[7] and is chemically simpler than the aged resin.[4] Resins that have been partially pyrolized by bush fires are the acaroid resins,[7] and fall into two principal categories that differ markedly:[6]

- *Yellow acaroid,* also known as *Botany Bay gum*,[8] is produced by *X. hastilis*[3,4] ("*Spear Grass Tree*"[5]), and is relatively rare.
- *Red acaroid*, also known as *Grass Tree gum*, *Blackboy gum*,[8] and *Red Gum*[9] is produced by *X. australis*[3] ("*Austral Grass Tree*"[5]), *X. preissii*,[3,10] *X. arborea*[3] ("*Great Resin Grass Tree*" or "*Dackowar*"[5]), *X. reflexa*,[11] and other *Xanthorrhoea* species.[3]

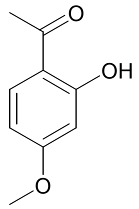
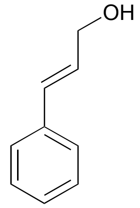
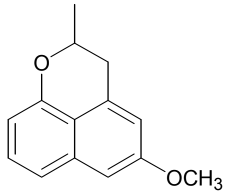
There are 28 species in the genus *Xanthorrhoea*,[12] and there seems to be general confusion in their individual identification[6,13] and from which species analytical samples originated.[6,10,13] An early report[10] attributed the yellow resin to *X. tateana*, but a more recent report[3] indicates that a red resin is produced instead. *X. australis*, on the other hand, produces a brittle red resin, and also a sticky yellow resin present at the leaf bases.[6] The presence of both color resins may be due, in part, to aging and natural oxidation.[3]

Unfortunately, there is no one, complete, composition for any of the resins. To make matters worse, each incomplete description differs significantly from the others. The experiment descriptions sometimes include vague values regarding the initial weight of resin extracted from the raw samples, or the amounts soluble in various solvents, etc. Estimates of the chemical composition and $\Delta_f H^o$ will be made, but the reader is cautioned to weigh these tentative estimates accordingly.

Early work[10,11] focused on the analysis of the *essential oils*, which constitute a small fraction of the total resin. See Table 1.

Later work focused on clarifying or correcting earlier works[13,14] and identifying specific *flavonoids* present in the resins.[4,6,15] Very little analytical work has been done, and the compositions of the bulk of the resins remains largely unknown.[5,6,15,16]

Table 1. Principle Components of Essential Oils from *Xanthorrhoea.*[a]

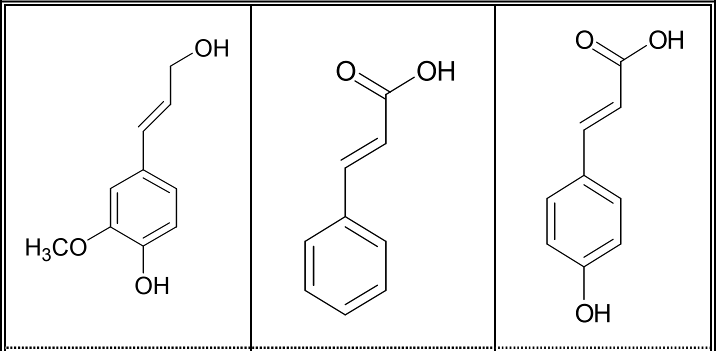
	X. arborea	*X. hastilis*	*X. reflexa*
Percent of resin	1.0 (approx.)	1.56	6.86
Component:			
Primary	Pæonol 50%	Cinnamyl alcohol 53%	Pæonol 62.8%
Secondary	—	—	Xanthorrhoein 17.5%
C_6 basis formula	$C_6H_{6.67}O_2$	$C_6H_{6.67}O_{0.67}$	$C_6H_{6.47}O_{1.65}$
Δ_fH^o (kJ/mole$_{liquid}{}^B$)	–513.3	–107.0	–460.4
Structure			
	Pæonol 89-84-9	Cinnamyl alcohol 104-54-1	Xanthorrhoein

Note: Xanthorrhoein –270.3, Pæonol –513.3, Cinnamyl alcohol –107.0, Δ_fH^o kJ/mole$_{liquid}{}^B$

[a] Components and percentages from reference 11.

Alcohols very closely related to coniferyl alcohol—see Figure 1—were shown to be present in the red acaroid resin.[17] The terms *resinotannol*,[3,10] *erythroresinotannol* ($C_{40}H_{40}O_{10}$),[8] or *xanthoresinotannol* ($C_{43}H_{46}O_{10}$)[8] were occasionally used as generic names for the alcoholic constituents that may be present in the resin, and which formed an ester with either p-*coumaric* or *cinnamic acid*.[8] See Figure 1. A more recent report uses the term *benzoresinotannol*.[7]

Resinotannols are related to *tannins*.[3] A partial definition of a vegetable tannin is a water-soluble phenolic compound having a molecular weight between 500 and 3000.[18] *Condensed tannins* are polymers derived from *flavonoid* monomers, and are very susceptible to polymerization by influence of heat.[19] This may account for part of the complexity of these resins, as bush fires frequent the localities of many of the grass tree species. Examples of flavonoids are the *flavan*, 4',5,7-trimethoxyflavan, and the *flavanones*, *hesperetin* and *pinocembrin*. See Figure 2. Condensed tannins are the most widespread and commercially significant plant phenolics; however, their chemistry is still



Coniferyl Alcohol 458-35-5	Cinnamic Acid 621-82-9	*p*-Coumaric Acid 7400-08-0

Figure 1. Coniferyl alcohol and closely related compounds.

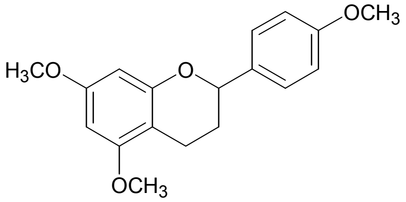
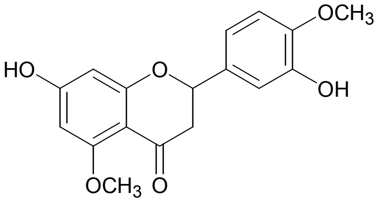
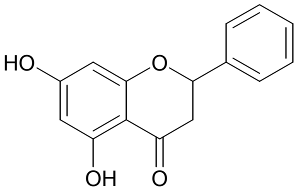
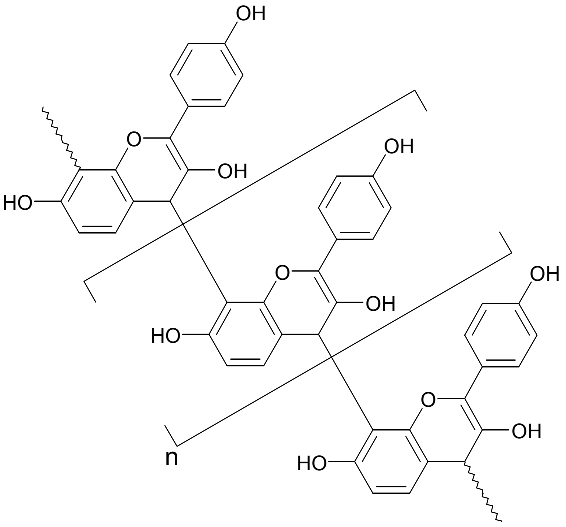
	
4',5,7-trimethoxyflavan	Hesperetin 520-33-2
	
Pinocembrin 51876-18-7	Generic Flavanol Polymer

Figure 2. Examples of flavanoids.

undeveloped.[18,20] Along with condensed tannins are found complex phenolic substances that are ill-defined.[19] An example of a generalized structure of a polymeric *flavanol* is depicted in Figure 2. If this arbitrary flavanol formed an ester with *p*-coumaric acid, the resulting hypothetical resinotannol would have a C_6 formula of $C_6H_4O_{1.5}$, Δ_fH^o –192 kJ/mole^B.

A recent report provides ultimate analysis data for resins of *X. preissii*, *X. reflexa*, and yacca gum, and also Δ_fH^o data for each in units of kJ/mole.[7] Unfortunately, chemical formulas or molecular weights were not provided in the report[7] or by the report's author;[21] thus there is no way to reconcile the molar-based Δ_fH^o values to the mass-based ultimate analysis data. Nevertheless, a representative chemical formula derived from the average of the ultimate analysis values for red acaroid resins is $C_6H_{5.95}O_{2.63}N_{0.01}$, and for yacca gum $C_6H_{6.78}O_{3.09}N_{0.05}$. The yacca gum oxygen and hydrogen both decrease, apparently as a result of the loss of volatiles[7] and hydroxyls[21] due to bush fire pyrolysis, when transformed into red acaroid resin.

Table 2. Constituents of *Xanthorrhoea* Resins.

Compound	*X. hastilis*	*X. australis*	Formula	$\Delta_f H^o$, kJ/mole
cinnamyl *p*-coumarate	50		$C_{18}H_{16}O_3$	-402.9^{B}
p-coumaric acid	4.17	35	$C_9H_8O_3$	-529.69[a]
methyl cinnamate	3.33		$C_{10}H_{10}O$	-290.79[a]
hesperetin	1.35		$C_{17}H_{16}O_6$	-992.57^{B}
cinnamic acid	0.83	9	$C_9H_8O_2$	-337.23[b]
cinnamyl alcohol	0.67		$C_9H_{10}O$	-131.3^{B}
cinnamyl cinnamate	[c]		$C_{18}H_{16}O_2$	-198.1^{B}
chrysophanic acid	[c]		$C_{15}H_{10}O_4$	-596.1^{B}
xanthorrhoeol		12[d]	$C_{15}H_{14}O_3$	-545.8^{B}
Percentage	60.35	56		
Formula	$C_6H_{5.59}O_{1.15}$	$C_6H_{5.42}O_{1.66}$		
$\Delta_f H^o$ kJ/mole^{B,R}	–414.8	–502.2		

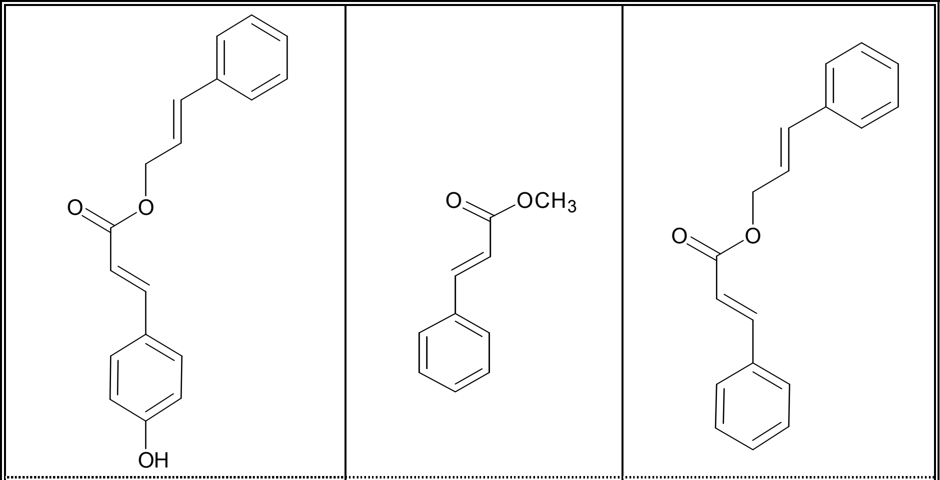
Note: all $\Delta_f H^o$ values for the solid phase. Percentages from reference 6.

[a] $\Delta_f H^o$ data from reference 23.

[b] $\Delta_f H^o$ data from reference 24.

[c] Present, but no percentages given.

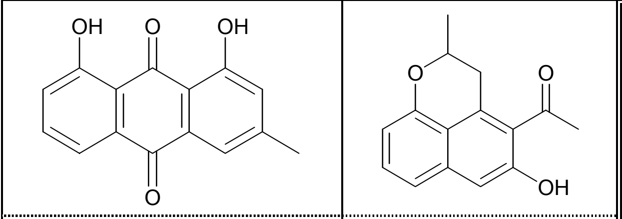
[d] At least 12 percent is present.



Cinnamyl *p*-coumarate

Methyl cinnamate
103-26-4

Cinnamyl cinnamate
122-69-0



Chrysophanic acid
481-74-3

Xanthorrhoeol
1485-31-0

Figure 3. Some constituents of Xanthorrhoea resin.

Table 3. $\Delta_f H^o$ Values for Some Acaroid Resins.

Resin	C_6-Basis Formula	$\Delta_f H^o$ (kJ/mol)[a]
Erythroresinotannol	$C_6H_6O_{1.5}$	–260^{E}
Xanthoresinotannol	$C_6H_{6.419}O_{1.395}$	–255^{E}
p-coumaric ester	$C_6H_{6.115}O_{1.5}$	–263^{E}
X. hastilis (60.35%)	$C_6H_{5.59}O_{1.15}$	–414.8^{B}, ref
X. australis (56%)	$C_6H_{5.42}O_{1.66}$	–502.2^{B}, ref.
Red acaroid	$C_6H_{5.95}O_{2.63}N_{0.01}$	–470^{E} [b]
Yacca gum	$C_6H_{6.78}O_{3.09}N_{0.05}$	–594^{E} [b]

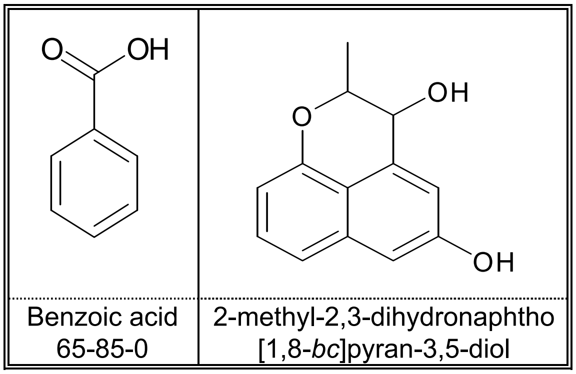
[a] Equation 5 used from reference 1.

[b] The nitrogen present is sufficiently small to ignore and allow a tentative estimate to be made using equation 5 from reference 1.

One reference[22] lists a composition for both red and yellow acaroid resin as 85% *p*-coumaric ester of xanthoresinotannol. An approximate chemical formula for this ester is $C_{52}H_{53}O_{13}$. In C_6 units this becomes $C_6H_{6.115}O_{1.5}$.

The soft resin of *X. hastilis* may consist chiefly of a polymer of *cinnamyl p-coumarate*.[4,6,15] The bulk of this resin may be a polymerization product of a variety of compounds isolated from this resin. See Table 2.

Trace compounds are present in *Xanthorrhoea* resins, many of which are strikingly similar to other compounds present in greater amounts (see Figure 4). *X. hastilis* contains *benzoic acid*,[8] *X. resinosa* contains free cinnamic and *p*-coumaric acids,[13] and *X. preissii* contains approximately 2 percent pinocembrin[6,15] ($C_{15}H_{12}O_4$, $\Delta_f H^o$ –642.3 kJ/mole^{B}). The red coloration of the resins may be due, in part, to the presence of 4',5,7-trimethoxyflavan[4] ($C_{18}H_{20}O_4$) and to *chrysophanic acid* ($C_{15}H_{10}O_4$), which is present possibly as a result of bush fire damage,[16] but has also been detected in *X. australis* resin that was undamaged by fire.[6] *X. australis* also contains 2-methyl-2,3-dihydronaphtho[1,8-*bc*]pyran-3,5-diol, which is unstable in the presence of light and air yielding red resins.[6] See Figure 4.



Benzoic acid 65-85-0

2-methyl-2,3-dihydronaphtho [1,8-*bc*]pyran-3,5-diol

Figure 4. Minor compounds present in some Xanthorrhoea resins.

Ethanol insolubles range from 6.6%–7%,[25,26] moisture 5.0%,[25] and ash less than 2%.[26] Unprocessed *X. hastilis* resin has up to 25 percent foreign matter such as husks and sand,[6] and approximately 23 percent of unprocessed *X. resinosa* resin derived from its "bark" is foreign matter.[13]

In the past, it was thought that supplies of this resin would last forever: "This resin is obtainable in inexhaustible quantities as the plants producing are abundant throughout Australia",[5] and "By suitable conservation of the trees a continuous supply could be maintained."[3] More recent perception is that acaroid resin is "a product of bush plants not suitable to cultivation; thus, a non-renewable resource with very limited availability."[7]

Acaroid resin is currently used in pyrotechnics,[3,9,27] and in the past was used in lacquers,[3,5,22] sealing waxes,[3,5,8,22] in the manufacture of picric acid,[3,8] and in the manufacture of the dye *nitropicric acid*, where up to ½ of the weight of the resin may yield dye.[5] See Table 3.

Shellac

Shellac (9000-59-3), also called *lacca*, *lac*,[28] *garnet lac*, *gum lac*, and *stick lac*,[29] is a resinous secretion of the insect *Laccifer lacca*,[28,29] which is continuously produced by the insect after consumption of the juices of the host tree *Kusum (Schleichera trijuga)*.[30] Its composition varies with the season.[28] Shellac is a combination of a hard resin secreted at a regular rate and a soft resin secreted at an irregular rate.[30]

Shellac contains 67.9% C, 9.1% H, and 23.0% O according to one reference,[30] and 67.0% C, 9.00% H, 23.87% O, and 0.13% ash according to another.[31] This corresponds to formulas of $C_6H_{9.58}O_{1.53}$ and $C_6H_{9.60}O_{1.60}$, respectively. The primary constituent of shellac is *aleuritic acid* (533-87-9, $C_{15}H_{30}O_4$, Δ_fH^o –1237.1 kJ/mole[B]), which accounts for up to 43% of the resin.[30] It is uncertain if shellac truly contains *shellolic acid* (4448-95-7, $C_{15}H_{20}O_6$)—reported in the past,[32] as some researchers have been unable to isolate it.[30] See Figure 5. Other acids are present, but their exact percentages have not been worked out.[30] In addition, waxes are present in amounts ranging from 3.5 to 5.5 percent, and are secreted in the form of long filaments.[30] Again, the results of the analysis of

Table 4. Δ_fH^o of Shellac[a] Derived from Pyrotechnic Colored Flame Formulations and Flame Temperatures.

Color Agent	Temp (K[b])	Δ_fH^o (kJ/mole[F])	Temp (K) (–440 kJ/mole)	Flame Temp. Percent Error
$SrCO_3$	2475	–401	2458	0.7
$SrC_2O_4 \cdot H_2O$[c]	2440	–443	2441	0.0
$SrCl_2 \cdot 6H_2O$	2475	–238	2387	3.6
$Sr(NO_3)_2$	2625	–247	2573	2.0
Na_2CO_3	2460	–485	2479	–0.8
$NaHCO_3$	2480	–419	2472	0.3
$Na_2C_2O_4$	2450	–518	2484	–1.4
NaCl	2540	–283	2476	2.5
$BaCO_3$	2430	–581	2491	–2.5
BaC_2O_4	2430	–569	2487	–2.5
$BaCl_2 \cdot 2H_2O$	2390	–588	2459	–2.9
$Ba(NO_3)_2$	2525	–603	2575	–2.0
$CuCO_3 \cdot Cu(OH)_2$	2430	–493	2452	–0.9
$CuSO_4 \cdot 5H_2O$	2390	–463	2401	–0.5
Cu (10%)	2460	–372	2430	1.2
Cu (5%)	2540	–343	2501	1.5

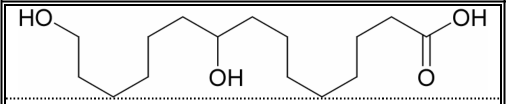
Shellac, $C_6H_{9.6}O_{1.6}$[a], –440 kJ/mole[F], standard deviation = 119.8 kJ/mole[F].

Notes: The copper-arsenic coloring agent formulations were not used due to the computer program[33] not including the element arsenic. Copper oxalate, $CuC_2O_4 \cdot H_2O$, was not used due to an Δ_fH^o value being unavailable at the time of this writing. One atmosphere (1 Bar) was used in all runs.

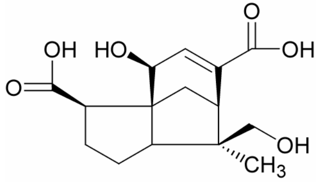
[a] $C_6H_{9.6}O_{1.6}$, from Shimizu.[31]

[b] Flame temperatures from the graphic chart "Figure 48 — Flame Temperature with Various Coloring Agents",[31] and is estimated to approximately ±10 K accuracy.

[c] Δ_fH^o data was not found for strontium oxalate hydrated by a single water molecule. The value used, –1666.24 kJ/mole, was interpolated from values for no hydration,[34] –1370.68 kJ/mole, and 2.5 water molecules,[35] –2109.57 kJ/mole.



Aleuritic acid
533-87-9



Shellolic acid
4448-95-7

Figure 5. Constituents of shellac.

the waxes give conflicting results.[30] Neither shellolic acid or the waxes will be considered here due to these circumstances.

Shimizu made a series of flame temperature measurements of various salts used in the production of colored flames.[31] Shellac was used as the fuel/binder in many of them. Most of the formulations using ammonium perchlorate as an oxidizer were used as input for a free energy minimization program,[33] and from these computer codes the $\Delta_f H^o$ was "reverse-engineered". See reference 1 for details on this method and a summary of important assumptions regarding its use.

Table 4 presents the coloring agent, the measured flame temperatures,[31] and the reverse-engineered $\Delta_f H^o$ values. An average value of –440 kJ/mole, standard deviation of 119.8 kJ/mole, was estimated using this method. An $\Delta_f H^o$ of –396 kJ/mole was calculated using equation 5 from reference 1, which is based on an analysis of 337 different CHO compounds. Clearly, either of these methods should only be used when laboratory-based values are unavailable and other estimation methods are not practical.

Shellac is used in pyrotechnic compositions[9,27,31]—probably less now than in the past due to its high cost,[9] and in a variety of varnishes, sealants, and cements.[28,29]

Charcoal

Charcoal is the solid, carbonaceous residue left remaining after the destructive distillation of carbonaceous materials.[36] The source material may be of animal, vegetable, or mineral origin. The charcoal outlined here is derived from wood or wood products. This charcoal is not to be confused with the briquette form used in outdoor grills, which typically contains many additional compounds and up to 25 percent ash.[37] A commercial brand of charcoal used in outdoor cooking contains wood charcoal, anthracite coal, mineral charcoal, starch, sodium nitrate, limestone, sawdust, and borax[38]—almost a pyrotechnic formulation in itself!

Hardwood charcoal is manufactured batchwise in kilns or continuously in a furnace[36,37,38] by a four-step pyrolysis process. Heat is applied to the wood, and as the temperature approaches 100 ºC, water and volatile hydrocarbons are released and distilled. Once the moisture content of the wood has been removed, the temperature of the wood rises higher, and the hydrocarbon distillate yield increases. This second stage continues to approximately 275 ºC. At this temperature the third stage begins, and external application of heat is no longer required as the carbonization reactions become exothermic. The bulk of the hydrocarbon distillates are produced as the temperature increases to 350 ºC. The exothermic reactions then end, and once again heat is applied to bring the charcoal to its final processing temperature, which is typically between 400 and 500 ºC. At these temperatures the less volatile tars and pitch are removed from the product.[36]

Table 6. Typical Charcoal Composition and Yield as a function of Temperature.[36]

Distillation Temp (ºC)	Charcoal Composition (%) C	H	O	Yield (%)
200	52.3	6.3	41.4	91.8
300	73.2	4.9	21.9	51.4
400	77.7	4.5	18.1	40.6
500	89.2	3.1	6.7	31.0
600	92.2	2.6	5.2	29.1
700	92.8	2.4	4.8	27.8
800	95.7	1.0	3.3	26.7
900	96.1	0.7	3.2	26.6
1000	96.6	0.5	2.9	26.3

If dry, ash-free wood is assigned the approximate formula $C_{42}H_{60}O_{28}$, then the following generalization of wood pyrolysis may be written:[36]

$$\underset{\text{(wood)}}{2\,C_{42}H_{60}O_{28}} \rightarrow \underset{\text{(charcoal)}}{3\,C_{16}H_{10}O_2} + \underset{\text{(water)}}{28\,H_2O} + \underset{\text{(carbon dioxide)}}{5\,CO_2} + \underset{\text{(carbon monoxide)}}{3\,CO} + \underset{\text{(acetic acid)}}{2\,C_2H_4O_2} + \underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(wood tar)}}{C_{23}H_{22}O_4}$$

These products are divided into four categories: charcoal, noncondensible gases, pyroligneous liquor, and insoluble tars. The distribution of these products varies depending on the raw materials used and the pyrolysis conditions. Table 5 lists a typical distribution. Pyrolysis temperature plays a key role in the composition of the charcoal. As expected, higher pyrolysis temperatures result in higher carbon percentages and lower charcoal yields—see Table 6.

Table 5. Typical Yields of Various Final Products per 1000 kg of Dry Wood.[37]

Product	Unit	
Charcoal	kg	300
Pitch	kg	33
Soluble tar	liter	91.8
Ethyl acetate	liter	61.3
Creosote oil	liter	12.5
Methanol	liter	12.5
Ethyl formate	liter	5.4
Methyl acetate	liter	4.2
Methyl acetone	liter	2.9
Ketones	liter	0.8
Allyl alcohol	liter	0.4
Noncondensible gas	meter^3	156

Charcoal composition varies not only due to the source material and pyrolysis conditions, but even within individual pieces of wood: one report[39] states that a 5 cm stick of elder charcoal had 45% volatiles at the edge, but only 30% at the midsection. In an analysis of different lots of maple charcoal from the same manufacturer, it was demonstrated that significant variations in composition, ash content, and heating values existed, where the latter varied 13%.[40] Charcoal used in the manufacture of black powder has no exact specification, but the industries manufacturing it generally conform to a composition of 75% ±5% carbon and a volatile content of 20–30%.[39] See Tables 7 and 8 for representative elemental compositions, $\Delta_f H^o$ values, and computed oxide-form ash compositions.

Wood charcoal is used in fireworks,[9,27,31] in the manufacture of black powder,[9,29,39,40] in cast iron production,[37] as a fuel for outdoor cooking,[29,36–38] and as a filtering medium (activated carbon).[29,36]

Table 7. Composition, Heating Value, and $\Delta_f H^o$ of Charcoals.

Source	Temp. °C	Elemental Analysis						HHV MJ/kg	$\Delta_f H^o$ MJ/kg[H]	Ref.
		C	H	O	N	S	Ash			
Pine[a]	400	75.3	3.8	15.2	0.8	0.0	3.4	28.1	–1.95	41
Pine[a]	500	80.3	3.1	11.3	0.2	0.0	3.4	31.1	0.41	41
Redwood	485[b]	75.6	3.3	18.4	0.2	0.2	2.3	28.8	–0.66	42
Redwood	700[b]	78.8	3.5	13.2	0.2	0.2	4.1	30.5	–0.29	42
Oak	NA	67.7	2.4	14.4	0.4	0.2	14.9	24.8	–0.80	42
Oak	NA	70.59	2.92	13.25	0.61	0.04	13.05	25.6	–1.66	40
Maple[c]	NA	71.96	2.06	15.27	0.46	0.03	10.22	26.7	0.20	40
Maple[c]	NA	76.87	3.49	16.03	0.32	0.01	3.30	29.2	–0.93	40
Maple[c]	NA	79.44	3.39	14.18	0.32	0.02	2.65	29.9	–0.93	40
Pine	750	88.4	7.8	2.88[d]	0.4	0.2	0.32	NA	NA	32
Willow	NA	82.2	3.5	10.35[d]	0.3	0.05	3.6	NA	NA	32

[a] Georgia Tech. Research Institute's "Tech-air" process using pine bark and sawdust

[b] Range of 694–822 K, an average of 485 °C used, and 733–1214 K, average of 700 °C used

[c] Sample #5—lowest percentage of carbon, #10—median, and #7—highest percentage of carbon of lots

[d] Oxygen by difference

Pitch

Pitch is a tar-like material produced from the destructive distillation of coal or biomass such as wood or wood by-products. It may be best described as "an awesome mixture of phenolic and nonphenolic compounds that has taxed the capabilities of several analytical laboratories for over a century."[43] The names tar and pitch seem to be used in the literature almost interchangeably. Very little data is available for biomass tars.[44] Pitch is a resin-based deposit of a widely varying and complex composition, and its analysis is made difficult because of this.[45] Sedimentation tar is fractionated into tar oils and tar pitch, and hundreds of compounds have been identified.[43] Data for a few *pyrolytic oils* is available, and is summarized in Table 9. Pitch that is a by-product of the pulping industry is generally considered a nuisance, clogging the machinery and reducing the quality of the paper produced.[45]

Shimizu[31] refers to two different types of pitch used in pyrotechnic formulations, *Pine Root Pitch I* and *II*. They are apparently derived from oil of turpentine.[27] An elemental analysis is provided for Pine Root Pitch II, however, Pine Root Pitch I was used in pyrotechnic formulations for flame temperature measurements. If the *assumption* is made that the elemental analysis is approximately the same for both varieties, then an $\Delta_f H^o$ may be estimated from the ammonium perchlorate based pyrotechnic composition in a manner similar to that used for shellac (see *Shellac* above; see reference 1 for important assumptions in this method's use). The resulting formula is $C_6H_{6.54}O_{1.03}$, $\Delta_f H^o$ –221 kJ/mole[F]. This compares favorably to –196.9[E] kJ/mole. Naturally, this should be considered a

Table 8. Charcoal Ash Composition, Computed Percentage Oxide Form.[40]

Source	CaO	SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	Na_2O	P_2O_5	TiO_2	Li_2O (ppm)
Maple[a]	40.44	25.73	13.53	10.45	3.33	2.85	1.74	1.63	0.30	1084
Oak	49.20	25.09	13.36	6.57	1.95	1.71	0.87	1.01	0.24	434

[a] Sample numbers 1, 3, 5, 7, and 9 were normalized to 100% ash recovered, then averaged.

Table 9. Pyrolytic Oil Compositions, Heating Values, and $\Delta_f H^o$.

	Elemental Composition					HHV	$\Delta_f H^o$	C_6-basis	$\Delta_f H^o$	
Source	C	H	O	N	S	MJ/kg	MJ/kg^H	Formula	kJ/mole	Ref.
Tech-air oil[a]	39.5	7.5	52.6	0.1	0	24.3	0.73	$C_6H_{13.58}O_6N_{0.01}$	133^H	46
Biomass oil	59	7	32	1	0.1	24.656	–4.59	$C_6H_{8.48}O_{2.44}N_{0.09}S_{0.004}$	–56^H	47
Tech-air oil	65.6	7.8	25.6	0.9	0.1	22.8	–9.73	$C_6H_{8.5}O_{1.76}N_{0.07}S_{0.003}$	–1070^H	41
#6 Heating oil[b]	85.7	10.5	2.0	—	1.8	42.3	–0.77	$C_6H_{8.76}O_{0.11}S_{0.05}$	–65^H	47
Pine root[c]	75.12	6.87	17.14	—	—	—	–2.3	$C_6H_{6.54}O_{1.03}$	–221^F	31

Note: All oils are liquid except Pine root.

[a] Oil produced at approximately 500° C.

[b] Included for comparison.

[c] Pitch. Included for comparison to pyrolytic oils. See text.

very tentative estimate due to the aforementioned assumption and the single data-point used.

Pitch is used in pyrotechnic compositions[27,31]—perhaps more so in Japanese fireworks than in the west,[27] and also in sealants, roofing compounds, and wood preservatives.[29,43]

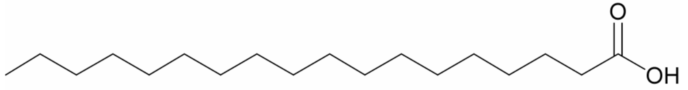
Gilsonite

Gilsonite (12002-43-6), also known as *uintahite*[48,49] and *North American Asphaltum*,[50] is a black, homogenous, solid hydrocarbon that is *asphaltene*-rich.[48,50,51] It is mined in northeastern Utah near the junction of the White and Green rivers south of Vernal, in an area approximately 3600 km^2.[48] It is found in vertical veins (dikes) that vary in width from millimeters up to 5.5 m, and up to 13 km in length. The Cowboy vein is the widest, measuring 5.5 m wide at its maximum, a depth of 305 m, and is estimated at containing over 16 million metric tons (includes the neighboring Bonanza vein).[49]

Gilsonite is sorted into the grades *Selects*, *Seconds*, and *Jet*.[49] The selects are taken from the center of the vein, and the seconds are taken from near the vein walls. Jet is mined from the middle of the Cowboy vein, and is characterized by a deep black color with bluish undertones. The fusing-point temperature increases, whereas the petroleum naphtha solubility decreases, from selects to seconds to jet.[49] Gilsonite, as mined, is almost completely free of mineral impurities.[48] Impurities present include vanadium, nickel, iron, and copper. The vanadium and nickel contribute the most, and even then typically average less than 100 ppm each.[51,52]

Gilsonite is part of a group of related bitumens including *ozocerite*, *asphalt*, *glance pitch*, and *grahamite*. They are all members of the maceral subgroup *asphaltite*, which is a *migrabitumen*.[51] See Table 10 for compositions and $\Delta_f H^o$.

Gilsonite is used in pyrotechnics,[27] as a binder for wood fibers,[48] as an oil substitute for paints and varnishes,[48,49] in the production of electrode coke and high-octane gasolines,[48,49] in asphalt paving products,[29,48] and as a high-energy component of certain explosives.[48]



Stearic acid
57-11-4

Figure 6. Stearic acid.

Wax

Wax is a low melting-temperature mixture of organic compounds of high molecular weight that typically repels water and is soluble in hydrocarbons.[29] Waxes may be of animal, vegetable, mineral, or synthetic origin.[29]

Wax is a naturally occurring fraction of petroleum. There are two general types of petroleum waxes: *paraffin* (untreated 8002-74-2, clay-treated 64742-43-4) waxes in petroleum distillates and *microcrystalline* (clay-treated 64742-42-3) waxes in petroleum residues.[51] Paraffin wax is a solid crystalline mixture of predominantly straight-chain hydrocarbons[51] ranging from C_{20} to C_{36}.[54] Microcrystalline wax hydrocarbons range from C_{30} to C_{75}.[54] *Cyclic* and *dicyclic* hydrocarbons are also present.[30,55] The composition of the wax varies with the particular wax-bearing crude oil from which it is derived.[55]

The simplest description of a paraffin wax would be an *alkane* with an approximate formula of C_nH_{2n+2}. This would result in a range of $C_{20}H_{42}$, Δ_fH^o –622.86 kJ/mole^B to $C_{36}H_{74}$ Δ_fH^o –1093.42 kJ/mole^B. In C_6 units this becomes $C_6H_{12.6}$ Δ_fH^o –186.9 kJ/mole^B to $C_6H_{12.3}$ Δ_fH^o –182.2 kJ/mole^B. For microcrystalline wax, the corresponding ranges would be $C_{30}H_{62}$ Δ_fH^o –916.96 kJ/mole^B to $C_{75}H_{152}$ Δ_fH^o –2240.41 kJ/mole^B, or in C_6 units $C_6H_{12.4}$ Δ_fH^o –183.4 kJ/mole^B to $C_6H_{12.16}$ Δ_fH^o –179.2 kJ/mole^B. If the *assumption* is made that paraffin wax is $C_{20}H_{42}$, then the Δ_cH^o of –46.61 MJ/kg[56] leads to a Δ_fH^o of –682.5 kJ/mole^C, or in C_6 units, $C_6H_{12.6}$ Δ_fH^o –204.8 kJ/mole^C, which is in reasonable agreement with the Benson Group based estimates.

Paraffin wax from a solvent de-waxing operation is commonly called "*slack wax*" (64742-61-6)[51] and may be categorized as *light neutral* and *heavy neutral*.[54] Slack wax may have between 5 and 50% oil content, which is removed such that the fully refined petroleum wax has an oil content of 0.5% maximum.[54] If paraffin oil is *assumed* to have an approximate composition of $C_{20}H_{42}$, then the Δ_cH^o of –41.00 MJ/kg[56] leads to an Δ_fH^o of –2294 kJ/mole$_{\text{liquid}}^C$, or in C_6 units, $C_6H_{12.6}$ and Δ_fH^o –688.2 kJ/mole$_{\text{liquid}}^C$.

Petrolatum (8009-03-8), also known as *petroleum jelly*, *white petroleum jelly*, *Vaseline*, and *Stanolene*,[28] is a colloidal system containing both non-straight chain solid hydrocarbons and high-boiling liquid hydrocarbons,[28] and is a low-melting microcrystalline wax.[51] The microcrystalline hydrocarbons of petrolatum wax range from C_{33} to C_{43}[29] with an approximate

Table 10. Elemental Composition, Heating Value, and Δ_fH^o of Bitumens.

	Elemental Composition						HHV	Δ_fH^o	C_6-basis	Δ_fH^o	
Bitumen	C	H	O	N	S	Ash	MJ/kg	MJ/kg^H	Formula	kJ/mole^H	Ref
Gilsonite	84.9	10.0	1.4	3.3	0.3	0.1	41.64	–0.325	$C_6H_{8.42}O_{0.07}N_{0.2}S_{0.008}$	–27.6	50
bitumen[a]	84.44	11.05	2.59[b]	1.00	0.75	0.17	41.87	–1.47	$C_6H_{9.36}O_{0.14}N_{0.06}S_{0.02}$	–125.2	53
bitumen	83.1	10.6	1.1	0.4	4.8	0.75	40.71	–1.93	$C_6H_{9.12}O_{0.06}N_{0.02}S_{0.13}$	–167.1	51

[a] P.R. Springs bitumen

[b] Oxygen by difference

formula of C_nH_{2n+2}.[28] The liquid form is *white mineral oil* (8012-95-1).[29] Aromatic compounds are highest in petrolatum (43%) and lowest in light neutral wax (3.2%).[54] Composition data sufficient to render an Δ_fH^o estimate was not found as of the time of this writing. The Δ_fH^o probably lies somewhere between paraffin wax (solid) and paraffin oil (liquid). The average of the aforementioned values based on the *assumed* composition of $C_{20}H_{42}$, in C_6 units, would be $C_6H_{12.6}$ Δ_fH^o –447 kJ/mole$_{\text{solid-liquid}}{}^{C}$.

Beeswax (*white* 8012-89-3, *yellow* 8006-40-4), is produced by various species of honeybees including *Apis mellifera*, *A. dorsata*, *A. flores*, and *A. Indica*. [30,57] Beeswax contains a variety of different compounds, each with a range of molecular sizes. See Figure 7 and Table 11. [*Note that most of the renderings in Figure 7 use an abbreviated notation,* $(CH_2)_X$, *which indicates that this* CH_2 *unit repeats "x" times, where "x" is variable. Without this notation, the renderings would be lengthy and difficult to compare to each other.*] The resulting formula based on this tabulated data is $C_{39.285}H_{78.296}O_{2.369}$ Δ_fH^o –1588.3 kJ/mole^B, or in C_6 units, $C_6H_{11.958}O_{0.362}$, Δ_fH^o –242.6 kJ/mole^B.

Paraffin waxes are used in pyrotechnics,[27,31,55] polishes, candles, crayons, paper coatings, packaging, and waterproofing.[29,54] Beeswax is used in cosmetics,[29,30,57] candles, shoe polish and polishes,[28–30,54] and furniture and floor waxes.[29] Petrolatum and paraffin oil are occasionally used in fireworks as *phlegmatizers*.[27] Other waxes are also used in pyrotechnics: *kauri* wax, *carnauba* wax,[55] and *stearic acid* (57-11-4, *octadecanoic acid*, $C_{18}H_{36}O_2$, Δ_fH^o –947.7 kJ/mole,[24] see Figure 6) to name a few.[9,27]

Table 11. Beeswax Composition and Formation Enthalpies.

Component	Weight Percent[a]	Typical Ranges	Representative Value[b]	Δ_fH^o kJ/mole^B
hydrocarbons	14	C_{23}–C_{31}	$C_{29}H_{60}$	–887.55
monoesters	35	C_{38}–C_{52}	$C_{46}H_{92}O_2$	–1724.39
diesters	14	C_{56}–C_{66}	$C_{60}H_{119}O_4$	–2477.41
triesters	3	NA	$C_{60}H_{118}O_6$	–2822.28
hydroxymonoesters	4	C_{24}–C_{34}	$C_{30}H_{61}O_3$	–1182.57
hydroxypolyesters	8	NA	$C_{46}H_{92}O_5$	–2274.33
acid monoesters	1	C_{16}–C_{20}	$C_{16}H_{30}O_4$	–1243.0
acid polyesters	2	NA	$C_{30}H_{56}O_6$	–2005.02
free acids	12	C_{14}–C_{36}	$C_{27}H_{52}O_2$	–1216.23
3-hydroxyflavanone	0.3	C_{15}	$C_{15}H_{12}O_3$	–418.88
unidentified	6.7[c]	NA	NA	NA

[a] All *Weight Percentages* and *Typical Ranges* from reference 57 except 3-hydroxyflavanone from reference 30. The *unidentified* component was given the value of 7 percent in reference 57, however, the author assigned it a value of 6.7 percent to account for the 3-hydroxyflavanone.

[b] Specific formula chosen by the author as representative of this component. See Figure 7 for the basic structures used in the estimates.

[c] Excluded from the beeswax representative formula and its Δ_fH .

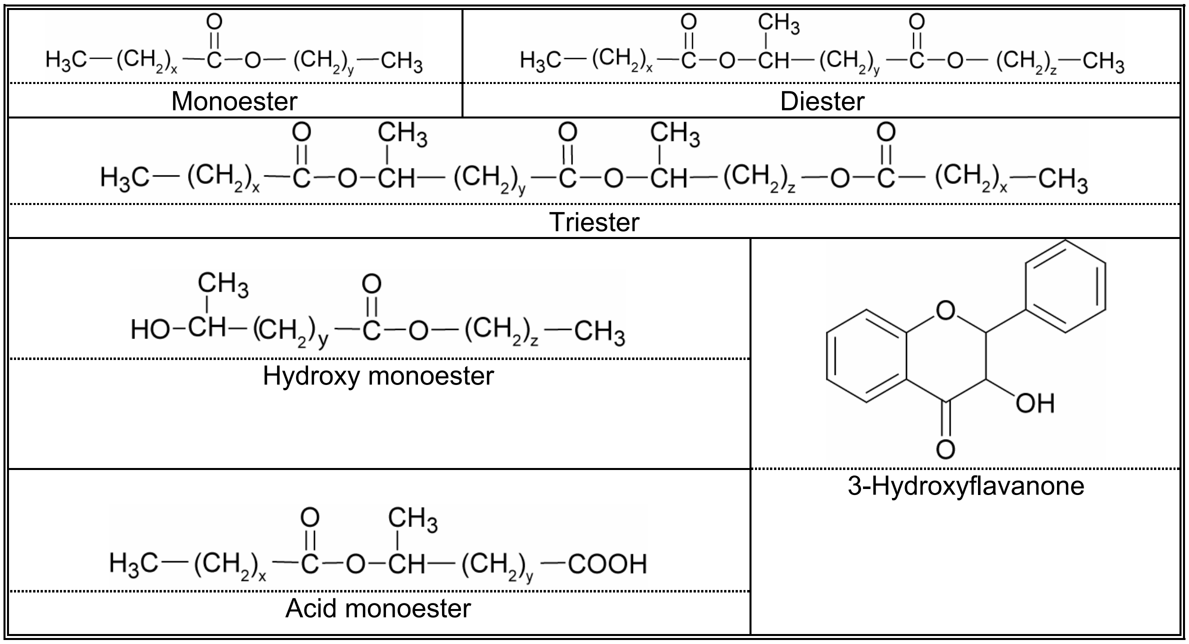


Figure 7. Some compounds contained in beeswax.

Miscellaneous Organic Compounds

Modern pyrotechnic compositions frequently utilize synthetic pure compounds and polymers. The choices made available by the chemical industries are truly remarkable. The polymers are made from a variety of different monomers in precisely controlled proportions. Blends of different polymers, and the introduction of additives such as plasticizers, stabilizers, ultraviolet light inhibitors, etc., make for a bewildering variety for the consumer to choose from. This is further complicated by the plethora of trade names given to each of these materials. For example, one reference[58] lists no less than 359 different names for polyvinyl chloride!

A sampling of some common, pure compounds and polymers are considered here for these reasons. See Table 12 for formulas and $\Delta_f H^o$, and Figures 8–12 for representative structures.

Naphthalene (91-20-3) finds occasional use in pyrotechnics for the generation of smoke,[9,27] and is also used in the production of smokeless powder, moth repellants, and preservatives.[29] *Anthracene* (120-12-7) is also used for smoke generation,[27] and is a carcinogen.[29]

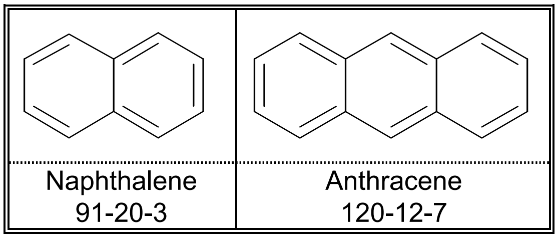


Figure 8. Naphthalene and anthracene.

Hexamethylenetetramine (100-97-0), also known as *hexamine* and *methenamine*,[9,29] is used in some pyrotechnic star formulations,[9] in the manufacture of adhesives, and in the high explosive *cyclonite*.[29]

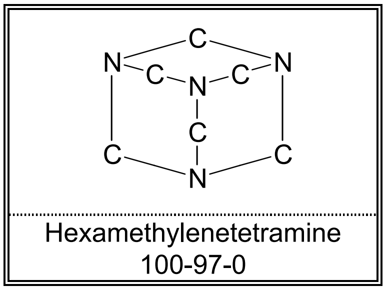


Figure 9. Hexamethylenetetramine.

Gallic acid (149-91-7) is used in the generation of pyrotechnic whistle effects,[27] in photography, and in the manufacture of tannins, inks,

Table 12. Composition and $\Delta_f H^o$ of Miscellaneous Organic Compounds.

Compound	Formula	$\Delta_f H^o$ kJ/mole	C_6 Basis Formula	$\Delta_f H^o$ kJ/mole	Ref.
Naphthalene	$C_{10}H_8$	77.9	$C_6H_{4.8}$	46.7	24
Anthracene	$C_{14}H_{10}$	129.2	$C_6H_{4.286}$	55.4	24
Hexamethylenetetramine	$C_6H_{12}N_4$	124.1	$C_6H_{12}N_4$	124.1	24
Poly(vinyl chloride)	C_2H_3Cl	$-96.90_{liquid}^{B\ [a]}$	$C_6H_9Cl_3$	$-290.7^{B\ [a]}$	
Poly(vinylidene chloride)	$C_4H_5Cl_3$	$-224.43_{liquid}^{B\ [a]}$	$C_6H_{7.5}Cl_{4.5}$	$-336.6^{B\ [a]}$	
Hexachlorobenzene	C_6Cl_6	–127.6	C_6Cl_6	–127.6	24
Gallic acid	$C_7H_6O_5$	–959.0	$C_6H_{5.143}O_{4.286}$	–822.0	23
Sodium benzoate	$C_7H_5NaO_2$	–595.38	$C_6H_{4.286}Na_{0.857}O_{1.714}$	–510.3	60
Sodium salicylate	$C_7H_5NaO_3$	-795.2^{PB}	$C_6H_{4.286}Na_{0.857}O_{2.571}$	-681.6^{PB}	
Tristearin	$C_{57}H_{110}O_6$	-2276.1^{B}	$C_6H_{11.579}O_{0.632}$	-239.6^{B}	

[a] Required Benson Group values were unavailable for the solid phase.

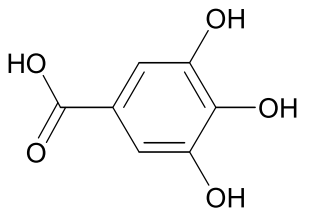
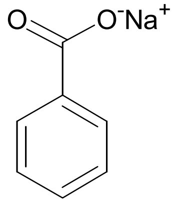
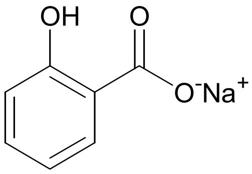
		
Gallic acid 149-91-7	Sodium benzoate 532-32-1	Sodium salicylate 54-21-7

Figure 10. Gallic acid, sodium benzoate and sodium salicylate.

and dyes.[29] *Sodium benzoate* (532-32-1)[9] and *sodium salicylate* (54-21-7)[9,27] are also used in pyrotechnic whistles. The former is used as a food preservative and the latter as a preservative for adhesives.29]

Polyvinyl chloride (9002-86-2), or *PVC*, is used in pyrotechnics as a *chlorine donor*[9,27] and as a fuel,[29] as a *plastisol* binder in composite propellants,[59] and in the manufacture of piping, siding, and plastic products.[29] *Polyvinylidene chloride* (9011-06-7), also known as *Saran*,[9,29] is also used as a chlorine donor in pyrotechnics,[9,27] for food packaging films, and in upholstery and fabrics.[29] *Hexachlorobenzene* (118-74-1) once found use in pyrotechnics as a chlorine donor,[9,27] but its use has declined due to a preference for PVC.[27] It is likely a carcinogen. [9] It is also used for fungicides and wood preservatives. [29]

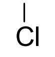
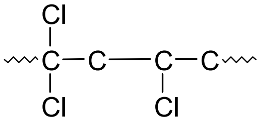
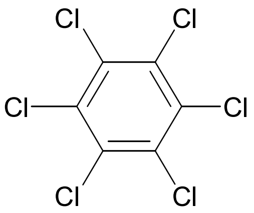
 $\sim\mathrm{C}-\underset{\mathrm{Cl}}{\mathrm{C}}\sim$	 $\sim\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\mathrm{C}-\underset{\mathrm{Cl}}{\mathrm{C}}-\mathrm{C}\sim$	
Poly(vinyl chloride) PVC 9002-86-2	Poly(vinylidene chloride) 9011-06-7	Hexachlorobenzene 118-74-1

Figure 11. Polyvinyl chloride, polyvinylidene chloride and hexachlorobenzene.

Tristearin (555-43-1), also known as *stearin* and *glycerol tristearate*,[9,29] is used in pyrotechnics as a phlegmatizing agent and for coating aluminum flakes,[9] and in soap, candles, adhesives, and polishes.[29]

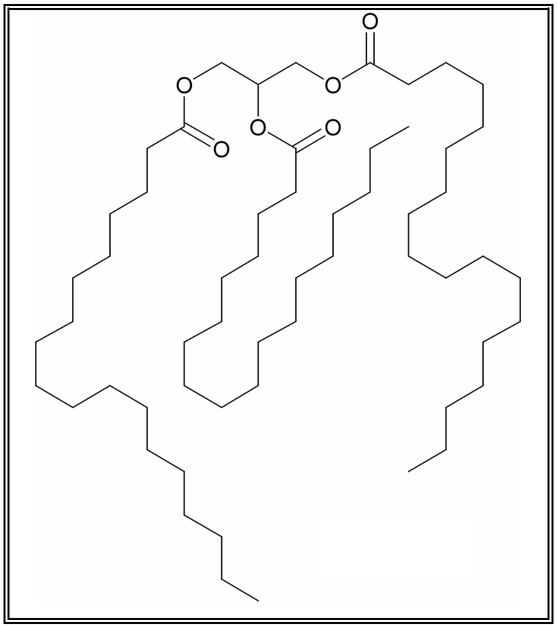


Figure 12. Tristearin.

Conclusion

A variety of disparate sources of data, as illustrated above, may be drawn on to gather, reduce, and estimate useful chemical formulas and formation enthalpies for fuels used in pyrotechnics until such time as exact, laboratory measured values become available. In this process of research and discovery, other potentially useful information may be found. For example, the trace elements present in many of the fuels might cause undesirable coloration of, say, a star's color purity. This ancillary information assists the energetics chemist in making informed decisions. It is the author's hope that the reader has a greater appreciation for the overall simplicity and variety of methods in which useful estimates may be made. The benefit one gets by estimating and using these values certainly outweighs the costs in getting them.

Acknowledgments

The author gratefully acknowledges the technical assistance of B. Jenkins, K. Kosanke, R. Kuzma, D. Meyer, and D. Wilson.

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(05/98)

Errata

Issue 8, Winter 1998, page 12, Table at bottom of page:

In the row for "Rha*p*" the "Formula" "$C_6H_{10}O_5$" should be "$C_6H_{12}O_5$".

Page 15, Table 5 at top of page:

In the row for " Nitrate, DS = 2.5" the "Formula" "$C_6H_{7.5}N_{2.5}O_{20}$" should be "$C_6H_{7.5}N_{2.5}O_{10}$".

Page 16, Reference 23 that appears at the end, should be Reference 25 and subsequent references renumbered.

Events Calendar

Pyrotechnics

17th Symp. on Explosives & Pyrotechnics

April 27–29, 1999, Essington, PA, USA

Contact:
Franklin Applied Physics, Inc.
Phone: +610-666-6645
FAX: +610-666-0173

2nd Workshop in the Use of Microcalorimetry to Characterize Energetic Materials

May 17–19, 1999, Leeds, UK

Contact: Dr. Trevor T. Griffiths
Phone: +44-1959-51-5321
FAX: +44-1959-51-6065
e-mail: ttgriffiths@deragov.uk

Grunelagen Pyrotechnik (Fundamentals of Pyrotechnics)

May 17–22, 1999, Weil-am-Rhein, Germany

Contact: Dr. G. A. Schröder
Carl-cranz-Gesellschaft e. V.
79576 Weil-am Rhein, Germany
Phone: +49-7621-75091
FAX: +49-7621-793026
Web site: www.ccg.dlr.de

7th International Seminar—Groupe de Travail de Pyrotechnie—EuroPyro 99 and 25th International Pyrotechnics Seminar

June 7–11, 1999, Ensieta Brest, France

Contact: Association Francaise de Pyrotechnie
EuroPyro 99
B.P. No. 121
45240 La Ferte
St. Aubin, France
FAX: +33-238-516-822
Web site: www.intlpyro.org

30th Int'l Annual Conference of ICT

June 29–July 2 1999

Contact: Mrs. Gesa Langer, Chair

Franuhofer-Inst. für Chemische Technologie
Attn: Manuella Wolff
PO Box 1240
D-76318 Pinfztal (Berghausen)
Federal Republic of Germany
Phone: +49-(0)721-4640-121
FAX: +49-(0)721-4640-111
e-mail: mw@ict.fhg.de
Web site: www.ict.fhg.de

3rd International Conference On Intrachamber Processes And Combustion In Devices Using Solid Propellants and in the Gun Tube Systems (ICOC99)

July 7–9, 1999, Izhevsk, Udmurt Rep., Russia

Chemistry of Pyrotechnics & Explosives

July 25–30, 1999, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: Pyrotechnics in the 21st Century — A Review of the State-of-the Art in 1999

Aug. 1–6, 1999, Chestertown, MD, USA

Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: 410-778-6825
FAX: 410-778-5013
e-mail: John.Conkling@washcoll.edu

American Pyrotechnics Association Conv.

Oct. 19–23, 1999, Las Vegas, NV, USA

Contact: American Pyrotechnics Association
PO Box 30438
Bethesda, MD 20824, USA
Phone: 301-907-8181
FAX: 301-907-9148
e-mail: julie@fireworksafty.com
Web site: www.americanpyro.com

26th International Pyrotechnics Seminar

Oct. 1–4, 1999, Nanjing, China

Contact: Jinhua Peng/Chongkai Sun, Chair.

Nanjing Univ. of Science and Technology
Nanging, 210084 P. R. China
Phone: 86-25-431-5225
FAX: 86-25-443-1622
e-mail: diecnust@publicl.ptt.js.cn

3rd International Autumn Seminar on Propellants, Explosives and Pyrotechnics

Oct. 5–8, 1999, Chengdu, China

Contact: Prof. Feng Changgen, Mech. & Engr.
Beijing Institute of Technology
PO Box 327
Beijing, 100081, China
FAX: +86-10-6841-2889
e-mail: cgfen@public.east.cn.net

(Continued on Page 50)

The Hazards Posed by Fragments from Rupturing Steel Fireworks Mortar Tubes — Predictions from a Computer Model —

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ABSTRACT

Fragments with masses of up to 100 g and velocities of up to 510 m/s can be produced from spiral-wound mild steel mortar tubes when firework maroon shells of diameters up to 150 mm are exploded in them. External ballistics calculations indicate that such fragments could travel up to 165±60 m, and possibly 30% further if ricochets on a concrete surface take place. Calculations indicate that these fragments possess sufficient kinetic energy density to penetrate the skin of spectators on landing. In addition, large slow–moving fragments of up to 7 kg are also produced and these could inflict blunt trauma injuries on operators.

Keywords: firework, mortar tube, safety, fragment, steel velocity, projection, injury, shell

Introduction

A firework accident in which a mortar shell exploded prematurely in its steel mortar tube resulted in the display operator having to have his leg amputated and members of the public being injured.[1] As a result, the UK Health and Safety Executive instigated a research programme into hazards associated with firework mortars.[2] A summary of this work was presented at the 4th International Symposium on Fireworks.[3] The need for the work was reinforced by subsequent mortar-related accidents which led to fatalities[4] and serious injuries[5–7]

At public firework displays, it is not uncommon for firework mortar tubes to be used without a means of mitigating the hazards from fragmentation of the mortar tube if a shell explodes prematurely in it.[8] Large numbers of fragments can be generated, particularly when maroon or large calibre cylindrical effect multi-break shells are used.[9] Some of the fragments are small and have high velocities, while others, which are produced from areas of the mortar tube away from the explosion point, are large (up to 7 kg) and relatively slow-moving. Plastic fragments from shell casings could also pose a hazard when shells are propelled out of the mortar tube but explode at low altitude (a 'low-burst'), or when a shell explodes prematurely in a mortar tube that does not fragment but ruptures, producing splits in its side that allow the plastic fragments to escape.

There was a need to estimate how far such fragments could travel and the types of injury they could inflict, so that estimates of hazard ranges could be made. Another factor to be considered was the possibility of fragments ricocheting off hard surfaces, and thus increasing the hazard range. Velocity and mass data for steel mortar and plastic shell case fragments (which allow such an analysis to be carried out) have been previously reported[10].

In the UK professional firework operators are covered by the Health and Safety at Work, etc.

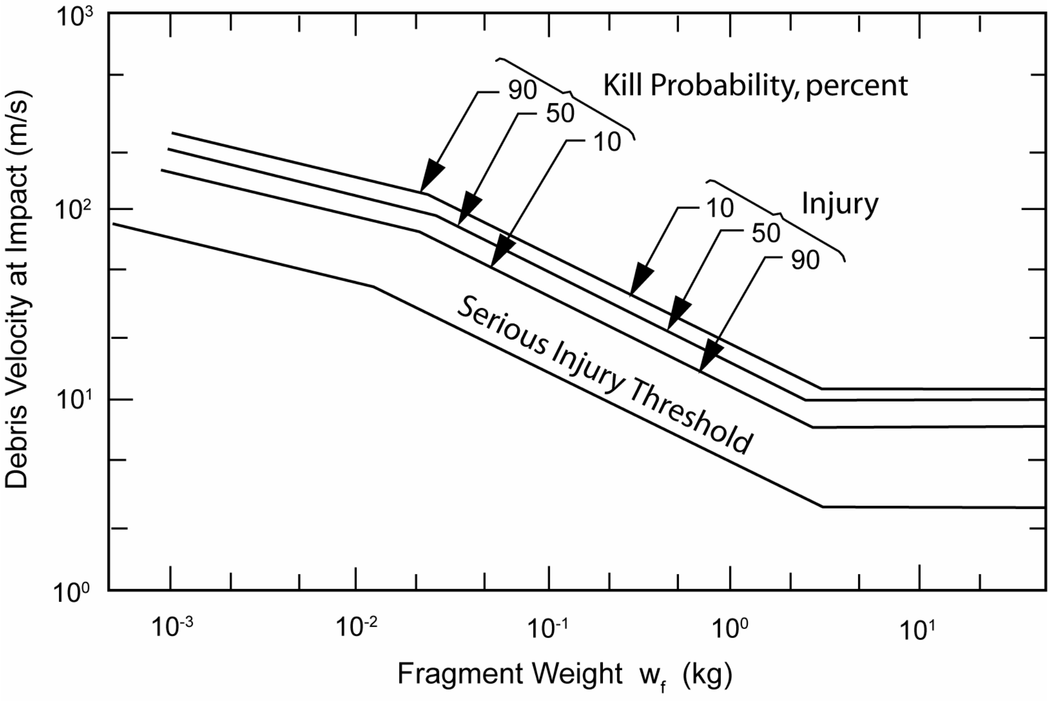

Figure 1: Effect of non-penetrating fragment impact on the human body (Abdomen and limbs)[12]
[Reproduced with kind permission from Elsevier Science–NL.]

Act, 1974. This places duties on operators who are employers to ensure, as far as is reasonably practicable, the health and safety of their employees at work and that of other people, including the public, who may be affected by their operations. Similar duties are placed on self-employed operators in respect of the health and safety of themselves and other people.

Possible injuries to spectators and operators can come from penetrating wounds, where the energy density of the fragment exceeds a threshold value, or from blunt trauma (where large non-penetrating projectiles impact with the surface of the body and impart their energy to it causing internal injuries), which is governed by the total kinetic energy of the fragment hitting the body.

The threshold energy densities required to penetrate various parts of the body[11] range from 0.06 J/mm^2 for the eye, 0.1 J/mm^2 for skin and 0.19 J/mm^2 for bone. Threshold energy density is defined as the kinetic energy of the penetrating fragment divided by the cross-sectional area of the penetrating edge of the fragment in the direction of motion. Thus a 40 g fragment with a penetrating edge of 1.6 mm × 0.1 mm (estimated to be equivalent to the sharp corner of a mortar tube fragment), will only need to be travelling at 0.9 m/s to break the skin.

Blunt trauma can range from bruising to death. Figure 1[12] shows that for a 100 g fragment, there is a 90% probability of death at a velocity of 100 m/s and that the onset of serious injury is at a velocity of 10 m/s. These values are all within the range of velocities measured for fragments from bursting steel mortar tubes,[10] suggesting a risk of injuries from blunt trauma, as well as from penetrating fragments.

Fragment ricochets will occur when there is insufficient vertical velocity to penetrate the ground. The possibility of ricochets will be higher when the ground is hard (e.g., concrete, rather than soil), and when the velocity vector has a small angle to the horizontal. Thus fragments that are fired near to the horizontal are most likely to ricochet. When assessing separation distances, consideration should therefore be given to the effects of ricochets, especially if displays are conducted on hard surfaces.

The aim of this work is to present computer model estimates for the likely flight distances of

Table 1: Calculated Projected Distance Against Frontal Area for 200 g Steel Fragment Travelling at 400 m/s.

	Drag Coefficient (C_d)	Presented frontal area (mm^2)	Equivalent calibre (mm)	Optimum elevation of fragment trajectory (degrees)	Maximum horizontal distance if exploded at ground level (m)
Maximum area	0.9	15400	140	22	85.40
Mean area		7880	100	23	151
Minimum area		204	16	35	2670
No drag	0	—	—	45	16000

fragments formed when maroon shells explode in free air (simulating a 'low-burst') and when they explode within, and fragment, steel mortar tubes. The data will be a parameter used to establish the separation distances required to protect both operators and spectators from penetrating and blunt trauma injuries.

Ballistics Calculations

The results obtained from the calculations performed during this study are based on the output from a computer model that requires specific data inputs. To satisfy these requirements a number of assumptions have been made regarding the behaviour of fragments during flight, and no experimental work has been performed to validate the model used. Therefore, the findings presented in this paper should only be considered as indicators of what is likely to happen when firework shells explode in steel mortar tubes or directly above them. Experimental work will be necessary to validate the model before the calculated flight distances can be verified.

The majority of calculations assumed that the fragment impact site was at the same height as the explosion site. A small sample of calculations assumed that the impact site was lower than the explosion site to simulate displays fired from buildings or bridges. These indicated that high velocity fragments at elevations of up to 50 m do not significantly affect projected distances (<10% increase in distance), and it was concluded that elevation of the explosion position in relation to the impact point was not a critical factor when considering separation distances.

To calculate the external ballistic behaviour of fragments it was assumed that they were square in section with a thickness equal to the wall thickness of the mortar tube from which the fragment was formed (i.e., 1.65 mm and 2 mm for 75 mm and 152 mm calibre steel tubes, respectively).

Using literature values for fragment mass (200 g)[13] and velocity (400 m/s),[14] it is possible to calculate projection distances of 2700 m, 85 m and 150 m for the fragment depending on whether it is presenting its minimum, maximum or mean frontal area to the direction of flight. See Table 1. The value obtained using the mean frontal area (150 m) is appropriate to those circumstances when the fragment is tumbling in flight and is in line with experimentally measured distances (120 m) reported in the literature for metal fragments.[15] These results, together with a report that "all orientations of bomb fragments are equi-probable",[16] indicate that it is reasonable to assume that fragments are aerodynamically unstable and tumble in flight.

The forces acting on the fragment will be gravity, drag, which will be a function of the shape of the fragment, its velocity and its cross-sectional area, and lift, which will be a function of the same variables as drag.

From the literature it has been reported that:

1) In velocity trials,[10] steel mortar fragments of up to 100 g mass can travel at initial velocities of up to 512 m/s. However, the one large fragment recorded (408 g) had a much

lower velocity (44 m/s) which suggests that ballistics calculations of large fragments at high velocities would be inappropriate,

2) In fragmentation trials,[9] the maximum mass of a fragment that had sufficient energy to penetrate into the wooden fragment-capture system was 533.5 g,
3) Initial trajectory data indicate that 72% of steel fragments have initial trajectories of ±15° from the horizontal with <10% having trajectories >45°.[9]
4) Drag coefficients (C_d) for tumbling fragments are likely to be 0.91±0.27,[16] which suggests that an average value of 0.9 should be used. In order to show the effect of reducing drag coefficients, a value of 0.6 was also used in our calculations.
5) Assuming that fragments tumble, a mean frontal area can be set equal to $S/4$, where S = fragment surface area.[16] The mean lift for a tumbling fragment can be assumed to be zero provided that the rotational speed is much less than the translational speed.

Using these assumptions, the parameters used to calculate steel fragment flight distances were as shown in Table 2.

Table 2: Fragment Parameters Used in Ballistics Calculations.

Drag coefficient (C_d)	Velocity (m/s)	Mass (g)	Trajectory (degrees)
0.6	19	4.9	0
0.9	246	30.3	5
	450	118.6	10
		533.5	15
			25
			45

Equations covering the movement of projectiles have been incorporated into many computer programs that can calculate the distance travelled by the projectile as a function of its mass, launch angle and launch velocity. The model used for this work[17] is due to be issued through the NATO Range Safety Working Party (NRSWP).

The effect of ricochets was calculated from a knowledge of the coefficient of restitution, e,[18] which was measured experimentally for concrete by carrying out drop tests with steel balls. These experiments generated a value of 0.56. For a projectile hitting the ground with horizontal velocity and vertical velocity (upward velocities being taken as positive), the ricochet velocity is given by:

Horizontal velocity = v_x

Vertical velocity = ev_y

Trajectory angle = $\tan^{-1}\left(\frac{ev_y}{v_x}\right)$

Thus, for successive ricochets, the resultant velocity will reduce and the trajectory will move closer to the horizontal.

Velocity trials[10] showed that plastic shell fragments of up to 7.1 g with velocities of 540 m/s were generated in mortar tubes that ruptured but did not fragment, and that smaller fragments with velocities of up to 964 m/s were generated from shell explosions in free air. These data were used to estimate the distances that such fragments could travel.

Analysis and Discussion of Results

Ballistics calculations indicated that maximum projected distances occurred when fast moving fragments had an initial trajectory of approximately 25°. Table 3 shows the projected distances that steel fragments could fly as a function of fragment mass and velocity (C_d=0.9 and 0.6). The data suggest that the distances that fragments will fly will increase with fragment mass and velocity, but that in the typical ranges of mass and velocity for the lighter fragments, the distance is not very sensitive to variations in either mass or velocity. However, in all cases, the distances travelled are well in excess of 50 m, a minimum separation distance commonly given in guidance material.[19–22] Thus, when staging firework displays, it is unlikely that an adequate separation distance could be provided at venues such as football grounds to allow the safe use of steel mortar tubes that are not surrounded by some form of

Table 3: Maximum Projected Distances for Tumbling Steel Fragments As a Function of Fragment Mass, Velocity and Drag Coefficient (Trajectory Angle 25°).

Fragment initial velocity (m/s)	Tube diameter (mm)	Fragment mass (g)	Mean Presented frontal area (mm^2)	Projected distance (m)		Projected distance after 2 ricochets on concrete (m)	
				C_d=0.6	C_d=0.9	C_d=0.6	C_d=0.9
246	75	4.9	221	175	126	225	160
		30.3	1250	188	135	242	172
		118.6	4730	193	139	248	177
	152	533.5	17300	228	165	297	212
450	75	4.9	221	204	145	252	178
		30.3	1250	221	157	272	193
		118.6	4730	227	162	279	198
	152	533.5	17300	n/a	n/a	n/a	n/a

fragment mitigation system. Results for a drag coefficient of 0.6 show the same relationship between distance travelled and fragment mass and velocity as for a value of 0.9, but the distance travelled is greater as a consequence of the reduced drag of the fragment.

Calculations using the minimum projected area, a mode of travel similar to that of a discus, suggest maximum projected distances of 1470 m, or 2000 m after two ricochets, for a 30.3 g fragment with initial velocity of 450 m/s. However, given the irregular shape of tube fragments, it is unlikely that they would fly in this fashion.

In addition to the distance travelled by fragments, their effect on the body must be considered. Table 4 summarises the velocity and energy density data that corresponds to the ballistics data given in Table 3. The energy density of the fragments on landing will range from 5.0 J/mm^2 for a 4.9 g fragment travelling at an initial velocity of 246 m/s to 151 J/mm^2 for a 118.6 g fragment with initial velocity of 450 m/s (assuming C_d = 0.9). Even after two ricochets, energy densities are only reduced to 1.88 J/mm^2 in the former case and 48.1 J/mm^2 in the latter. These values are all substantially greater than the 0.1 J/mm^2 required to cut skin,[11] indicating that unacceptable injury would be inflicted if the bare skin of a spectator were to be hit by a steel fragment.

In connection with blunt trauma injuries, the key factor is the total kinetic energy of the fragment. Table 5 lists the velocity required to exceed the serious injury threshold and the 50% kill probability threshold (Figure 1) for fragments of masses of 4.9–533.5 g. At a velocity of 246 m/s it can be seen that fragments in the mass range indicated will have sufficient kinetic energy to cause serious injury and exceed the 50% kill probability. At the point of first impact with the ground, total kinetic energies will be reduced but the serious injury threshold will still be exceeded for the 118.6 g and 533.5 g fragments and the 50% kill probability will be exceeded for all velocities of the 533.5 g fragment. The greatest risk of blunt trauma injury would be to an operator who fired shells in a display using flame ignition assuming the tube to be completely without any form of mitigation. Such an operator might be very close to a mortar tube at the time of its disintegration. Measurement of fragment velocities[10] has shown that very few fragments of mass greater than 100 g have initial velocities of greater than 100 m/s, and thus the risk of serious blunt trauma injury to spectators, standing at the distances of 50–100 m from the mortar tube recommended by current codes of practice, will be lower.

Table 4: Velocity and Kinetic Energy Densities for Tumbling Steel Fragments As a Function of Fragment Mass and Velocity (Drag Coefficient 0.9, Trajectory Angle 25°).

Fragment initial velocity (m/s)	Tube diameter (mm)	Fragment mass (g)	Presented frontal area (mm^2)	Initial energy density (J/mm^2)	Velocity after 1st flight (m/s)	Kinetic energy density after 1st flight (J/mm^2)	Velocity after 2 ricochets (m/s)	Kinetic energy density after 2 ricochets (J/mm^2)
246	75	4.9	221	925	0.8	5	0.3	1.88
		30.3	1250	5730	5.6	35	1.8	11.3
		118.6	4730	22400	22.8	143	7.2	45
	152	533.5	17300	101000	125	781	38.9	243
450	75	4.9	221	3100	0.9	5.63	0.3	1.88
		30.3	1250	19200	6	37.5	1.9	11.9
		118.6	4730	75100	24.2	151	7.7	48.1
	152	533.5	17300	n/a	n/a	n/a	n/a	n/a

It should be noted that even if the steel mortar tube is fully protected by burial or being surrounded by sandbags, there will still need to be a separation distance between tube and spectators. This will reduce the likelihood of plastic fragments from the firework shell or debris from burning stars from reaching spectators if the shell explodes above the mortar tube but at a low altitude (a 'low–burst'). Plastic fragments are likely to travel up to 40 m with an energy density just sufficient to damage the eye,[9] while the radius of the star debris is likely to be around 70 m for a 152 mm diameter mortar tube, since the burst diameter of star shells that fit that tube has been estimated to be 130 m by Shimizu[23](Figure 2).

Overall, it appears that in order to prevent fragments generated from unmitigated firework mortar tubes from injuring spectators, extremely large separation distances would have to be implemented. Such precautions would not protect firework operators when they have to work within the separation distance between the mortar tubes and the spectators. Clearly, the implementation of such large separation distances would preclude the use of many of the venues currently used for firework displays.

A better approach for operators and spectators would be to protect steel mortar tubes. This would enable the minimum separation distance to be reduced and provide some protection to operators. A minimum separation distance will still be necessary to protect spectators from plastic fragments from firework shells and from burning debris from stars.

Table 5: Blunt Trauma Injury to the Body by Projectiles as a Function of Mass and Velocity.

Fragment mass (g)	Fragment velocity to exceed the serious injury threshold (m/s)	Fragment velocity to exceed the 50% kill probability (m/s)
4.9	52	109
30.3	26	85
118.6	11	34
533.5	3	11

Conclusions

This paper has indicated that:

1) For shells of up to 150 mm diameter, steel mortar tube fragments of up to 100 g mass are likely to travel up to 165±60 m.
2) Ricochets, which will tend to occur on concrete surfaces, can increase the distance traveled by fragments from steel mortar tubes by up to 30%. Ricochets will present a significant additional hazard on concrete surfaces, and a negligible hazard on grass, except when it is compacted and dry.
3) The risks to spectators from mortar tube fragments are likely to be from penetrative injuries. Calculations indicate that at the current minimum recommended separation distances all fragments that are not hindered by a mitigation system will have sufficient kinetic energy density to puncture bare skin.
4) Hazards to operators can come from both penetrative and blunt trauma injuries.

It is suggested that the following steps should be considered to reduce the hazard to spectators and display operators:

1) Steel mortar tubes should have some form of mitigation system in place to retain any fragments produced as a result of a shell exploding in the tube.
2) Remote firing of mortars should be encouraged because operators can then fire the display from a sheltered position, or from a position outside the separation distance between the mortar tubes and the spectators.
3) Even when there is a mitigation system around the tube, appropriate separation distances are required between mortars and spectators to protect them from shell fragments and debris from burning stars. This varies with the size and type of shell being fired (Figure 2) and is approximately 70 m for a 150 mm diameter shell.

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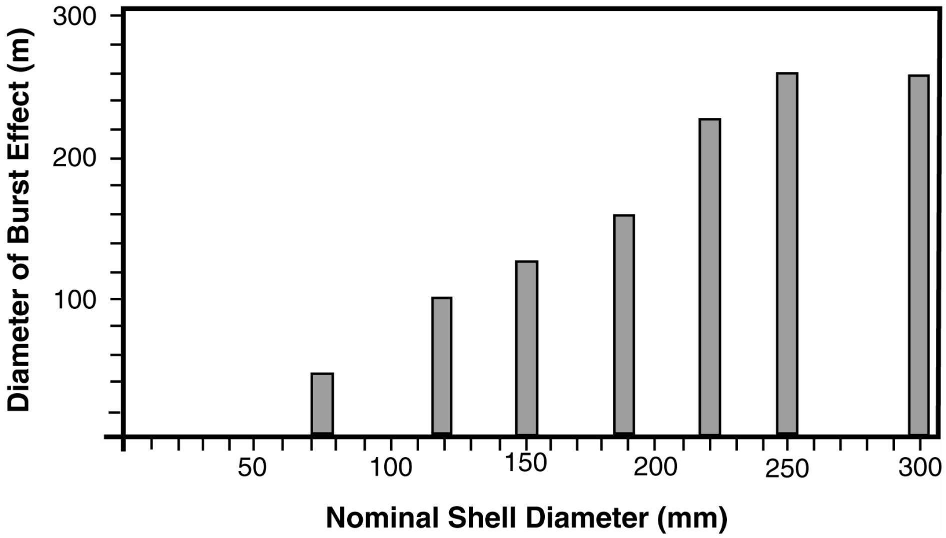

Figure 2: Shell burst diameter as a function of star shell diameter (Data from Shimizu).[23]

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An Introduction to Chemical Thermodynamics
Part 1 — Matter, Energy and the First Law

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ABSTRACT

This is the first in a series of articles presenting an introductory outline of chemical thermodynamics and chemical kinetics, with emphasis on those aspects of particular relevance to pyrotechnics. A brief comment on the molecular theory of matter is followed by a discussion of basic mechanics to introduce the concepts of work and energy. The non-conservation of mechanical energy leads to the idea of heat as a form of energy, and to the Law of Conservation of Energy. The concepts of temperature and thermal equilibrium are then introduced. An introduction to thermodynamic systems, thermodynamic states and state functions is presented. The first Law of Thermodynamics is introduced as a statement of the Law of Conservation of Energy in terms of changes in internal energy, heat and work. The enthalpy is shown to be a useful thermodynamic state function; the enthalpy change in a process corresponds to the heat transferred between a system and its surroundings at constant pressure. Calculations of the heat transferred in chemical reactions are demonstrated. A Table of standard enthalpies of formation of a range of pyrotechnically interesting materials is included for use in such calculations.

Keywords: thermodynamics, thermochemistry, energy, heat, flash powder

Introduction

Pyrotechnic devices use the energy released by chemical reactions to produce a variety of effects including heat, light, sound and motion. The relationship between chemical change and energy is of central importance to a scientific approach to pyrotechnics. The branch of science that deals with this relationship is *chemical thermodynamics.* Thermodynamics can predict whether or not a chemical reaction is possible, and how much energy would be released or absorbed by that reaction. It cannot, however, predict how fast a reaction will be. That is the concern of *chemical kinetics.* The energy involved in chemical reactions and the speed of those reactions are both of obvious interest to the pyrotechnist. This series of articles will give an introduction to chemical thermodynamics and chemical kinetics, with an emphasis on those aspects of relevance to pyrotechnics.

The following sections will often contain mathematics. To a newcomer to science, it can be rather intimidating to see lines of mathematical symbols appearing in the middle of a discussion about some aspect of the physical world. It is by no means obvious how these symbols can have anything to do with what happens in the world outside. Some writers add to the confusion by claiming that the behavior of the real world is in some mysterious way "governed" by mathematics. What really happens is this: Scientists take some aspect of the real world and treat it *as if* it were one of the abstract objects dealt with by mathematics. You do this, perhaps without realizing it, all the time. Suppose you were packing eggs, and you packed twelve eggs to a box, and twelve boxes per crate, and someone asked you how many eggs you had packed. You would count the crates and multiply 12 to get the number of boxes and multiply that number by 12 to get the number of eggs. You would treat the eggs, boxes and crates as if they were *numbers*, obeying the rules of arithmetic. This is a very simple example of a *mathematical model*, whereby a real situation is converted to a problem in mathematics. The reason for making mathematical models is that mathematics provides a very powerful set of procedures for reasoning in a completely logical and consistent way. If the model is well chosen, the mathematical argument can reveal all sorts of relationships between aspects of the real world. If the results of the mathematical reasoning are consistent with what is observed, it is evidence that the mathematical model was indeed well chosen. Instead of saying that the behavior of the physical world is "governed" by mathematics, we should say that aspects of it are *described* or *modeled* by mathematics.

The mathematics in this article is set out in more detail than is usual, in an effort to avoid the frustration that arises when a reader cannot follow a step that might be obvious to the mathematically-minded.

Chemical Thermodynamics

Chemical thermodynamics can provide an understanding of what drives chemical change. It provides ways to calculate whether a particular reaction is possible and what energy changes would be associated with that reaction. Calculations, using tables of thermodynamic data, can reveal the maximum possible amount of energy that could be provided by a particular reaction, such as that between potassium nitrate, charcoal and sulfur in Black Powder. A calculated value for the energy released in a pyrotechnic reaction can then be used to estimate the maximum possible temperature that could be reached. Such information can be useful when designing compositions for producing colored flames, for example. Thermodynamic calculations can provide useful information about the composition of chemical systems at equilibrium that would be difficult, or impossible, to obtain by experimental measurement. Such information is useful in calculations for the design of efficient rocket motors.

Thermodynamics originated from efforts to understand the limitations of steam engines. Its application to chemistry happened at about the same time that the molecular theory of matter was being developed. Thermodynamics makes no assumptions whatsoever about the structure of matter. It is much easier, however, to understand the application of thermodynamics to chemistry if the behavior of molecules is brought into the picture.

A Preamble about Matter

Since chemical thermodynamics is concerned with matter and energy, it is appropriate first to review some relevant ideas about matter. The most obvious characteristic of matter is its complexity. Stars, planets, plants, rocks, people, cities – all are aggregates of matter in varying degrees of complexity. The task of understanding such complexity might seem impossible. Chemistry approaches the understanding of matter by focusing attention on the forms with the least complexity. Over the past few centuries, chemists have subjected matter to various processes of chemical analysis, reducing structures and objects to materials, and then attempting to reduce each material to its simplest constituents. This led to the recognition of a relatively small number of **chemical elements**, materials that could not be decomposed into simpler substances by chemical analysis. The next level of complexity is the **chemical compound**. Chemical compounds are substances made up of chemical elements, in *constant proportions by mass*. Elements and compounds, because they are of constant chemical composition, are called **pure substances**. Compounds are formed from their elements (either directly or indirectly by way of intermediate compounds) by **chemical reactions**. During some chemical reactions, **energy** is released. In others, it is absorbed from the surroundings by the reacting materials.

The Molecular Structure of Matter

Probably the most important idea in physical science is the notion that matter is made up of very small particles, called **molecules**. Each pure substance consists of molecules of the same kind. Molecules can be broken down into smaller particles, called **atoms**. The molecules of each of the chemical elements are made up of atoms having the same, unique set of chemical properties. They may vary in mass (atoms of the same chemical type but having different masses are called **isotopes**) but their chemical properties are essentially identical. The molecules of elements may consist of single atoms (helium, neon, argon and gaseous mercury are examples), or of two or more atoms bound together. Examples include oxygen (O_2, a pair of oxygen atoms), white phosphorus (P_4, a tetrahedron of phosphorus atoms) and sulfur (S_8, a ring of eight sulfur atoms). The word "atom" means "indivisible", and at one time it was thought that the atom represented the limit to the breaking down of matter. These days, it is known that atoms consist of an extremely small, but massive, central **nucleus** surrounded by a rather complex outer structure of **electrons**. Chemical reactions occur when the outer electrons of atoms rearrange themselves. These rearrangements can result in atoms of various sorts becoming linked together by new electronic structures, forming molecules. Only the outermost electrons are involved the rearrangements that take place in chemical reactions. An arrangement of electrons that links two atoms together is referred to as a **chemical bond**.

The simplest type of electronic rearrangement to imagine is the loss of a single electron from an atom. The electron-deficient atom left after this process is called a positive **ion**. Metals, such as sodium, iron and gold, are made up of positive ions, stacked in regular patterns, surrounded by a "sea" of loose electrons that can move around freely, provided they do not move too far from the ions. These mobile electrons are responsible for the high electrical conductivity of metals and for their characteristic metallic luster. Other atoms, such as those of non-metallic elements like oxygen and chlorine, can gain electrons and form negative ions. Compounds such as magnesium oxide (MgO) and sodium chloride (NaCl) consist of positive metal ions and negative non-metal ions stacked in regular patterns. These compounds are examples of **ionic compounds**. In substances such as elemental sulfur (S_8) and oxygen (O_2), and compounds such as water (H_2O) and alcohol (C_2H_5OH) and also in ions such as the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-), the atoms are linked by pairs of electrons shared between the atoms. These shared pairs of electrons are called **covalent bonds**.

Molecular Structure of the States of Matter

Most pure substances can occur in three physical states: solid, liquid and gas. The three physical states differ in the way in which the molecules are arranged in space. Molecules in every state of matter are in constant motion. In a solid, molecules are close together and move mainly by vibrating about their rest positions. In a gas, molecules are relatively far apart and move at random through the entire volume available to be occupied by the gas. In a liquid the molecules can move freely, but tend to remain close to each other.

A Digression into Mechanics

Already in this discussion several *mechanical* concepts have been mentioned without definition or explanation. These concepts included motion, mass and energy. While these ideas might already be quite familiar, it is useful to review them. This requires a brief look at the classical Laws of Motion. It will be assumed that the ideas of space, distance and time can be taken for granted. The aim is to review the rules that describe how objects move; that is, how their position in space changes with time.

Displacement, Speed and Velocity

If you see an object at one place, and some time later see it somewhere else, the object has undergone a **displacement**. Displacement is measured in units of length or distance, and in scientific work the unit of length is the **meter (m)**. By timing the object as it moves from one place to another, you can work out how far it travels in a unit of time, such as one second. That gives its **average speed** in **meters per second (ms^{-1})**. If the speed is the same from one instant to the next, and if the object is moving in a straight line, the object is travelling at constant **velocity**. Velocity has the same units as speed (meters per second), but speed is only one aspect of velocity. The other aspect is direction. Left to its self, an object will maintain its velocity. It will keep moving with the same speed, in the same direction, forever. This might seem an absurd statement, because everyday observation shows that moving objects usually stop moving unless something is done to keep them in motion. The point is that the objects in everyday life are not left to themselves, but are always interacting with something else. Another way of looking at it is that a change in the velocity of an object requires an explanation, but a constant velocity does not.

Acceleration, Force, Newton's First Law

If the velocity of an object changes, either in speed or direction, the object has undergone **acceleration**. The units of acceleration are **meters per second per second (ms^{-2})**. In ordinary conversation, the term "acceleration" means an increase in speed. In physics, acceleration means any change in velocity. This can be an increase or decrease in the speed of an object, or a change in its direction of motion. Acceleration, being a change in velocity, requires an explanation. By definition, acceleration is the result of a **force.** In everyday language the word "force" is associated with pushing, shoving, compelling, making something happen. In physics, force is that which causes acceleration. All the discussion of motion so far can be summarized in a simple statement: "An object will remain at rest, or in uniform motion in a straight line, unless acted on by a force". This is **Galileo's Law of Inertia**, or **Newton's First Law of Motion**.

Mass, Newton's Second Law of Motion

It is obvious from everyday experience that a push or shove that produces a certain change in the motion of one object will not necessarily have the same effect on a different object. By definition, the ratio of the force on an object to the resulting acceleration is the **mass** of the object.

force ÷ acceleration = mass or
force = mass × acceleration.

This relationship is **Newton's Second Law of Motion**.

It is known from experiment that in the absence of air, objects near the surface of the earth fall towards the ground at the same speed. That means that they all experience the same acceleration, known as the **gravitational acceleration**, g meters per second per second. The force that acts on bodies near the earth's surface is therefore $m \times g$, where m is the mass (units not yet defined). The mass of an object can most easily be described by comparing the gravitational force acting on it to that acting on some reference object. The comparison is readily carried out using a **balance**.

For historical reasons, the reference object for mass is a piece of platinum-iridium alloy called the standard **kilogram**.

In scientific work, mass is measured in **kilograms (kg)**. Force is measured in terms of the acceleration that it produces in an object of unit mass. A force that produces an acceleration of one meter per second per second when acting on an object having a mass of 1 kilogram is called a **newton (N)**.

Mass and Weight

It is worth recalling that mass is a fundamental property of an object and does not vary from place to place. In contrast, the **weight** of an object is the force exerted by the gravitational interaction between the object and the earth (or the moon, if the object happens to be on the moon). Because the gravitational acceleration near the earth's surface is constant, it is convenient to describe weight in units of mass, when really we should use units of force. If the day ever comes when people regularly travel between the earth and the moon, the distinction between mass and weight will be common knowledge. Spring balances and electronic balances would need to be re-calibrated for use on the moon. A beam balance, of course, would be accurate in either location.

Pressure

Having introduced the concept of force, it is appropriate to mention **pressure**, which is simply the force applied per unit area of a surface. Pressure is extremely important in discussing the behavior of gases. It is measured in **pascals (Pa)**. A pressure of one pascal corresponds to a force of one newton per square meter. Living as we do at the bottom of a vast ocean of air, we are subjected to a relatively constant pressure of around 100 kilopascals. A pressure of 101.33 kilopascals is *defined* as one **atmosphere**, and is often used as a unit of pressure in thermodynamics. To avoid confusion, however, the pascal will be used as the unit of pressure in this discussion. It should be mentioned, too, that pressure gauges, even though they might be calibrated in pascals, often take their zero point as 1 atmosphere. Such gauges actually read the difference between the measured pressure and one atmosphere, the so-called gauge pressure. In thermodynamic calculations, pressure must be measured from a true zero point of zero newtons per square meter.

Newton's Third Law of Motion

Much of the discussion so far has really been giving definitions. Now it is time to introduce some results of experiments and observations. One important result is that acceleration always involves the interaction of at least two objects. There is a general rule that summarizes the results of many experiments and observations. "If two isolated objects interact in a manner that results in their acceleration, the accelerations of the two objects will be in opposite directions". The objects are described as "isolated" to indicate that the only force acting on them is the one involved in the interaction. If the two interacting objects are identical, the accelerations will not only be in opposite directions but of the same magnitude. If the two interacting objects are different, their accelerations will be inversely proportional to their masses. In other words, when two objects interact, the force acting on one object will be of the same magnitude, but in the opposite direction, as the force acting on the other. This is **Newton's Third Law of Motion**. The traditional statement of that Law is "For every action, there is an equal but opposite reaction".

Work

When a force acts on an object and accelerates it, the force is said to have done **work**. The amount of work is obtained by multiplying the force by the distance over which it acts. The units of work are **newton meters (Nm)**. A good example of work is the lifting of a weight. To raise a weight of mass m kilograms, you must apply a force of ($m \times g$) newtons to overcome the gravitational force of mg newtons acting on the object. If you lift the object h meters, you will have exerted a force of mg newtons over a distance of h meters. You will have done mgh newton meters of work.

When you lift a weight,
work done
= force × distance

= mass × acceleration × distance

= m kilograms × g meters per second per second × h meters

= mgh newton meters.

Energy

Energy is one of the most important concepts in physical science. Perhaps because of its central role in scientific explanation, it is also one of the most difficult concepts to define. Fortunately, the ultimate nature of energy is irrelevant for the purposes of this discussion. In mechanics, energy can be defined as the *capacity to do work,* and it is expressed in the same units as work; the amount of energy required to do one newton meter of work is the **joule (J)**. Conversely, the joule can be used as a unit of work, exactly equivalent to the newton meter.

This definition of energy as the capacity to do work is not entirely satisfactory, because in thermodynamics situations arise where energy is not available to do work. It could be argued that to speak of a "capacity to do work" that is not available to do work is not particularly meaningful. As will be seen, however, this idea of "unavailable energy" is of fundamental importance in thermodynamics and is easy to understand from the molecular perspective.

For the moment, it is necessary only to review energy in simple mechanical systems.

Potential Energy

Imagine a small heavy object, of mass m_1 kilograms, at rest on the floor, attached to a string threaded through a pulley fixed to the ceiling. You will also need to imagine that the pulley is absolutely perfect, offering no resistance whatsoever to the motion of the string. If you pull downwards on the other end of the string, the string will eventually become tight and will exert a force on the object. If you increase the force until it exceeds the weight of the object (m_1g newtons, where g is the gravitational acceleration), the object will be accelerated and will rise toward the ceiling. If you keep pulling the string until the object is a distance of h meters above the ground, you will have exerted a force of m_1g newtons over a distance of h meters and you will have done m_1gh newton meters (i.e., joules) of work in lifting the object.

Suppose now that you tie your end of the string to another object, and release it. The string will exert an upward force on the second object equal to the weight m_1g newtons of the first object. The earth's gravity will exert a downward force m_2g newtons on the second object. If m_2 is less than m_1, then the second object will be subjected to a net upward force of $(m_1g - m_2g)$ newtons. It will accelerate upwards. Meanwhile, the first object, experiencing a net downward force of $(m_1g - m_2g)$ newtons, will accelerate towards the floor. It will fall a distance of h meters before it crashes into the floor. The second object, having been accelerated to a certain upward velocity, will now experience only the downward force of gravity m_2g. If it has reached a sufficiently high upward velocity, it may hit the ceiling or reach the end of the string, but ultimately it will come to rest hanging h meters above the floor. The overall effect has been to lift a weight of mass m_2 kilograms to a distance h meters above the floor. The net work that has been done is m_2gh newton meters (joules). Notice that the work done in lifting the second object (m_2gh newton meters) is *less* than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1.

Suppose now that the mass m_2 of the second object is only a few milligrams less than that of the first object. The second object will experience a very small upward force, and it will accelerate upwards very slowly. At the same time the first object will accelerate downwards very slowly until it lands gently on the floor. The second object, having reached only a very small velocity, will very quickly come to rest at a height h meters above the floor. The net work that has been done is again m_2gh newton meters. Notice that the work done in lifting the second object (m_2gh newton meters) is again less than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1.

Carrying this line of argument to its limit, as the mass of the second object approaches that of the first, the net force acting on each object will approach zero. When the second object is only a tiny amount less massive than the first, the second object will take an extremely long time to rise to its ultimate height of h meters above the floor and will overshoot its rest position by only a minute distance. The work done will be m_2gh newton meters, which in this case is very close to the work m_1gh newton meters that was done when the first object was lifted h meters above the ground.

Ultimately, a weight of mass m kilograms hanging h meters above the floor has the capacity to do mgh newton meters of work in falling to the floor. It therefore possesses a **potential energy** of mgh joules. In this example, the object possesses potential energy because of its *position* in the gravitational field of the earth. Potential energy is also possessed by objects such as compressed springs, to which a force has been applied over a distance to distort the shape of the object.

Equilibrium

When the masses of two objects hanging from a string on either side of a pulley are exactly equal, the upward and downward forces acting on each object are exactly balanced. The forces are said to be in **equilibrium**. Once a system is in equilibrium, there are no net forces available to do work. *A system in equilibrium can do no work. The available energy is zero.*

When the masses of the two objects are unequal, the system will come to rest with one weight on the floor and the other hanging in the air. Again, the forces acting on each weight are exactly balanced, the available energy is zero, and the system can do no work. The system has come to equilibrium, but the equilibrium is clearly very different from that achieved when the two weights were equal. In that case, a tiny change in the mass of either weight would upset the equilibrium. This leads to the idea of a *reversible* process. A process is **reversible** if its direction can be reversed by an infinitesimally small change.

Equilibrium and Reversibility

The thought experiment with the hanging weights provides a useful mechanical example of a reversible process.

Imagine that the two weights are of exactly equal mass, and that they are hanging at equilibrium on either side of a perfect pulley that offers absolutely no resistance to motion. Now, imagine that the mass of one object be increased by a very small amount. Perhaps a very tiny speck of dust falls on it. The forces on the two weights are no longer equal. The heavier weight will start to accelerate downward, with an extremely small acceleration. Now suppose that the speck of dust is blown off the weight with a gentle puff of air that imparts no vertical acceleration to either weight. The net forces acting on each object will again be zero, and acceleration will cease. According to Newton's First Law, each body will keep moving upward or downward at the very tiny velocity that it had acquired after its very small acceleration. After an extremely long time, the system will come to equilibrium with one object on the floor and the other object h meters above the ground. At any instant, the addition of a tiny mass to the rising object would cause it to experience a net downward force so the direction of motion would reverse. Such a process, that can be set into reverse by an infinitesimally small change, is an example of a **reversible** process.

Notice that when this reversible process eventually comes to equilibrium, the system will have done the maximum possible amount of work.

In thermodynamics, a process carried out reversibly will always perform the maximum possible amount of work, but will take an infinitely long time to do so. All natural processes take place in a finite amount of time, and are thus irreversible. None the less, the concept of a reversible process is important in thermodynamics because of the link between reversibility and maximum work. This will be discussed further in the section dealing with the Second Law of Thermodynamics.

Kinetic Energy

Kinetic energy is the energy possessed by a body because of its *state of motion*.

A thought experiment can show how a moving body can do work in being brought to rest. Imagine a body of mass m_1 kilograms moving with a uniform velocity of v meters per second over the surface of an ideal, friction-free table. At the edge of the table is a perfect pulley, over which passes a string attached to a small object of mass m_2 kilograms sitting on the floor. The moving object is travelling away from the pulley. At a certain point the string is suddenly attached to the moving object. It pulls tight, and lifts the second object off the ground. The string exerts a force on the moving object, causing it to accelerate in the opposite direction to its direction of motion. Eventually the moving object comes momentarily to a stop after having moved through a distance of h meters. The small object has been raised a height of h meters above the ground, so the moving object has done m_2gh newton meters of work.

In bringing the moving object to a halt, the force m_2g newtons has been applied over a distance of h meters. This force was applied to an object of mass m_1 kilograms and accelerated it from an initial velocity of v meters per second to a final velocity of 0 meters per second.

The distance h over which the force acted is given by the average velocity v_{av} multiplied by the time t:

$$h = v_{av}\, t$$

The average velocity v_{av} is half the sum of the initial velocity (v) and the final velocity (0 meters per second), so

$$\begin{aligned} h &= \tfrac{1}{2}(v+0)t \\ &= \tfrac{1}{2}vt \end{aligned}$$

The final velocity (0 meters per second) is given by the initial velocity (v) plus the acceleration $-a$ multiplied by the time t. Notice that the acceleration is given a negative sign, because it is acting in the opposite direction to the initial velocity v.

$$0 = v - a\,t,$$

so $t = v \div a$

and
$$\begin{aligned} h &= \tfrac{1}{2}\, v\, t \\ &= \tfrac{1}{2}\, v\, (v \div a) \\ &= \tfrac{1}{2}\, v^2 \div a \end{aligned}$$

But

$$\begin{aligned} \text{force} &= \text{mass} \times \text{acceleration} \\ &= m_1 a \end{aligned}$$

and
$$\begin{aligned} \text{work} &= \text{force} \times \text{distance} \\ &= m_1 a\, h \\ &= m_1 a\, (\tfrac{1}{2}\, v^2 \div a) \\ &= \tfrac{1}{2}\, m_1 v^2 \text{ newton meters} \end{aligned}$$

The work done by a body of mass m_1 kg being to rest from an initial velocity of v meters per second is $\frac{1}{2}\, m_1 v^2$ newton meters. A body of mass m kg moving with a velocity v meters per second has a kinetic energy of $\frac{1}{2}\, mv^2$ joules.

Conservation of Energy

In the thought experiment just described, the moving body on the table top was brought momentarily to rest, while the small body suspended from the pulley was raised a distance h meters above the floor. The potential energy of the suspended body became m_2gh joules, while the kinetic energy of the body on the table became 0 joules. Obviously this situation can only last for an instant. The stationary body, under the influence of the force m_2g in the string, will begin to accelerate in the opposite direction as the suspended object falls towards the floor. The falling object will end up on the floor, having fallen through a distance h meters, and its potential energy will again be zero. By reversing the arguments in the previous section, it is easy to show that the object on the table will end up with a velocity of v meters per second, in the opposite direction to that of its initial velocity. Its kinetic energy is again $\frac{1}{2}\, m_1 v^2$ joules. Energy has been converted from kinetic energy to potential energy and back again.

In some mechanical devices, conversion from potential to kinetic energy and back again can (at least in theory) proceed indefinitely. An example is the pendulum. At the top of its swing, the pendulum is momentarily at rest, so its kinetic energy is zero and its potential energy is at a maximum. At the bottom of its swing, the pendulum is moving at its maximum velocity, its kinetic energy is at a maximum and its potential energy is at a minimum. As the pendulum swings to the top at the other side, the kinetic energy decreases to zero and the potential energy rises back to the maximum value. In principle, if there were no losses of energy, this process could repeat indefinitely. Such a system is called a **conservative system**, because the total mechanical energy is conserved. A real pendulum does not keep swinging indefinitely but eventually comes to a halt. This indicates that the transformation of potential energy to kinetic energy and back again is not 100% efficient. What happens to the lost energy? Part of it goes to stir up the air through which the pendulum moves, and some is used in moving the parts of the suspension device past each other (fibers in a string, for example, move against each other as the pendulum swings). Ultimately, this energy is converted to **heat**. The air and the rope are a little bit warmer at the end of the process than they were at the beginning.

In the last century the British scientist James P. Joule carried out careful experiments that showed that mechanical work could be converted entirely into heat. Before then, heat and work were measured in different units. Now, (at least in scientific work), the same units are used for both.

The conversion of mechanical work into heat is important in pyrotechnics. Devices such as the friction match, the party popper, the pull-wire igniter and the percussion cap all rely on the conversion of mechanical work into heat that subsequently ignites a pyrotechnic composition. Unintended initiation of pyrotechnic mixtures during manufacturing and processing can result from the mechanical work associated with friction, shock or impact being transformed into heat. The heat produced in such processes is highly localized and can be very effective in initiating certain sensitive mixtures.

It is a fundamental postulate of thermodynamics that when heat is taken into account, the total amount of energy in the universe is constant. This is the **Law of Conservation of Energy**.

Heat as a Form of Energy

As outlined in the preceding sections, energy is transferred between mechanical systems as work. The Law of Conservation of Energy is based on the recognition that energy can also be transferred as heat. There are several other processes that can transfer energy. Electric currents and various types of radiation are two examples. In this discussion of chemical thermodynamics, however, it will be sufficient to consider only heat and work.

Classical chemical thermodynamics made no reference to the molecular structure of matter. It is, however, very useful to interpret thermodynamic properties by relating them to the behavior of molecules. Heat can be thought of as the energy associated with the random motion of molecules. This makes the connection between mechanical work and heat much easier to understand. In Joule's experiments, water stirred by mechanically driven paddles became hotter. From a molecular perspective one can imagine the uniform motion of the molecules in the paddles moving nearby water molecules, initially in a rather uniform way. The motion of the water molecules would quickly become randomized as one molecule collided with another, so ultimately the effect of the stirring paddles would be to increase the random motion of the molecules—in other words, to heat the water. Each molecule has a certain mass m, and at any instant of time has a certain velocity v. At that instant the molecule has a kinetic energy $\frac{1}{2} mv^2$. The average kinetic energy of the molecules is directly related to the t**emperature** of the material.

As well as energy being transferred between molecules by direct mechanical impact, it can also be transferred by **electromagnetic radiation**. A proper discussion of this would take up considerable space. It is sufficient to note that this radiation is familiar to us as **light** and **radiant heat** (or **infra-red** radiation), the only fundamental difference between these being the energy with which the radiation is associated. The energy of electromagnetic radiation can be thought of as being packaged into little particles called **photons**. The energy of a photon is related to the wave properties of the radiation through **Planck's relationship**:

$$E = \mathrm{h}\nu = \mathrm{hc} \div \lambda,$$

where ν is the **frequency** in cycles per second (units**: inverse seconds**, $\mathbf{s^{-1}}$, often called **Hertz, Hz**), c the velocity of light (2.9979×10^8 meter per second in vacuum) and λ the wavelength in meters. The constant of proportionality h is **Planck's Constant** (6.6262×10^{-34} joule seconds). Radiation emitted by a molecule travels through space and can be absorbed by another, resulting in a transfer of energy from one molecule to another without any direct contact between them.

Temperature

The idea of temperature is familiar from everyday life, as an indicator of 'hotness' or 'coldness'. Historically, people have chosen some property of matter that varies with 'hotness' or 'coldness' and used it as the basis of a system for measuring temperature. Such a property is the volume of a fixed mass of gas or liquid. A fixed mass of gas or liquid, arranged in such a way that changes in volume can be readily measured, can be used as a temperature measuring instrument or **thermometer**. The thermometer is calibrated by placing it in environments where the temperature is reproducible. One such environment is a mixture of pure water and ice. The temperature of this mixture has been assigned the value of 0 degrees Celsius (ºC). The temperature of pure water boiling at atmospheric pressure has been assigned the value of 100 degrees Celsius. The liquid or gas in the thermometer has a certain volume in the melting ice, and another, larger volume in the boiling water. This range of volumes is divided into 100 equal parts, and a change of one of these units of volume is defined to correspond to a change in temperature of 1 degree Celsius. It is found experimentally for gases that one degree Celsius corresponds to a change of 1/273 of the volume at 0 degrees Celsius. This suggests that if the temperature were reduced to –273 degrees Celsius, the volume of the gas would shrink to zero. While this is only a "thought experiment", because all real gases turn into liquids before the temperature reaches –273 degrees Celsius, it suggests the very important idea of an absolute zero of temperature at –273 degrees Celsius. More accurate estimates give the value as –273.15 degrees Celsius. The temperature scale used in scientific work, the kelvin (or absolute) scale, uses the same degrees as the Celsius scale but starts at absolute zero. The kelvin temperature is obtained by adding 273.15 to the Celsius temperature. The unit of temperature on the absolute scale is the **kelvin (K)**.

The Zeroth Law of Thermodynamics

Temperature could be defined as the property that is measured by thermometers. This is expressed in a formal way as follows:

Two bodies that are in thermal equilibrium with a third body are in thermal equilibrium with each other. They share a common property called *"temperature"*.

This statement is the **Zeroth Law of Thermodynamics**.

The 'third body' referred to in the Zeroth Law is the thermometer. Being in thermal equilibrium means that the transfer of heat from the body to the thermometer is exactly balanced by the transfer of heat from the thermometer to the body. This situation is easily recognized, because the reading of the thermometer is then constant.

Molecular Interpretation of Temperature

As will be shown later, temperature is a measure of the **average kinetic energy** associated with **random motion of the molecules**.

Heat Capacity

It is found experimentally that different amounts of energy are required to change the temperature of the same mass of different substances by the same amount. The **heat capacity** of a substance is the quantity of energy required to raise the temperature of a specified amount of the substance by 1 kelvin. In thermodynamics, particularly when dealing with gases, it is necessary to distinguish between C_v, the heat capacity at constant volume, and C_p, the heat capacity at constant pressure.

Amount of a Substance

In chemical thermodynamics the **amount of a substance** is specified in **moles (mol)**. One mole of any substance is the molecular weight of that substance expressed in grams. The molecular weight is simply the sum of the atomic weights of all the atoms in one molecule of the substance. The atomic weight is the ratio of the mass of that atom to the mass of an atom of the most common type of carbon atom, which has been assigned a mass of exactly 12 **atomic mass units** or **daltons**. One mole of a substance contains 6.022×10^{23} molecules. This enormous number

602,200,000,000,000,000,000,000

molecules per mole is called **Avogadro's Number**.

Thermodynamic Systems

Like all sciences, thermodynamics attempts to gain some understanding of the incredibly complex world by focusing attention on small, simple aspects of it. In any thermodynamics experiment, whether done in the laboratory or in the imagination, the objects that are being studied are very carefully defined and are called the **system.** Everything else in the world is called the **surroundings**. The system may interact with the surroundings, or it may be kept separate from the surroundings so that there is no interchange of matter or energy between it and the surroundings. The system is then said to be **isolated**. A system that cannot exchange matter with its surroundings, but may exchange energy, is called a **closed** system. A system that can exchange both matter and energy with its surroundings is called an **open** system. The combination of system and surroundings is called the **universe**.

Thermodynamic States and State Functions

Having decided what the system of interest is, the next step is to describe it as completely, yet as concisely, as possible. The aim is that anyone given the description should be able to reproduce the system in all its relevant aspects. Thermodynamics does not concern itself with the molecular structure of matter, so the position and energy of all the individual molecules in the system is not relevant. That is just as well. On the molecular level, the world is in a state of constant change. If the position and energy of all the molecules in the system (the **microscopic state** of the system) could ever be described, the description would be correct only for an instant. It could be reproduced only by pure chance, and then only for an instant.

Thermodynamics deals only with those aspects of a system that can be measured by large-scale devices such as thermometers, measuring rods and pressure gauges. Such properties are called **macroscopic** properties, and it is those properties that are used to describe thermodynamic systems. A complete description of the macroscopic properties of a system is called the **thermodynamic state** of the system. The thermodynamic state can be described by a relatively small number of properties, called **state functions**. State functions are *chosen* so that their values depend only on the thermodynamic state of the system, and not on the path that was taken to reach that state. There are two sorts of state functions: **intensive functions**, such as temperature and pressure, do not depend on the amount of matter in the system. **Extensive functions,** such as mass and volume, depend on the amount of matter (number of moles) present. It is obvious that mass must be an extensive function. One can, however, imagine a system of fixed volume, into which any quantity of gas might be compressed. In such a system volume would not be an extensive function, but a constant. For volume to be an extensive function, the *volume of the system must be variable*. Such systems are often modeled as a cylinder closed with a perfectly sealed, massless piston that offers no resistance to motion.

State functions are always indicated by capital letters, but not all quantities indicated by capital letters are state functions. A quantity indicated by a lower-case letter will not be a state function, and its value may depend on the path that was taken by the system to arrive at its present state.

The algebraic relationship between the state functions is called the **equation of state** of the system. An example is the **equation of state for a perfect (or ideal) gas**. A perfect gas is simply one in which the physical volume of the molecules is negligible in comparison to the volume of the gas, and in which forces between the molecules are negligible. The system to which the equation of state for a perfect gas applies is a fixed amount of perfect gas in a container of variable volume, such as a cylinder sealed with a perfect, frictionless, massless piston. The container is equipped with a thermometer and a pressure gauge. The volume can be calculated from the position of the piston. The equation of state is

$$PV = n\mathrm{R}T$$

P is the pressure in pascals, V is the volume in cubic meters, n is the number of moles of the gas, R is the **universal gas constant** (8.3143 joules per mole per kelvin) and T is the temperature in kelvins.

Each side of this equation can be expressed in units of energy:

The left-hand side is the energy associated with the *mechanical* properties of the system:

$$\begin{aligned} PV &= \text{newtons per meter}^2 \times \text{meter}^3 \\ &= \text{newton meters} = \text{joules} \end{aligned}$$

The right hand side is the energy associated with the *thermal* properties:

$$\begin{aligned} n\mathrm{R}T &= \text{number of moles} \times \text{joules per mole per kelvin} \times \text{kelvins} \\ &= \text{joules} \end{aligned}$$

The equation of state is simply the Law of Conservation of Energy applied to a perfect gas.

The equation indicates that for a fixed amount (n moles) of gas, there are only *two* properties that need to be specified. For example, if the pressure and the temperature are specified, the volume of the gas is fixed. This is a consequence of the Law of Conservation of Energy, as expressed in the equation of state.

The equation of state can be re-arranged to indicate how the volume varies with the other parameters.

$V = n\mathrm{R}T \div P$ indicates that the volume (V) of a fixed amount (n moles) of gas at a constant temperature T is inversely proportional to the pressure P. This relationship was established experimentally in the 17th century and is known as **Boyle's Law**. $V = n\mathrm{R}T \div P$ also shows that the volume of a fixed amount (n moles) of gas at a fixed pressure P is proportional to the absolute temperature T. This relationship, also first established experimentally, is known as **Charles' Law**. Finally, $V = n\mathrm{R}T \div P$ shows that a fixed volume of any perfect gas under the same conditions of temperature and pressure contains the same number of moles, and hence the same number of molecules. This was first proposed by Avogadro, and is called **Avogadro's hypothesis**.

A great deal of information about the behavior of gases is thus summarized in the simple equation $PV = n\mathrm{R}T$.

Changes in State Functions

If a system undergoes a change from one thermodynamic state to another, the new state will, by definition, be described by a new set of values of the state functions. The values of the state function after the change will depend only on the properties of the new state. They will not be influenced in any way by any properties that the system might have had while it was in the process of undergoing the change. Many thermodynamic calculations deal with changes in state functions. Such changes are always calculated by subtracting the value of the initial state function from that of the final one. For example, for a temperature change from a starting temperature T_1 to a final temperature T_2 the change of temperature ΔT is given by

$$\Delta T = T_2 - T_1.$$

The symbol Δ that indicates "change of" is the capital form of the Greek letter delta. The symbol "ΔT" is read "delta tee".

State Functions and Equilibrium

A system is in equilibrium when the values of the state functions are constant in all parts of the system. In other words, for a system at equilibrium

$$\Delta X = 0$$

where X is *any* state function. This is one definition of thermodynamic equilibrium.

Internal Energy and the First Law of Thermodynamics

So far, three state functions have been introduced. These are the temperature, T, the volume, V, and the pressure, P. All of these can be measured easily. There are other state functions that are not measured directly. Such a state function is the **internal energy** of a system, denoted by the symbol U. This is the sum total of the energy, in whatever form, stored in a system. The total energy will obviously vary according to the amount of substance in the system, so internal energy is an extensive function. The absolute value of the internal energy of a system is not of concern to thermodynamics, but changes in internal energy are of central importance. Suppose a system undergoes a change in internal energy from an initial (unknown) value of U_1 joules to a final value (unknown) value of U_2 joules. Then the change in internal energy, ΔU, is

$$\Delta U = U_2 - U_1$$

This might not seem very useful, since U_2 and U_1 are both unknown. The equation is nothing more than another statement of the law of conservation of energy. The change in internal energy, ΔU, represents the net energy that has come into the system from the surroundings or that the system has lost to the surroundings. For the purposes of this discussion, only two ways of a system exchanging energy with the surroundings are relevant. Energy can be transferred *mechanically*, as **work**, denoted by w. For example, if a gas expands against an external pressure, the gas does work. Energy can also be transferred as **heat**, denoted by q. The change in internal energy can now be written:

$$\Delta U = q - w.$$

This states that the change in internal energy, ΔU, of a system is given by the heat, q, *absorbed by the system* minus the work, w, *done by the system* on its surroundings.

This statement, which is again a statement of the Law of Conservation of Energy, is the **First Law of Thermodynamics**.

Heat or work going *into* the system from the surroundings increases the internal energy of the system, and heat or work leaving the system *decreases* the internal energy.

The Enthalpy

The four state functions introduced so far are the intensive functions temperature, T, and pressure, P, and the extensive functions volume, V, and internal energy U.

It is convenient to define another state function, called the **enthalpy**, H. This is given by

$$H = U + PV$$

Notice that H has units of energy. Since U, P and V are all state functions, H is necessarily one as well. Notice, too, that U and V are extensive functions, and consequently H is also an extensive function. Since the purpose of state functions is to give the most concise description of a system, it might seem counterproductive to introduce another function that combines three others. Why use five when four would be enough?

The reason will emerge from the following discussion. The change in enthalpy when a system with an original enthalpy H_1 changes to a final enthalpy H_2 is given by

$$\begin{aligned}\Delta H &= H_2 - H_1\\ &= U_2 + P_2V_2 - (U_1 + P_1V_1)\\ &= U_2 - U_1 + P_2V_2 - P_1V_1\\ &= \Delta U + \Delta(PV)\\ &= q - w + \Delta(PV)\end{aligned}$$

Chemical reactions are often carried out in systems open to the atmosphere, that is, under conditions of constant pressure. Then,

$$\Delta(PV) = P\Delta V, \text{ and}$$

$$\Delta H = q - w + P\Delta V$$

At constant pressure the work w done by the system on the surroundings is simply the pressure P multiplied by the change in volume, ΔV.

$$w = P\Delta V.$$

Therefore, at constant pressure,

$$\begin{aligned}\Delta H &= q - w + P\Delta V\\ &= q - P\Delta V + P\Delta V\\ &= q\end{aligned}$$

The change in enthalpy is thus a measure of the heat transferred between the system and the surroundings at conditions of constant pressure. This is what makes the enthalpy such a useful function in chemical thermodynamics. If the enthalpy change is positive, the system will absorb heat from the surroundings. An example is ammonium nitrate dissolving in water. Such a process is **endothermic** (heat taken in). If the enthalpy change is negative, the system will release heat into the surroundings. Such a process is **exothermic** (heat given out). An example is sodium hydroxide dissolving in water.

Thermochemistry

To find the heat emitted or absorbed in a chemical reaction at constant pressure, all that is required is the enthalpy change associated with that reaction. Enthalpy changes are very easily calculated from tables of **the standard enthalpy of formation,** ΔH_f^o, of various substances (see Table 1 at end of article). The superscript (º) indicates that the change in state function is calculated for reactants and products at some standard set of conditions, usually 298.15 K (25 ºC) and 1 atmosphere pressure.

Recall that enthalpy is an extensive property, that is, it is proportional to the amount of substance present. Recall, too, that only *changes* in enthalpy are relevant. For convenience, the standard enthalpy of formation of the most stable form of any chemical element at 298.15 K and one atmosphere pressure (101.33 kilopascals) is given the value of 0 joules per mole. The standard enthalpy of formation of any compound that can be formed by direct reaction of the elements is then very easily obtained, at least in principle. Experimental details may well be quite difficult. All that is required is to measure the heat emitted or absorbed when a known amount of the compound is formed from the elements at 1 atmosphere pressure and 298.15 K. Since enthalpy is a state function, the intermediate values of temperature and pressure during the reaction are irrelevant. As long as the reactants and products end up at 1 atmosphere and 298.15 K, the heat emitted or absorbed will correspond to the change in enthalpy.

Hess's Law of Heat Summation

The fact that the enthalpy change in a chemical reaction does not depend on the path was first stated by Germain H. Hess in 1840, and is often referred to as **Hess's Law**. Its usefulness can be illustrated by the classic example of how it can be used to calculate a quantity that would be impossible to measure experimentally: the standard enthalpy of formation of carbon monoxide.

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO \qquad \Delta H^o = x \text{ kJ/mol}$$

The **standard enthalpy of formation** of carbon dioxide is easily calculated from the **molar heat of combustion**, the heat released when one mole of carbon is burned in an excess of oxygen:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^o = -393.5 \text{ kJ/mol}$$

The same approach is not possible for carbon monoxide, because it is impossible to burn carbon in oxygen to produce only carbon monoxide.

Carbon monoxide can, however, be burned in excess oxygen to produce carbon dioxide:

$$CO + \tfrac{1}{2}\,O_2 \rightarrow CO_2 \qquad \Delta H^o = -283.0 \text{ kJ/mol}$$

The combustion of carbon to carbon dioxide can now be *imagined* to take place in two steps:

Step 1:

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO \qquad \Delta H^o = x \text{ kJ/mol}$$

Step 2:

$$CO + \tfrac{1}{2}\,O_2 \rightarrow CO_2 \qquad \Delta H^o = -283.0 \text{ kJ/mol}$$

By addition:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^o = (x - 283.0) \text{ kJ/mol}$$

For this reaction $\Delta H^o = -393.5$ kJ/mol, so

$$\begin{aligned}(x - 283.0) \text{ kJ/mol} &= -393.5 \text{ kJ/mol}\\ x &= -393.5 \text{ kJ/mol} + 283.0 \text{ kJ/mol}\\ &= -110.5 \text{ kJ/mol}\end{aligned}$$

Thus, for the reaction to form carbon monoxide

$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H^o = -110.5$ kJ/mol.

Application to Pyrotechnics

As an example, consider the thermochemistry involved in a *flash powder* consisting of a mixture of powdered aluminium and potassium perchlorate.

Potassium perchlorate decomposes on heating to form potassium chloride and oxygen:

$KClO_4 \rightarrow KCl + 2\ O_2$

This reaction can be *imagined* to take part in two stages:

$KClO_4 \rightarrow K + \frac{1}{2} Cl_2 + 2\ O_2$

$K + \frac{1}{2} Cl_2 \rightarrow KCl$

Of course the reaction certainly does not take place by these two steps. The enthalpy of the reaction must, however, equal the sum of the enthalpy changes of these two reactions. The enthalpy changes of these reactions can be obtained from tables of thermochemical data, such as Table 1.

The first reaction is the decomposition of 1 mole of potassium perchlorate into its elements. The enthalpy change is, therefore, *minus* the standard enthalpy of formation of potassium perchlorate, –(–430 kJ/mol) = 430 kJ/mol.

The second reaction is the formation of 1 mole of potassium chloride from its elements, and the enthalpy change is the standard enthalpy of formation of potassium chloride, –437 kJ/mol.

The total enthalpy change for the decomposition of 1 mole of potassium perchlorate is the sum of these two enthalpy changes:

$KClO_4 \rightarrow K + \frac{1}{2} Cl_2 + 2\ O_2 \qquad \Delta H^o = 430$ kJ/mol

$K + \frac{1}{2} Cl_2 \rightarrow KCl \qquad \Delta H^o = -437$ kJ/mol

$KClO_4 \rightarrow KCl + 2\ O_2 \qquad \Delta H^o = -7$ kJ/mol

The decomposition of 1mole of potassium perchlorate releases 7 kJ of heat.

Now consider the combustion of aluminium in oxygen to form 1 mole of aluminium oxide:

$2Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad \Delta H^o = -1676$ kJ/mol.

The enthalpy change for this reaction is, of course, the standard enthalpy of formation of aluminium oxide.

The reaction of aluminium with potassium perchlorate in flash powder is

$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3$

This can be imagined as taking place in two steps:

Step 1: decomposition of 3 moles of potassium perchlorate:

$3 \times (KClO_4 \rightarrow KCl + 2\ O_2 \quad \Delta H^o = -7$ kJ/mol)

i.e.,

$3\ KClO_4 \rightarrow 3\ KCl + 6\ O_2 \qquad \Delta H^o = -21$ kJ

and

Step 2: Combustion of aluminium in oxygen to form 4 moles of aluminium oxide:

$4 \times (2\ Al + 3/2\ O_2 \rightarrow Al_2O_3 \qquad \Delta H^o = -1676$ kJ/mol)

i.e.,

$8\ Al + 6\ O_2 \rightarrow 4\ Al_2O_3 \qquad \Delta H^o = -6704$ kJ

The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:

$3\ KClO_4 \rightarrow 3\ KCl + 6\ O_2 \qquad \Delta H^o = -21$kJ

$8\ Al + 6\ O_2 \rightarrow 4\ Al_2O_3 \qquad \Delta H^o = -6704$ kJ

$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3 \qquad \Delta H^o = -6725$ kJ

The reaction of 3 moles of potassium perchlorate with 8 moles of aluminium releases 6725 kilojoules of heat.

It is useful to convert the units of measure of the amounts of the chemicals from moles to grams, because pyrotechnic mixtures are not usually specified in moles.

One mole of aluminium weighs 26.98 grams, and one mole of potassium perchlorate weighs 138.55 grams. These values are obtained from the formula weights of these materials, listed in Table 1.

Three moles of potassium perchlorate weigh

3 × 138.55 grams = 415.65 grams.

Eight moles of aluminium weigh

8 × 26.98 grams = 215.84 grams.

Three moles of potassium perchlorate plus eight moles of aluminium weigh

(415.65 + 215.84) grams = 631.49 grams.

This quantity of mixture releases 6725 kilojoules, so the heat released per gram is:

6725 kJ ÷ 631.49 g = 10.64 kJ/g

The percentage composition of this mixture is:

Potassium perchlorate:

415.65 grams ÷ 631.49 grams × 100% = 65.8%

Aluminium:

215.84 grams ÷ 631.49 grams × 100% = 34.2%

Lancaster[1] quotes two mixtures for European style flash composition. One of these (66% potassium perchlorate and 34% aluminium) is almost identical to the mixture just discussed.

Such a mixture, in which the ratio of the components is exactly as required for the balanced chemical reaction, is called a **stoichiometric** mixture.

Lancaster[1] also lists some flash mixtures that contain sulfur. One of the mixtures he quotes is 67% potassium perchlorate, 17% aluminium and 16% sulfur. It is instructive to calculate the heat output of this composition.

First, the percentage by weight is converted to moles per 100 grams, by dividing the percentage of each component by its formula weight:

Potassium perchlorate:

67.00 ÷ 138.55 = 0.4836 moles per 100 grams

Aluminium:
17.00 ÷ 26.98 = 0.6301 moles per 100 grams

Sulfur:
16.00 ÷ 32.06 = 0.4991 moles per 100 grams.

From the previous discussion, every 8 moles of aluminium require 3 moles of potassium perchlorate. To find the amount of potassium perchlorate needed to burn the aluminium, divide the number of moles of aluminium by 8 and multiply by 3:

Amount of potassium perchlorate required to burn the aluminium:

0.6301 ÷ 8 × 3 = 0.2363 moles.

Amount left to burn the sulfur:

0.4836 – 0.2363 = 0.2473 moles.

From the reaction

$KClO_4 \rightarrow KCl + 2\ O_2$,

each mole of potassium perchlorate releases 2 moles of oxygen. The 0.2473 moles of potassium perchlorate left after burning the aluminium therefore release 2 × 0.2473 = 0.4946 moles of oxygen. This is available to burn the 0.499 moles of sulfur. The ratio of oxygen to sulfur is 0.4946 ÷ 0.4991 = 0.991, very close to 1. The chemical equation for the burning of sulfur in oxygen is

$S + O_2 \rightarrow SO_2$,

with a ratio of 1 mole of oxygen 1 mole of sulfur. This composition is therefore very close indeed to having exactly enough potassium perchlorate to burn the aluminium and sulfur to their oxides. It is another example of a stoichiometric mixture.

The heat released when aluminium burns with a stoichiometric quantity of potassium perchlorate has already been shown to be 10.69 kJ/g. It now remains to calculate the heat released when sulfur burns with a stoichiometric quantity of potassium perchlorate. The reaction for the decomposition of potassium perchlorate has already been discussed:

$KClO_4 \rightarrow KCl + 2\ O_2 \qquad \Delta H^o = -7$ kJ/mol

The burning of sulfur to sulfur dioxide

$S + O_2 \rightarrow SO_2$

is the formation of one mole of sulfur dioxide from its elements, so the enthalpy change is the standard enthalpy of formation of sulfur dioxide, which from Table 1 is –297 kJ/mol.

The total reaction can be thought of as proceeding as follows:

Step 1: Decomposition of half a mole of potassium perchlorate to release a mole of oxygen:

$\frac{1}{2} \times (\text{KClO}_4 \rightarrow \text{KCl} + 2\ \text{O}_2 \quad \Delta H^o = -7\ \text{kJ/mol})$

i.e.,

$\frac{1}{2}\ \text{KClO}_4 \rightarrow \frac{1}{2}\ \text{KCl} + \text{O}_2 \qquad \Delta H^o = -3.5\ \text{kJ}$

Step 2: Combustion of one mole of sulfur in one mole of oxygen to form one mole of sulfur dioxide:

$\text{S} + \text{O}_2 \rightarrow \text{SO}_2 \qquad \Delta H^o = -297\ \text{kJ}$

The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:

$\frac{1}{2}\ \text{KClO}_4 \rightarrow \frac{1}{2}\ \text{KCl} + \text{O}_2 \qquad \Delta H^o = -3.5\ \text{kJ}$

$\text{S} + \text{O}_2 \rightarrow \text{SO}_2 \qquad \Delta H^o = -297\ \text{kJ}$

$\frac{1}{2}\ \text{KClO}_4 + \text{S} \rightarrow \frac{1}{2}\ \text{KCl} + \text{SO}_2 \qquad \Delta H^o = -300\ \text{kJ}$

The next step is to convert the units from moles to grams. Half a mole of potassium perchlorate weighs

$\frac{1}{2} \times 138.55$ grams = 69.275 grams.

One mole of sulfur weighs 32.06 grams. Half a mole of potassium perchlorate plus a mole of sulfur weighs

(69.275 + 32.06) grams = 101.34 grams.

This quantity of mixture releases 300.5 kilojoules, so the heat released per gram is:

$300.5 \div 101.34 = 2.965$ kJ/g.

One hundred grams of the original mixture can be thought of as being made up of two stoichiometric mixtures:

Mixture A: A mixture of 17.00 grams (0.6301 moles) of aluminium with the stoichiometric amount of potassium perchlorate (0.2363 moles or 32.74 grams). Total amount of mixture A:

$17.00 + 32.74 = 49.74$ grams $\div$ 100 grams.

Mixture B: A mixture of 16.00 grams (0.499 moles) of sulfur with the stoichiometric amount of potassium perchlorate (0.2495 moles or 34.57 grams). Total amount of mixture B:

$16.00 + 34.57 = 50.57$ grams $\div$ 100 grams.

Total (Mixture A + Mixture B) = (49.74 + 50.57) grams = 100.31 grams per 100 grams. The mixture is clearly very close to a 50:50 mix of mixtures A and B. The heat output per gram is therefore:

$\frac{1}{2} \times$ heat output per gram Mixture A +
$\frac{1}{2} \times$ heat output per gram Mixture B =
$\frac{1}{2} \times (10.69\ \text{kJ/g}) + \frac{1}{2} \times (2.965\ \text{kJ/g}) =$
$(5.345 + 1.483)\ \text{kJ/g} = 6.828\ \text{kJ/g}$

The heat output per gram of the flash mix containing sulfur is 6.828 kJ/g, while that of the mix containing no sulfur is 10.69 kJ/g.

This shows that the heat output is only one aspect of a pyrotechnic mixture. Another very important factor is the speed or rate of the reaction. While adding sulfur to the flash mix reduces the heat output, it might (and the evidence is that it does) increase the rate of the reaction. A discussion of how this might be so is outside the scope of this article, as it relates to chemical kinetics, not thermodynamics.

Another relevant difference between the two mixtures is that the one with no sulfur generates products that are solids at room temperature. The conversion of these to liquids and/or gases at the temperature of the reaction absorbs large amounts of heat. The only way in which the reaction can do mechanical work is by the heat of the reaction causing the expansion of a gas. This gas can include vaporized products (if there is sufficient heat to vaporize them) and the surrounding air that gets raised to high temperatures by the heat released in the reaction.

Suppose 1 gram of each mixture is ignited in a closed container of fixed volume V. An estimate of the maximum pressure reached in the container can be obtained from the equation $PV = n\text{R}T$. This gives the pressure as

$P = n\text{R}T \div V$

For a fixed volume (V) this equation predicts that the pressure will be proportional to the temperature (T) and to the number of moles of gas (n).

For the mixture of aluminium and potassium perchlorate, the chemical equation

$3\ \text{KClO}_4 + 8\ \text{Al} \rightarrow 3\ \text{KCl} + 4\ \text{Al}_2\text{O}_3$

shows that 3 moles of potassium perchlorate react with 8 moles of aluminium to produce 3 moles of potassium chloride plus 4 moles of aluminium oxide. Potassium chloride boils at 1437 K at atmospheric pressure, while aluminium oxide does not boil until 2950 K.[3] The procedure for calculating the maximum temperature in a reaction will be explained in a later section. For the moment, it can be assumed that the temperature of the reaction is sufficient to vaporize the potassium chloride but not the aluminium oxide. From the equation, 3 moles of potassium perchlorate react with 8 moles of aluminium to produce 3 moles of potassium chloride vapor. As shown previously, 3 moles of potassium perchlorate and 8 moles of aluminium correspond to 631.49 grams of mixture. The amount of potassium chloride vapor produced by 1 gram of mixture is therefore 3 ÷ 631.49 moles per gram = 4.75×10^{-3} moles per gram.

Now, for the reaction of sulfur and potassium perchlorate

$$\tfrac{1}{2}\,KClO_4 + S \rightarrow \tfrac{1}{2}\,KCl + SO_2$$

it has been shown previously that ½ mole potassium perchlorate and 1 mole of sulfur corresponds to 101.34 grams of mixture. The amount of potassium chloride produced is therefore
½ ÷ 101.34 moles per gram = 4.93×10^{-3} moles per gram. The amount of sulfur dioxide produced is 1 ÷ 101.34 = 9.86×10^{-3} moles per gram.

As shown previously, the aluminium/sulfur/potassium perchlorate flash mixture was close to 1 part by weight of the aluminium/potassium perchlorate mixture and 1 part by weight of the sulfur/potassium perchlorate mixture.

The aluminium/potassium perchlorate mixture produces 4.75×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.445×10^{-3} moles of potassium chloride to the reaction products.

The sulfur/potassium perchlorate mixture produces 4.93×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.465×10^{-3} moles of potassium chloride to the reaction products. The total amount of potassium chloride produced per gram of mixture is therefore (2.445 + 2.465) $\times 10^{-3}$ moles = 4.91×10^{-3} moles. This is very similar to the amount of potassium chloride (4.75×10^{-3} moles) produced by 1 gram of the aluminium/potassium perchlorate mix. However, the sulfur/potassium perchlorate mix also generates 9.86×10^{-3} moles of sulfur dioxide per gram of mixture. Half a gram of mixture will therefore contribute 4.93×10^{-3} moles of sulfur dioxide to the reaction products. The total number of moles of gas at the temperature of reaction is thus 4.91×10^{-3} moles (KCl) plus 4.93×10^{-3} moles (SO_2) = 9.84×10^{-3} moles of gas per gram of mixture. This is close to twice the number of moles of gaseous products formed by the aluminium/potassium perchlorate mixture. So, while the mixture that contains sulfur produces less heat per gram, it produces much more gas per gram. An estimation of the total pressure produced by the same mass of each mixture in a fixed volume requires an estimation of the maximum temperature. This calculation will be done in a subsequent article in this series.

It is worth emphasizing that the enthalpy of a reaction depends only on the reactants and products, and not on the path taken to go from one to the other. Consequently the possible formation of aluminium sulfide by reaction of the sulfur and aluminium can contribute nothing to the enthalpy of the reaction. While the reaction of aluminium and sulfur is indeed highly exothermic:

$$2\,Al + 3\,S \rightarrow Al_2S_3 \qquad \Delta H^o = -724\ \text{kJ/mol}$$

the heat released in this reaction would be exactly balanced by the heat absorbed when the aluminium sulfide was (conceptually, if not in reality) broken down into its elements before they were oxidized to form aluminium oxide and sulfur dioxide.

Effect of Temperature on the Enthalpy

Tables of standard enthalpies of formation usually list values at 298.15 K (25 ºC).[2,3] Barin's tables[4] list enthalpies of formation at intervals of 100 K, so it is easy to calculate enthalpy changes at any desired temperature in the range listed.

It is useful to understand how enthalpy changes for reactions at other temperatures can be calculated from the standard enthalpies of formation of the reactants and products at 298.15 K.

Suppose you wanted to calculate the enthalpy change for some reaction at 500 K:

Reactants at 500 K → Products at 500 K

From tables, you have the enthalpy change for the reaction at 298.15 K.

Step 1. Imagine the reactants at 500 K are brought to 298.15 K, and calculate the enthalpy change for this process. For the simplest cases, this will be the heat capacity at constant pressure of the reactants multiplied by the temperature change. This is complicated by the fact that the heat capacity varies with temperature; formulae are available for some materials that give the heat capacity as a function of temperature. If one or more of the reactants undergoes a phase change (melts, for example) over the temperature range of interest, the enthalpy change for that process must also be included.

Step 2. Imagine that the reaction takes place at 298.15 K, forming products at that temperature. You can calculate the enthalpy change from tables.

Step 3. Imagine that the products at 298.15 K are heated to 500 K. The enthalpy change for this process is at least the heat capacities at constant pressure of the products multiplied by the temperature change. Again, it is necessary to account for the variation of heat capacity of each substance with temperature. The enthalpy changes associated with any melting or vaporization of the products must also be included.

The enthalpy change for the reaction at 500 K is simply the sum of the enthalpy changes for steps 1, 2 and 3.

For reactions with large enthalpy changes, the contributions of steps 1 and 3 can be small compared with that of step 2. In such cases, and for relatively small temperature changes, the enthalpy change of the reaction will vary to only a small extent with temperature.

Table 1. Some Formula Weights and Enthalpies of Formation for Some Substances Relevant to Pyrotechnics.

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]
Aluminium	Al	26.98	0
carbide	Al_4C_3	143.96	–209
oxide	Al_2O_3	101.96	–1676
sulfide	Al_2S_3	150.16	–724
Ammonium			
chloride	NH_4Cl	53.49	–315
nitrate	NH_4NO_3	80.04	–366
perchlorate	NH_4ClO_4	117.49	–296
Antimony	Sb	121.75	0
oxide	Sb_2O_3	291.50	–720
sulfide	Sb_2S_3	339.69	–142
Arsenic	As	74.92	0
oxide	As_2O_3	197.84	–657
sulfide	As_2S_3	246.04	–167
Barium	Ba	137.34	0
carbonate	$BaCO_3$	197.35	–1216
chlorate	$Ba(ClO_3)_2$	304.24	–772
chloride	$BaCl_2$	208.25	–859
nitrate	$Ba(NO_3)_2$	261.35	–992
oxide	BaO	153.34	–554
peroxide	BaO_2	169.34	–634
sulfate	$BaSO_4$	233.40	–1473
sulfide	BaS	169.40	–460

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]
Boron	B	10.81	0
oxide	B_2O_3	69.62	–1272
Calcium	Ca	40.08	0
carbonate	$CaCO_3$	100.09	–1207
oxide	CaO	56.08	–635
sulfate	$CaSO_4$	136.14	–1434
Carbon	C (graphite)	12.01	0
monoxide	CO(g)	28.01	–111
dioxide	CO_2(g)	44.01	–394
Chlorine	Cl_2(g)	70.91	0
atomic chlorine	Cl(g)	35.45	121
Copper	Cu	63.54	0
(I) chloride	CuCl	98.99	–156
(II) chloride	$CuCl_2$	134.45	–218
(I) oxide	Cu_2O	143.09	–171
(II) oxide	CuO	79.55	–155
carbonate, basic	$CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$	221.10	–1051
Hydrogen	H_2(g)	2.02	0
chloride	HCl(g)	36.46	–92
sulfide	H_2S(g)	34.08	–21
(water)	H_2O(l)	18.02	–286
Iron	Fe	55.85	0
(III) oxide	Fe_2O_3	159.69	–824
(II,III) oxide	Fe_3O_4	231.54	–1118
Lead	Pb	207.20	0
(IV) oxide	PbO_2	239.20	–274
(II,IV) oxide	Pb_3O_4	685.60	–719
Magnesium	Mg	24.31	0
carbonate	$MgCO_3$	84.31	–1096
chloride	$MgCl_2$	95.22	–642
oxide	MgO	40.30	–601
Manganese	Mn	54.94	0
dioxide	MnO_2	86.94	–520
Nitrogen	N_2(g)	28.01	0
(nitrous oxide)	N_2O(g)	44.01	82
(ammonia)	NH_3(g)	17.03	–46
Oxygen	O_2(g)	32.00	0
atomic oxygen	O(g)	16.00	249
Phosphorus	P(red amorph.)	30.97	–17
(V) oxide	P_4O_{10}	283.89	–3010
Potassium	K	39.10	0
chlorate	$KClO_3$	122.55	–398
chloride	KCl	74.55	–437
dichromate	$K_2Cr_2O_7$	294.19	–2062
nitrate	KNO_3	101.10	–495
oxide	K_2O	94.20	–361
perchlorate	$KClO_4$	138.55	–430
permanganate	$KMnO_4$	158.04	–837
sulfide	K_2S	110.26	–377
Silicon	Si	28.09	0
dioxide	SiO_2 (quartz)	60.08	–911
Sodium	Na	22.99	0
bicarbonate	$NaHCO_3$	85.00	–951
carbonate	Na_2CO_3	105.99	–1131
chlorate	$NaClO_3$	106.44	–366
chloride	NaCl	58.44	–411
nitrate	$NaNO_3$	84.99	–468
oxalate	$Na_2C_2O_4$	134.00	–1318
oxide	Na_2O	61.98	–418
perchlorate	$NaClO_4$	122.40	–383
Strontium	Sr	87.62	0
carbonate	$SrCO_3$	147.63	–1220
chloride	$SrCl_2$	158.53	–829
nitrate	$Sr(NO_3)_2$	211.63	–978
oxalate	SrC_2O_4	175.64	–1371
oxide	SrO	103.62	–592
Sulfur	S (rhombic)	32.06	0
dioxide	SO_2(g)	64.06	–297
trioxide	SO_3(g)	80.06	–396
Titanium	Ti	47.88	0
dioxide	TiO_2	79.88	–396
Zinc	Zn	65.39	0
oxide	ZnO	81.39	–350
sulfide	ZnS	97.46	–192

[a] Unless otherwise indicated, these are crystalline solids. Gases are indicated as (g) and liquids as (l).

[b] Values are for 298.15 K, with units of kJ/mol.

Data are from References 2, 3, and 4. If data were inconsistent in the references, the most recent value is quoted. Data were rounded to the number of significant figures presented in the Table.

References

Specific to Text

1) R. Lancaster, "Fireworks Principles and Practice", 3rd ed., Chemical Publishing Co. Inc., New York, N.Y., 1998, p 246.
2) R. C. Weast, Ed, M. J. Astle, Assoc. Ed., *CRC Handbook of Chemistry and Physics*, 63rd ed., CRC Press, Inc., Boca Raton, 1982–1983.
3) G. Aylward and T. Findlay, *SI Chemical Data*, 4th ed., John Wiley & Sons, Brisbane, New York, Chichester, Weinheim, Singapore, Toronto, 1994.
4) I. Barin, "Thermochemical Data of Pure Substances", Parts 1 and 2, 2nd ed., VCH Verlag. MbH, Weinham, Germany, 1993.

General References and Suggestions for Further Reading

This article includes information from a number of references, including the following, cited in order of publication of the work used. More recent editions of some of the books may be available; others may be out of print.

General Chemistry Texts

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K. W. Whitten and K. D. Gailey, *General Chemistry*, 2nd ed., Saunders College Publishing, Philadelphia, 1984.

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A. Findlay, *Introduction to Physical Chemistry*, 2nd ed., Longmans, Green & Co, London, New York and Toronto, 1933.

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Thermodynamics Texts

I. M. Klotz, *Chemical Thermodynamics*, Prentice-Hall, Inc, Englewood Cliffs, 1950.

B. H. Mahan, *Elementary Chemical Thermodynamics*, W.A. Benjamin, Inc., New York, 1964.

E. B. Smith, *Basic Chemical Thermodynamics*, 3rd ed., Clarendon Press, Oxford, 1982.

I. Barin, "Thermochemical Data of Pure Substances", Parts 1 and 2, 2nd ed., VCH Verlag. MbH, Weinham, Germany, 1993.

For further reading, there are many books that deal with this subject. The simplest treatments are to be found in the general chemistry texts, followed by the physical chemistry texts and then the specialized texts on chemical thermodynamics. There are also many texts on engineering thermodynamics that contain little of direct relevance to chemical thermodynamics. Of the books listed, that by E. B. Smith and the two books by B. H. Mahan are particularly recommended. The work by P. W. Atkins is a comprehensive physical chemistry textbook with an excellent treatment of chemical thermodynamics. The first volume of I. Barin's superb 2-volume collection of thermochemical data contains a concise overview of chemical thermodynamics and some useful worked examples.

Events Calendar

(Continued from Page 20)

Explosives

Computational Mech. Assoc. Courses–1999
Explosive Initiation and Initiators
Introduction to Explosives

Contact: Computational Mechanics Associates
PO Box 11314,
Baltimore, MD 21239-0314 USA
Phone: 410-532-3260
FAX: 410-532-3261

Fireworks

Benson & Hedges Pyrotechnic Competition

Montreal 1999

June 19	Panzera (Opening)
June 26	Kimbolton Fireworks (UK)
July 3	Bugano (Switzerland)
July 8	Igual (Spain)
July 14	Ampleman (Canada)
July 18	Soldi (Italy)
July 25	Performance Pyro. Assoc. (USA)
July 28	Panzera (Closing)

Toronto 1999

June 19	Concept Fiatlux (Canada)
June 26	Beijing Zhong Fa (China)
June 30	Parente (Italy)
July 3	C5 Pyrotechnic (France)
July 8	Antonio Caballer (Spain)
July 10	Closing

Montreal 1999

July 31	Concept Fiat lux (Canada)
Aug. 4	C5 Pyrotechnic (France)
Aug. 7	Antonio Caballer (Spain)
Aug. 11	Closing

Summer Fireworks Festival

July 26–30, 1999, Clearfield, PA USA

Contact: Charlie Hill
4533 Foster Valley Road
Endicott, NY 13760 USA
Phone: (607) 748-0667
FAX: (607) 748-0899

Pyrotechnics Guild International Conv.

Aug. 8–13, 1999, Fargo, ND USA

Contact: Erv Haman, Chairman
13225 Bradley Blvd.
Becker, MN 55308 USA
Phone: (612) 261-2793
FAX: (612) 261-2795
e-mail: stargate99@sherbtel.net
Web site: www.pgi.org

11th Western Winter Blast

Feb. 11–14, 1999, Lake Havasu, AZ USA

Contact: Steve Rhodes
Phone: 906-685-2968
e-mail: remains4u@aol.com
Web site: wpa.pyrotechnics.org

Fireworks Display Operator Training

March 8–9, 2000, Gatton, Qld, Australia

Contact: Clive Featherby
Freepost 99, PO Box 1103
Nambour, Qld 4560, Australia
Phone: +61-7-5446-8236
FAX: +61-7-5446-8456
e-mail: firework@dcc.net.au
Web site: www.kcsfireworks.com.au

High Power Rocketry

LDRS XVIII

July 20–Aug 1, 1999

Contact: John Baumfalk
e-mail: johnb@southwind.net
Web site: www.kloudbusters.org

Model Rocketry

NARAM–41

For launch information visit the NAR Web site: www.nar.org

Performance Study of Civil War Vintage Black Powder

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ABSTRACT

A sample of Black Powder dating to the time of the US Civil War (ca. 1863) was harvested from cannon balls uncovered during an excavation on what had previously been the grounds of the Allegheny Arsenal near Pittsburgh, PA. A portion of this powder was eventually made available for an investigation of its properties. It was found to be in excellent condition, both physically and in its performance. Physically, it is essentially indistinguishable from high quality Black Powder of current production. Its performance under conditions replicating its normal use was only slightly less than that produced by a high quality powder of current production.

Keywords: Black Powder, US Civil War, Bormann fuse, quickness test, Eprouvette

Introduction

The stability and aging characteristics of Black Powder are occasional topics of discussion among pyrotechnists. A related question is, have the performance characteristics of Black Powder changed significantly over the years, possibly as the result of differences in raw materials or manufacturing methods? Having obtained a sample of Black Powder, dating to the time of the US Civil War (ca. 1863), the authors were able to investigate some of those interesting questions. This short article is the first in a series planned to report on those investigations.

Source of Powder Sample

Many of the exploding cannon shells produced by the North during the US Civil War were assembled at the Allegheny Arsenal, located in Pittsburgh, PA.[1] While some of the original site of the arsenal remains as a national historic site, much of it has been developed for other purposes, one of which is a gas (petrol) station. In 1972 there was an excavation at the gas station to install a new fuel storage tank. In the course of that excavation, approximately 1000 explosive cannon balls and rifled shells, dating to the Civil War (ca. 1863), were uncovered.[2] The shells were seized by the police for destruction by a bomb disposal unit. However, some of the shells in the best condition were saved from destruction. These shells were subsequently provided for analysis.

Since the shells were still potentially explosive, a remotely operated, barricaded, and water-cooled drill press was used to gain entry to the contents of the shells. For some of the shells, it was found that the seals on their fuses had failed. This allowed water to enter during the period of approximately a hundred years that the shells had been buried, thus ruining the powder they contained. However, the 32–pounder cannon balls were exceptions. These had a casing about 6 inches in diameter with a cast iron wall about an inch thick. Contained inside each shell were several pounds of Black Powder in apparently perfect condition, free flowing and showing no sign of deterioration. The lead-based "Bormann" time delay fuses,[3,4a] screwed into these cannon balls, provided sufficient integrity to protect the contents from intrusion of water over the preceding century of burial. It is the Black Powder from some of these 32 pounders that was provided for use in this study.

The organization of this article is such that the results of a series of physical and performance tests are presented, mostly without comment. This is then followed by a discussion of those results.

Physical Testing

A sieve analysis was performed on a sample of the recovered Black Powder, with the results listed in Table 1. Table 2 provides information on various granulations of Black Powder dating to about the time of the US Civil War and for recently produced powders. In comparing the granulations, it must be considered that current sieves have square holes produced by the interwoven wires forming screens, whereas the sieves of the Civil War era had round holes in thin sheet metal.[4b]

Table 1. Sieve Analysis of the Civil War Black Powder Sample.

Mesh(a)	Size (in.)[5]	Percent(b)
+12	> 0.066	0
–12 +16	0.047–0.066	15
–16 +20	0.033–0.047	45
–20 +30	0.023–0.033	30
–30	< 0.023	10
	Total Percent	100

Note that sieve sizes are US Standard. To convert inches to millimeters, multiply by 25.4.

(a) Minus (–) means the material passes through this mesh sieve. Plus (+) means the material is retained on this mesh sieve.

(b) Rounded to the nearest percent.

Table 2. Size Ranges of Black Powder Granulations.

Civil War Era[4b] Black Powder	Passing(a) (in.)	Retained(a) (in.)
Musket	0.06	0.03
Mortar	0.10	0.06
Cannon	0.35	0.25
Current Black Powder[6]	**Passing Mesh(b)**	**Retained Mesh(c)**
2Fg (Sporting)	16 (3%)	30 (12%)
Class 4 (Military)[7]	16 (3%)	30 (5%)
Musket (Military)	14 (3%)	25 (5%)
Fg (Sporting)	12 (3%)	16 (12%)
4F (A Blasting)	12 (3%)	20 (12%)

Note that sieve sizes are US Standard. To convert inches to millimeters, multiply by 25.4.

(a) These are for sieves made with round holes.

(b) Maximum percent retained on this mesh sieve.

(c) Maximum percent passing through this mesh sieve.

The Civil War powder's bulk and grain density were determined and compared with a recently produced powder. A bulk density for the 16- to 20-mesh fraction of the Civil War powder was determined by placing 5.00 g of powder into a 10 cc graduated cylinder (10 mm ID), and vibrating to produce a minimum volume. The bulk volume occupied by the powder was then read to the nearest 0.1 cc. The results were reported in terms of mass per cubic centimeter, see Table 3. Following this, the interstitial sample volume was estimated by determining the volume (to the nearest 0.1 cc) of a light weight oil required to fill the air spaces between the powder grains. To limit possible migration of the oil into the powder grains, a minimum time was allowed to elapse during the measurement. Grain density was then determined after subtracting the interstitial volume from the bulk volume. Similarly, the bulk and grain densities were determined for a sample of Black Powder recently produced by Goex[8] and sieved to the same 16- to 20-mesh range.

Table 3. Density and Moisture Content of Black Powder Samples.

Powder Type (16–20 mesh)	Bulk Density (g/cc)	Grain Density (g/cc)	Moisture (%)
Civil War	0.98	1.67	0.67
Goex	1.03	1.75	0.53
Mil Spec 1962[7]	—	1.69–1.76	< 0.70
Mil Spec 1862[4]	—	≥1.75	—

Following the current military protocol for Black Powder moisture determination, samples of both the Civil War and Goex powders were weighed, placed in a 75 °C oven for 4 hours, allowed to cool briefly, then reweighed. The mass loss, expressed as a percentage, is the reported moisture content of the powder. These results are also reported in Table 3.

Performance Testing

An early instrument used to gauge the performance of Black Powder is an "Eprouvette", which is a pistol-like device, see Figure 1. The device has a small combustion chamber into which a charge of Black Powder is loaded. One end of the chamber is blocked with a spring-loaded pivoting baffle, with a ratchet to hold it in position against the closing force of a spring. When the powder is fired, using a standard percussion primer, the force of the explosion is determined by noting the extent to which the baffle has rotated. Five test shots were conducted using the 16- to 20-mesh samples of the Civil War powder and again using current production powder manufactured by Goex. The results, including the averages and their standard errors, are reported in Table 4. (Note that these results are dimensionless.)

Figure 1. Photo of Eprouvette,[9] an early Black Powder Tester.

Table 4. Eprouvette Test Results.

Trial	Civil War	Goex
1	4.0	3.5
2	3.5	3.5
3	2.5	2.5
4	2.5	3.5
5	2.5	3.5
Average	3.0	3.3
Std. Error	0.3	0.3

Note that the standard error is the standard deviation, using the *n*–1 method, divided by the square root of *n*, the number of measurements.

A modern test of powder performance is the quickness test.[10] In this test, a small sample of powder is burned in a closed vessel, while recording internal pressure as a function of time. Typically, for this type of test, the level of confinement is sufficient to withstand the pressures produced without venting. However, the instrument used in this study had been assembled for use in studying fireworks lift and burst powders.[11] Accordingly, it was designed to operate in a relatively low pressure regime, typically using one of a series of rupture disks that limit the maximum pressure to a few hundred psi (a few MPa). The volume of this quickness tester is quite low (6.3 cc) to allow testing of very small powder samples. The standard procedure with this apparatus is to crush the powder sample using a mortar and pestle, then load 0.15 g of the 60- to 100-mesh fraction into the combustion chamber for test firing. In each case, ignition is accomplished using a tiny hot-wire igniter.[12]

In this study of Civil War Black Powder the standard method described above was used. Figure 2 is an example of the pressure versus time data from one quickness test. The figure also illustrates the simplified method used to deter-

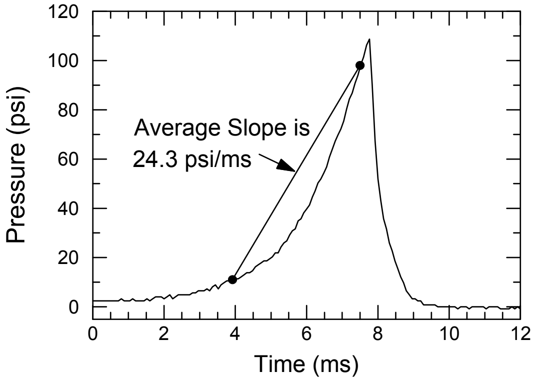

Figure 2. An example of a quickness determination for a sample of Civil War Black Powder.

mine its quickness value. The reported quickness values are the average slope of the pressure rise curve between the points equaling 10% and 90% of the peak pressure observed. A series of eight measurements were made, alternating between measurements for Goex and the Civil War powders. The results and averages are reported in Table 5.

Table 5. Results of Quickness Testing.

Trial	Goex (psi/ms)	Civil War (psi/ms)
1	35.5	24.0
2	36.1	24.2
3	33.3	19.4
4	35.8	22.8
Average	35.2	22.6
Std. Error	0.6	1.1

To convert psi per millisecond to kPa per millisecond, multiply by 6.89.

Note that the standard error is the standard deviation, using the *n*–1 method, divided by the square root of *n*, the number of measurements.

As a test of performance more nearly replicating the powder's use during the period of its production, test firings were made using a Black Powder rifle. Four test firings were made, using the 16- to 20-mesh fractions of samples of the Civil War and Goex powders. The rifle used was a Connecticut Valley Arms 50-caliber rifle with a 26-in. (0.66-m) barrel, firing a 360-grain (23-g) maxi ball using a powder charge of 50 grains (3.2 g). Projectile muzzle velocities were measured using a Prochrono Plus Chronometer (Model CEI–3200).[13] Test firing results are reported in Table 6, along with their averages and standard errors.

Table 6. Black Powder Rifle Results.

Trial	Civil War (ft/s)	Goex (ft/s)
1	1028	1078
2	1034	1068
3	981	1123
4	1019	1071
Average	1016	1085
Std. Error	12	13

To convert feet per second to meters per second, divide by 3.28.

Note that the standard error is the standard deviation, using the *n*–1 method, divided by the square root of *n*, the number of measurements.

Discussion

The physical appearance of the Civil War Black Powder retrieved from the cannon balls is consistent with its still being of high quality. The grains are hard and show absolutely no sign of physical deterioration. The powder is free flowing with minimal dust present. There is possibly a very subtle difference in color, as compared with current production powder (Goex), with the Civil War powder being ever so slightly lighter in color. Based on its general physical appearance, it would not be possible to detect that the Civil War powder was not of current production.

The granulation of the Civil War powder fits well with the range reported for Musket powder of that era, especially if it is recognized that, in 1860, the holes in military sieves were round and not square as they are today. Further, it would seem that the granulation is still consistent with today's US military specification for Musket powder. (See Tables 1 and 2.)

The grain density for the Civil War powder (1.67 g/cc) is close to that of current production powder and to the current US military specification. The grain density of the Civil War powder is a little lower than the reported standard of that time. It is uncertain whether there has been a slight change in the powder's density over time or if the powder had been manufactured to a somewhat different standard. The moisture content of the powder (0.67%) is still within current military specification. (See Table 3.)

In terms of its performance under significant confinement, in the Eprouvette and Black Powder rifle tests, the Civil War powder produces results within 7 to 10% of that of current production Goex powder. (See Tables 4 and 6.) (Note that even though the powder samples had both been sieved to 16–20 mesh, it is possible that relatively small particle-size differences within this mesh range could have contributed to the difference observed in this study.) To help put this 7 to 10% performance difference into perspective, it should be noted that past examinations of other current production Black Powder (non-Goex) performed significantly poorer than the Civil War powder examined in the present study.[14]

At this time, it is not possible to say whether the small difference between the Goex and Civil War powders under confinement represents a degradation of its performance, as opposed to being the result of performing a limited number of tests, or the powder having been less effective originally. Such lesser performance could easily have been the result of less pure potassium nitrate and sulfur, or charcoal having not been processed optimally. It is also possible (likely?) that processing methods have improved somewhat over the intervening 135 years. (Another phase of this study is planned to look into some questions of the purity of the materials and differences in processing in comparison with current materials and methods.)

The only significant difference observed in this study are from the relatively low pressure quickness tests, where the average rate of pressure rise for the Civil War powder was about 35% slower than Goex Black Powder. (See Table 5.) At this time, the authors have no explanation for why this difference is so large, or why it is so much greater than differences observed in the other performance tests. It is possible that particle-size differences, within the 60–100 mesh range used, had an effect. Another possibility is that crushing the powder grains affected the samples differently, perhaps introducing microfractures in the particles. Of course, a third possibility is that it reveals a fundamental difference between the Civil War and Goex powders that is only significant in a relatively low pressure regime.

Additional Historical Background

The method of entry into the shells called "32 pounders" was not by the easier (and less hazardous) drilling through their relatively soft fuse (a 50:50 lead / tin alloy). Rather it was by drilling through the iron casing of the shell. This was done because the Bormann fuses have great historical value. Many deactivated shells from the war have been preserved and are available for study. However, in most cases, their fuses had previously been removed or destroyed.

The Bormann fuses were a type of time delay fuse wherein a compacted semi-circular ring of Black Powder meal was protected by a lead alloy covering. Access to the powder, for the purpose of its ignition, was gained by cutting a hole in the covering, thus exposing the powder to the burning gasses as the shell was fired from its cannon. Accordingly, various delay times could be selected on the battle field by selecting the point along the powder ring, where the lead was cut. Delays up to 5.5 seconds, in quarter-second increments, were possible. (See Figure 3.) Some of the fuses on the recovered shells had the delays marked in numbers, while others had them in Braille. (Most of the rifled shells had an inertia type of fuse designed to explode the shell on impact, and some of these still had their percussion caps in place.) It might be of interest to note that a variation of the Bormann fuse principle is still used on some military items today (e.g., some illuminating flare rounds[15]).

Figure 3. A photo of a Bormann fuse in place on a 6-pounder cannon ball.

At the end of the Civil War, many of the unused shells were returned to the Allegheny Arsenal for deactivation. Apparently this deactivation was accomplished by inserting a spanner wrench into holes in the fuses, and unscrewing them to remove the powder contained in the shells. In the case of the recovered shells, all the spanner wrench holes showed severe rounding indicating a failure of the attempt to remove the fuses. Apparently this inability to easily deactivate these shells was the reason for burying them.

The Allegheny Arsenal was a major supplier of munitions for the North during the US Civil War and was operational until 1901. However, it is most remembered as the site of a horrific explosion during the war that took the lives of 78 children employed for assembly work.[1] The children ranged in age from 12 to 14 and were mostly girls. Children were employed for economic reasons and because their small fingers aided in assembly of some munitions. The explosion occurred early in the morning hours of September 17, 1862. (This is the same date as the battle of Antietam, the single bloodiest date in the war.) The children were buried in a mass grave in the Allegheny Cemetery, just outside the grounds of the arsenal.

Acknowledgements

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The Rare Earths As Possible Flame Color Agents

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ABSTRACT

Colors observed when solutions of scandium, yttrium and the lanthanide elements were sprayed into an inductively coupled plasma are reported. It is suggested, but without experimental evidence, that the colors seen in the lower temperature regions of the plasma (and in a pre-mixed air-acetylene flame) might also be produced by appropriate pyrotechnic mixtures. The color-emitting species (metal monoxide molecules) are remarkably stable, as shown by the dissociation energies of the M-O bonds. These monoxides might be able to exist in useful concentrations at the high temperatures of the glitter flash reaction, thus providing colored glitter. The possibility of using yttrium or erbium, or corrosion resistant alloys thereof, to produce red or green sparks is also suggested.

Keywords: rare earth element, colored flame, colored glitter, colored spark

Introduction

Only a very limited number of chemicals have been found to be useful for the production of colored pyrotechnic flames. Those that have found practical application include compounds of calcium, strontium, barium and copper (the emitting species are predominantly the gaseous monochlorides, MCl, where M is the metal) and sodium (the emitting species is predominantly the atomic vapor, Na). Other, much less widely-used, color agents include compounds of boron (the emitting species is predominantly the gaseous dioxide, BO_2), and lithium and potassium (the emitting species are predominantly the atomic vapors, Li and K).

Clive Jennings-White[1a] surveyed the periodic table for materials potentially useful in pyrotechny and discussed several other possible color agents including rubidium, cesium, indium and thallium. None of these were expected to be useful.

Of the rare earth elements, Jennings-White remarked "...nor do these elements produce useful flame spectra". The rare earth metals include scandium, yttrium and the lanthanides.[2a] A review of the flame spectroscopy of these elements is presented in Reference 3. The Italian scientist G. Picardi described the oxyhydrogen flame spectra of most of the rare earth elements in a series of papers published from 1929 to 1941.[3a] He, and the Swedish spectroscopist H. Lundegardh, discussed the use of the characteristic band emission spectra for the analytical determination of the rare earths by flame photometry.[3a] Many chemists since them will have observed that some of the rare earths produce beautiful colors when sufficiently concentrated solutions are sprayed into a flame or into an inductively coupled plasma. Despite this, there have been (as far as I am aware) no reports of the use of these elements or their compounds as color agents in pyrotechny.

It is common practice to introduce 0.1% yttrium solution into an inductively coupled plasma spectrometer to check that the plasma is properly adjusted. The atomic (actually predominantly ionic, from Y^+) emission shows up as blue, and the yttrium monoxide emission as red. That makes it easy to see if the various gas flows, and the power level, are correct.[4] As indicated by Crawford,[4] solutions of some of the other rare earths can also be used. I tried all the rare earths (except of course the radioactive lanthanide promethium). The colors I observed are reported in this paper, along with some speculations about the possible applications of these novel color agents in pyrotechny.

Table 1. Colors Observed When Solutions of 1 g/l of Individual Rare Earth Elements Were Introduced into a 1 kW Inductively Coupled Plasma.

Element, Symbol	Monoxide emission	Atomic (ionic) emission
Scandium, Sc	Orange-red	Blue-violet
Yttrium, Y	Red	Blue
Lanthanum, La	Faint, yellowish	Pale blue
Cerium, Ce	Pale yellow-orange	Pale blue
Praseodymium, Pr	Pale yellow	Pale greenish blue
Neodymium, Nd	Faint yellow	Greenish blue
Samarium, Sm	Red	Blue-violet
Europium, Eu	Pale pink	Violet
Gadolinium, Gd	Orange	Blue
Terbium, Tb	Yellow	Blue
Dysprosium, Dy	Greenish yellow	Blue
Holmium, Ho	Yellowish green	Blue
Erbium, Er	Green	Pale blue
Thulium, Tm	Green	Pale blue
Ytterbium, Yb	Green	Green
Lutetium, Lu	Deep bluish green	Yellow-green

Experimental

The inductively coupled plasma system was a Labtest Model 2000 (Labtest Equipment Company, Moorabbin, Victoria, Australia), operated at 1 kW. The pre-mixed air-acetylene burner system was part of a Varian Model AA1275 atomic absorption spectrometer (Varian Techtron Pty Ltd, Mulgrave, Victoria, Australia).

The test solutions each contained 1 gram per liter of a single rare earth metal as the chloride or nitrate in dilute nitric acid. Some were commercial spectroscopic calibration solutions, others were prepared in the laboratory by dissolving the equivalent amount of the appropriate rare earth oxide in acid and diluting to volume with distilled water.

Results and Discussion

The colors I observed are shown in Table 1. Some, but not all, were consistent with Crawford's observations, and I have included some elements that were not reported by Crawford. I viewed the colors through green welding glass, and this must have changed the perceived colors to some degree. Given the range of colors seen, it appears that most regions of the visible spectrum were transmitted to some extent.

The atomic/ionic emission colors were seen only in that part of the plasma called the "normal analytical zone".[5] This is the region of the plasma that is used for spectrochemical measurements, and it has been well characterized. The temperature in this zone in a 1 kW inductively coupled plasma is around 5000 K (4727 ºC).[6] These atomic/ionic emitters are most unlikely to be useful in pyrotechnic flames because the temperatures would be too low to break up the very stable monoxides into atoms.

The colors emitted at temperatures likely to be feasible in pyrotechnic flames are evidently produced by the molecular emission bands of the gaseous metal monoxides, MO. The spectrum of the colored light consists of bands, rather than lines, showing that the emitter is a molecule, not an atom or ion. For Sc, Y, and La the emitter has been identified as the metal monoxide.[7a] The other rare earth elements are so similar in their electronic structure to these three that it can be presumed that their emission bands also come predominantly from the monoxides. Some of the bands in the flame spectra of Eu and Yb, however, have been attributed to the monohydroxides, MOH.[7b] Spectra showing the emission bands are published; for example, see references 3b and 8.

There is some analogy between the rare earth monoxides and the monochlorides of calcium, strontium and barium. The latter metals are divalent, having two electrons in their outer shells. Chlorine is monovalent, requiring just one electron to complete its outer shell. In the metal monochloride molecules one of the two outer electrons of the metal atom is tied up in the covalent bond linking the metal atom and the chlorine atom. The other electron readily absorbs energy from molecular collisions by moving into molecular orbitals of higher energy. When it returns to a lower energy orbital, the excess energy is emitted as light of wavelengths characteristic of the energy difference between the orbitals. The molecule thus converts thermal energy (random molecular motion) into light of specific wavelengths. There are discrete energy sublevels associated with the vibration and rotation of the diatomic molecule. Consequently, many slightly different energies are available to the electron, and the spectrum appears as a series of bands.

The rare earth metals are trivalent, and have three electrons in their outer shell. Oxygen is divalent, requiring two electrons to complete its outer shell. When a gaseous monoxide molecule is formed, two of these electrons are tied up in the covalent bond linking the two atoms, and once again a single electron is left in a molecular orbital. In the periodic table, scandium is adjacent to calcium, and yttrium to strontium. It is noteworthy that the colors emitted by the monoxides of scandium and yttrium are rather similar to those emitted by the monochlorides of calcium and strontium, respectively.

The monoxide emission colors were seen in the lower temperature regions of the plasma, located just below the normal analytical zone and just above it. They are also seen when the solutions are introduced into a pre-mixed air-acetylene flame. The maximum temperature of this flame is around 2550 K (2277 ºC).[9] Yttrium solution sprayed into a premixed air-acetylene flame gave a deep red color, while ytterbium solution gave a bright grass green.

The fact that a material can color a laboratory flame does not mean that it is automatically a suitable color agent for pyrotechnics. Lithium compounds color the pre-mixed air-acetylene flame a vivid red, but as Jennings-White noted, they are not particularly effective for making a red pyrotechnic flame.[1b] In the experiments reported in this article, the materials were introduced into the flame (or plasma) as an aerosol by passing the solutions through an appropriate nebulizer and spray chamber system to produce a mist of very fine droplets. On entering the flame or plasma the aerosol droplets evaporate, leaving the dissolved solids as sub-micron sized particles. This provides almost ideal conditions for the volatilization and decomposition processes needed to form the emitting species. These processes might not be so efficient in a burning pyrotechnic mixture.

It might be thought pointless even to consider the use of the rare earths as color agents, because their practical application in fireworks is ruled out by their high cost. The cost might decrease in the future, however, as commercial applications for the rare earths increase. These elements occur together in nature and only some of them are useful in industry. The others, being essentially by-products, might become less costly. If it should turn out that unique effects are indeed possible with these materials, it would do no harm to know. It would be a shame to have to find out by analyzing some Chinese product in years to come. China, by the way, is a major producer of rare earths.

Some values of relevant properties of the rare earth metals and their oxides are listed in Table 2. The values sometimes differed from one reference to another; in such cases, the tabulated value is from the most recent reference.

The gaseous rare earth monoxides are extremely stable, as indicated by the bond dissociation energies. They are the last materials to disappear when solutions of these elements are atomized in the inductively coupled plasma; indeed, the ratio of CeO^+ to Ce^+ is widely used to assess the performance of inductively coupled plasmas when they are used as ion sources for elemental mass spectrometry. The stability of rare earth monoxides suggests that they might be effective color agents for glitter. Most color emitting species cannot survive the high temperatures of the glitter flash reaction, but these may very well be able to do so. Of course, any color produced might be swamped by white

Table 2. Properties of the Rare Earth Metals and their Oxides. Aluminum, Magnesium and Titanium Are Included for Comparison.[2b,10,11,12]

Element, Symbol	Melting Point of Metal (ºC)	Boiling Point of Metal (ºC)	Melting Point of Oxide (M_2O_3, unless otherwise indicated) (ºC)	Boiling Point of Oxide (ºC)	Bond Strength of M-O bond (kJ mol^{-1})
Scandium, Sc	1540	2832	~2500	unknown	670
Yttrium, Y	1525	3337	2430	unknown	720
Lanthanum, La	920	3464	2305	4200	800
Cerium, Ce	798	3433	~2500 (CeO_2)	unknown	800
Praseodymium, Pr	931	3520	~2200 (Pr_6O_{11})	unknown	750
Neodymium, Nd	1021	3074	2320	unknown	700
Samarium, Sm	1074	1794	2335	unknown	620
Europium, Eu	822	1429	2350	unknown	560
Gadolinium, Gd	1313	3273	2420	unknown	720
Terbium, Tb	1365	3230	~2410 (Tb_4O_7)	unknown	710
Dysprosium, Dy	1412	2567	2408	unknown	610
Holmium, Ho	1474	2700	2415	unknown	620
Erbium, Er	1529	2868	2418	unknown	610
Thulium, Tm	1545	1950	2425	unknown	560
Ytterbium, Yb	819	1196	2435	unknown	400
Lutetium, Lu	1663	3402	2490	unknown	700
Aluminum, Al	660.37	2467	2072	2980	510
Magnesium, Mg	648.8	1107	2852 (MgO)	3600 (MgO)	400
Titanium, Ti	1660	3287	1830–1850 (TiO_2)	2500–3000 (TiO_2)	660

light emission from Al_2O_3. It would be worth investigating, none the less.

The identification of suitable compounds for introducing rare earth elements into pyrotechnic compositions will require some research. The oxides are the most readily available compounds of these elements, but they may not be particularly useful. Some of them can be quite reactive, and this might lead to problems with spontaneous heating of mixtures containing them. Additionally, the oxides are so refractory that they may not volatilize to any useful extent in the flame. Many of the salts of the rare earths are deliquescent. Rare earth salts of organic acids would perhaps be useful. Ideally, the compound should vaporize at a relatively low temperature so that it would be in the gaseous state before it decomposed to the oxide. If the decomposition occurred in the solid or liquid state, it might be difficult to get sufficient material into the flame, because the oxides are extremely stable and have very high melting and boiling points (Table 2).

A highly desirable, yet elusive, firework effect is the colored spark. Some of the rare earth metals might produce colored sparks if they could be included in appropriate compositions as filings or coarse powders. The melting points of yttrium, erbium, thulium and lutetium are similar to that of titanium. This suggests that these metals would behave similarly to titanium in a spark-producing composition. If the monoxide emission colors were sufficiently intense to be visible above white light from hot oxide particles, yttrium would be expected to produce red sparks, and the other three metals, green. As noted by Jennings-White, however, the rare earth metals themselves are almost certainly too reactive to be used in pyrotechny.[1c] Alloys of appropriate rare earths with metals that form protective oxide films (aluminum or titanium, for example), might be more stable, and would be worth investigating.

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Communications

Brief technical articles, comments on prior articles and book reviews

Comment on:

Composite Colored Stars, Issue 8.

Scot Anderson's article states that "The calcium [impurity that interferes with flame color] may be present as a trace element in the water used during processing". (p 25, "Green" section) That is certainly possible, though I rather doubt it. Another potential source is the addition of "TCP"—tricalcium phosphate—also known as "anti-cake"—to the ammonium perchlorate (AP).

Two specific Kerr-McGee 200 micron rotary round AP lots from 1992 (without TCP) and 1993 (with TCP) had the following analysis (certificates of analysis from the manufacturer):

	1993	1992
NH_4ClO_4	99.8	99.2
NH_4Cl	0.005	0.009
NH_4ClO_3	0.005	0.002
Moisture (total)	0.033	0.025
Moisture (surface)	0.011	0.002
TCP	0.17	none

The TCP is more than a "trace" amount; quite possibly a significant contributor to the observations when one considers the inherent intensity of calcium spectra.

The article is indeed very interesting and informative—I enjoyed it very much!

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Comment on:

Glitter Chemistry, Issue 8.

Having read Clive Jennings-White's excellent article on glitter chemistry, I have re-visited the writings of M. Stanbridge on this topic.

The following refers to material published in Stanbridge's letter in *Pyrotechnica* XII, June 1988, p 3 ff.

1. On page 4, there is a table of thermodynamic quantities associated with various "flash reactions", calculated for a temperature of 3800 K. These are not consistent. If the ΔG values are calculated from the listed ΔH and ΔS values using $\Delta G = \Delta H - T \cdot \Delta S$, the results are very close to the listed values for 4 of the 5 reactions. The calculated ΔG value for the Al_4C_3/K_2SO_4 reaction, however, differs from the published one by over a factor of 2.
2. A temperature of 3800 K was used by Stanbridge because this is the "limiting temperature" reached in the flash. It would be more appropriate to use the temperature at which the flash initiates, which, according to Stanbridge, is around 1100 ºC (1373 K). When his numbers are recalculated using this temperature, however, they do not change the arguments that follow, which apply equally well in either case.
3. Stanbridge appears to have been confused about the significance of ΔG and ΔH. ΔG indicates the "driving force" behind a chemical reaction. Fundamentally, it is derived from the change in entropy of the Universe that would result if the reaction occurred. If ΔG is negative, the entropy of the universe will increase when the reaction proceeds to equilibrium, and the reaction will be thermodynamically spontaneous. Once initiated, the reaction will spontaneously proceed to equilibrium. If ΔG is large and negative, the equilibrium position will overwhelmingly favor the products. This is the case for *all* the reactions he lists. That means that if all

the reactants were present at the temperature being considered, the reactions would *all* be thermodynamically spontaneous. Stanbridge writes “The Al_4C_3/K_2SO_4 reaction increases its output with temperature, exceeding all the others in its output”. Here he clearly is using ‘output’ to mean ΔG. Curiously enough, the values of ΔG calculated from his ΔH and ΔS values do *not* give the most negative ΔG to the Al_4C_3/K_2SO_4 reaction. That honor belongs to the Al_2S_3/K_2SO_4 reaction. See the Table.

T = 3800 K Reaction	Published			Calculated	Ratio
	ΔH (kJ/mol)	ΔS (kJ/K)	ΔG_{3800} (kJ/mol)	ΔG_{3800} (kJ/mol)	Pub./Calc.
Al_4C_3/K_2SO_4	–1274	0.289	–5074	–2372	2.14
Al_4C_3/O_2	–4322	–0.575	–2141	–2137	1.00
Al/O_2	–3352	–0.625	–980	–977	1.00
Al/K_2SO_4	–3656	–0.386	–2190	–2189	1.00
Al_2S_3/K_2SO_4	+1772	1.698	–4545	–4680	0.97

Obviously the flash reaction must be spontaneous, and once initiated must proceed to completion (the equilibrium position must overwhelmingly favor the products), so its ΔG must be large and negative. The magnitude of ΔG, however, has *no relevance* to the “energy” of the flash reaction as perceived by an observer. The relevant quantity is ΔH. The released enthalpy of reaction, indicated by ΔH, increases the temperature of the reaction products and causes them to emit light. The flash reaction must be highly exothermic, so its ΔH must be large and negative.

There are many examples of processes having a large negative ΔG (i.e., they are thermodynamically spontaneous, and the equilibrium overwhelmingly favors the products) but which absorb heat from the surroundings (i.e., they have a positive ΔH). The melting of ice is one example; the dissolving of ammonium nitrate in water is another. For a third example, we need only look at Stanbridge’s figures for the Al_2S_3/K_2SO_4 reaction. This reaction is thermodynamically spontaneous, but it has a positive ΔH. That is to say, when this reaction takes place, it soaks up heat from the surroundings. This, by the way, refutes the Troy Fish theory that Al_2S_3 is the fuel in the flash reaction. I have calculated the ΔH value independently, using data from the *CRC Handbook of Chemistry and Physics* and confirmed that ΔH is indeed large and positive as Stanbridge’s figures indicate.

4. Of the reactions between a fuel and K_2SO_4, the one having the most negative ΔH (i.e., the greatest heat output) is the Al/K_2SO_4 reaction. This is so whether one calculates the heat per gram of Al (relevant if K_2SO_4 is present in excess) or the heat per gram of K_2SO_4 (relevant if Al is in excess).

5. My calculations indicate that if all the Al were to be converted to Al_4C_3 before the flash reaction, the effect would be to *lower* the heat output of the flash reaction by about 38%. This is assuming excess K_2SO_4 and calculating the heat evolved *per gram of Al.* Alternatively, the reaction could be assumed to be limited by the availability of K_2SO_4. Calculation of the heat evolved *per gram of* K_2SO_4 then indicates that the heat output of the flash reaction is reduced by 59% if all the Al is converted to Al_4C_3 before the flash reaction. This is consistent with the observations of Clive Jennings-White on the reaction of Al_4C_3 with K_2SO_4, compared to that of Al and K_2SO_4.

6. Stanbridge wrote “… the rate at which the reaction proceeds is not indicated by the free energy magnitude”. This is absolutely correct. The kinetics will be at least as important as the thermodynamics in determining what actually happens. He then writes, “An initial examination of the rate equations for these reactions does, however, suggest that the Al_4C_3/K_2SO_4 reaction should be faster than the others.” This almost throw-away line actually implies a great deal. The “rate

equations" could only be derived if one knew the detailed mechanism for these reactions. If Stanbridge has indeed worked out the mechanisms and figured out the rate equations, it was very modest of him not to have provided more details. Even today, the kinetics of much simpler high-temperature solid state or heterogeneous reactions than these is controversial. See, for example, "Forty years of electrothermal atomic absorption spectrometry. Advances and problems in theory", Boris V. L'vov, *Spectrochimica Acta* Part B, 52, (1997) 1239-1245 and references therein.

7. Setting aside the question of whether or not the rate equations for these reactions are known, it has to be said that Stanbridge's claim that "the Al_4C_3/K_2SO_4 reaction should be faster than the others" does not really support his case. If the reaction were indeed faster than the others, the Al_4C_3 would be consumed quickly. How, then, could enough accumulate to cause the flash? Whatever the flash reaction is, it must have a sufficiently high activation energy to allow the reactants to persist unreacted to quite a high temperature.

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Review: *Introduction to the Technology of Explosives*

Paul W. Cooper and Stanley R. Kurowski

Wiley–VCH, Inc., 1996
[ISBN: 0-471-18635-X] 204 pages

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This book is intended as an introduction to some of the technologies associated with explosives, propellants, and pyrotechnics.

In contrast to some earlier similar books, the authors saw fit to include enough mathematics to allow the reader to accomplish some useful tasks after having read the book. However, the amount, and level, of the mathematics used should not present any problems to even a reasonably non-technical reader. Similar to other works, the emphasis is on military and government applications. The chapters are summarized below:

Chemistry of Explosives

In this first, and very important, chapter the authors introduce some of the important chemical concepts required to understand the reactions that explosives, propellants, and pyrotechnics undergo. Included are the concepts of oxygen balance, stoichiometry, and some typical formulations.

Mechanics of Burning

The simple mechanics of burning, including some geometrical considerations, and gas states are presented.

Sound, Shock, and Detonation

The physical properties of materials are presented, followed by sound and shock waves, finishing with a description of some output tests.

Initiation and Initiators

Various mechanisms of initiation and descriptions of various technical and safety tests that may be used to quantify sensitivity to initiation are presented. A comprehensive description of various initiators is shown along with some analysis of their methods of function.

Scaling in Design and Analysis

This chapter is a treatment of the effects of scaling in explosive design and effects, including a brief analysis of the effects of explosives in air, water, and earth, and of jet formation and penetration.

Off-the Shelf Explosive Devices

Herein is a brief "catalog" of some available explosive items from various manufacturers.

Classification, Transportation, and Storage of Explosives

Some regulatory items concerning how explosives are to be classified, transported and stored are briefly covered.

Explosive Facilities and Explosive Operations

Considerations concerning facility structures, manufacturing operations, testing, safety and some regulatory matters are examined.

Each chapter ends with a "Related Reading" section which will assist the reader in obtaining further information.

A book such as this, especially one that gives more than a superficial look at a number of topics, should have had better editing. Some of the errors are merely typographic. However, a typographic error calls into question any value which might be given in, say, a table. Some typographic errors are more serious, such as the one just below 2.1 on page 42 where an explanation of the dimensions of the burning rate coefficient are given as (in./s/ psi^n), where, I suspect, what was intended was (in./s– psi^n).

Other errors such as listing IMR propellant as a double base composition on page 43, are errors of fact and may call into question other factual data.

In some cases the inconsistency may cause problems for a reader who is unfamiliar with the subject. As an example, toward the bottom of page 10, two examples of negative oxygen balance given are given. One is listed as (85.57%) and the other as (–35.9%). Is one to use the "–" sign, or not?

The explanation of the National Electric Code for hazardous location wiring, on page 180, may give an inexperienced user the completely wrong idea as to how to proceed with the design of a safe electrical system.

While the book is a welcome addition to the literature, this reviewer finds it difficult to whole-heartedly recommend the book in its present state. If some details were to be "cleaned" up in a second edition it would become a very useful addition to a technical library.

Review: *Theater of Fire*

Philip Butterworth

Special Effects in Early English & Scottish Theatre

The Society for Theatre Research, London, 1998.
[ISBN 085430 0627] 272 pages

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As a safety expert, I fell in love with this book before I finished the introduction. Author Philip Butterworth introduces his subject with a discussion of the difference in safety-consciousness between the Middle Ages and today. This is appropriate if readers are to appreciate the boisterous and hazardous theatrical pyrotechnic experimentation in this historical period.

The author surveyed five major renaissance and medieval data bases for information on period pyrotechnics:

- guild, civic and ecclesiastical records
- firework writers' recipes;
- eye-witness accounts;
- recipes in Books of Secrets; and
- stage directions in plays.

From these sources, Butterworth gives us a glimpse of pyrotechnics of the period through diagrams and illustrations of pyrotechnic effects, recipes, and written accounts transliterated from the original old English and old Scottish manuscripts.

Especially engaging are the descriptions of royal firework pageants. Often these began with the building of two realistic-looking castles and a monstrous pyro-spitting dragon. Then troops using real gunnery and fireworks-wielding actors staged battles which resulted in the complete demolition of the enemy castle and the dragon.

It is not surprising that these pageants got a bit exuberant. In one instance, one of the "balles of fyre" was accidentally projected "over the Castell, and into the myds of the Towne" where it was responsible for damage which "made a hole as big as a man's head".

My only criticism of the book is that the Glossary is not more complete. I would like to see almost every pyrotechnic term used in the text defined in the Glossary. The meanings of words have changed greatly over the last 400 years. In fact, I suggest reading the Glossary before the text. Readers who ignore the definitions are likely to be "hoisted on their own petards" or, at least, misled by a words like "lances", "coffins", and "stouple".

Stouple is a good case in point. Its synonyms include: cotton wick, cotton weeke, quickmatch, gunmatch, and match. But the stouple is unlike the matches and wicks of today. Readers must consult the Glossary to learn how cotton wicks were made if they want to understand how the stouples worked.

It is just as important to read the Glossary's descriptions of how the ingredients were manufactured. Then it becomes clear that most of the chemicals were so impure that the contaminants must have affected the pyrotechnic reactions. The impurities also render all the weights and measures in the old recipes unreliable. In addition, the author points out that some writers of the period withheld "significant information in order to retain control and apparent secrecy of processes which ironically prevent recipes from working". For all these reasons, *Theater of Fire* is not a "how to" book.

However, some "how to" aspects in the chapter on Flame as Light just might give ideas to Lighting Designers. I was awed by the inventive lighting devices and effects that were created with candles, lanterns, globes of liquid, and mirrors.

Special Effects Technicians also will find their roots here. However, they should not try the Medieval methods for creating shooting fire, devils on fire, devils spitting fire, lightning and lightning storms, thunderbolts, smoke, boilings, and burnings. For example, actors today probably would not be pleased if they were directed to

> *... take Brimstone [sulfur], Orpiment [arsenic trisulfide], and common Oyle, of these make an ointment, with the which anoint thy garment all about & thy head and handes, and after light the same & it will burne all at once without harme*

And if accidents did happen, well....

> *... the man who played Satan, when he prepared to enter through his trapdoor underground, his costume caught fire round his buttocks so that he was badly burned. But he was so swiftly succored, stripped, and reclothed that without giving any sign [of pain] he came and played his part, then retired to his house.*

I'll bet he did! Clearly, the show-must-go-on tradition was already established in the Middle Ages. And Butterworth documents the fact that pyrotechnics and special effects were an important part of that tradition. *Theater of Fire* is a masterfully researched and documented text that belongs in the libraries of all designers of special effects and lighting and every lover of pyrotechnics.

[*Editor's Note*: This book can be obtained directly from the Society for Theatric Research in London. The address is:

The Society for Theatric Research
IE Tavistock Street
London WC2 7PA
United Kingdom

At press time the cost was £24.00]

Review:

Fire Protective Clothing

A Guide for Those Who Manufacture or Store Pyrotechnics or Propellants

Confederation of British Industry
Explosives Industry Group, 1995
[ISBN 0-85201-513-5] 23 pages

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This relatively short publication (23 pages, including references) provides an enlightening look at protective clothing and the various materials—modern and otherwise—used in its manufacture. Though a substantial part of the content relates specifically to British and European standards and regulations which readers in other parts of the world may not find directly relevant, there is still much of potential interest.

This publication deals only with protection from transient thermal effects, such as might arise from accidental ignition of pyrotechnic compositions or propellants. That it does not address blast or projectiles is not surprising, given that guarding against these hazards is largely beyond the capability of mere clothing. Burn injuries, on the other hand, can in many cases be prevented or minimized even by rather unsophisticated work attire of the proper materials.

The most useful information in this publication concerns the classification, selection, and performance of various materials including aramids, polybenzimidazole, carbon fiber, treated cellulose, leather, and aluminum-coated fabrics. Qualitative comparisons are given, but no quantitative performance data are provided. This apparent shortcoming is acknowledged in the text, which refers to on-going research involving the measurement of thermal effects from burning explosives and the development of a manikin assessment method for protective clothing. More detailed data will apparently be forthcoming in future editions of this or related documents.

The work also discusses protection for specific parts of the body, and gives recommended practices for the maintenance of protective equipment. It concludes with a rather extensive list of documents and references where more detailed information on protective clothing may be found, the majority of which are British Standards and other government publications.

While not a comprehensive reference in its present state, this publication is useful as a quick source of basic information, and provides useful directions for further reading.

Studies on Low Smoke Photoflash Compositions

NOTE: This article originally appeared in *Proceedings of the 19th International Pyrotechnics Seminars*, Christchurch, NZ, February, 1994.

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ABSTRACT

There have been numerous reports in recent years of problems with the use of certain pyrotechnic photoflash compositions in noise simulators. The most common has been the gassing problem caused by the oxidation, during storage, of the magnesium metal fuel. In addition the quantity of particulate smoke produced by the combustion reaction can cause a number of undesirable effects when the simulators are deployed in confined environments during training operations. A study has been undertaken to investigate compositions that use alternative reactants to generate the pyrotechnic effects. The relative noise, light and smoke emissions of the compositions have been measured.

Preliminary results suggest that a formulation which uses powdered hexamine as the fuel may offer a satisfactory alternative as the filling in noise simulators.

Introduction

Pyrotechnic photoflash compositions have been used for many years in noise simulators and thunderflash devices to produce impulse noise and light effects. The compositions have been largely based on magnesium–potassium perchlorate formulations, the British compositions SR 801C and SR 813 being typical examples. A number of problems has been reported with the use of these compositions.

Firstly, the limited service life associated with devices incorporating magnesium-fuelled photoflash compositions has been well documented.[1] This is caused by the gradual oxidation of the uncoated magnesium metal powder in the presence of entrapped moisture. The reaction results in the liberation of hydrogen gas which can, in sealed devices or storage containers, cause degenerative effects (case swelling) which generally result in the failure of the devices to comply with the performance or safety specifications. As the result of several investigations at Material Research Laboratory (AMRL) it was recommended that the magnesium fuel could be replaced by aluminium powder which is less affected by moisture.[2,3] This approach was found to overcome the gassing problem and even enhance the noise and light emissions.[4]

The second problem reported by the Australian Defence Force (ADF) concerning the use of photoflash-filled devices has been the obscurating effect of the particulate smoke produced by the combustion reaction. This is of concern, particularly when the devices are fired in confined environments such as below deck on ships. The quantity of smoke produced has been found to have adverse effects on personnel and the operational requirements of training operations.

A study was undertaken at AMRL to look for alternative reactants which would maintain the noise and light emissions but reduce the quantity of smoke produced to minimal levels. After initial screening of candidate formulations was done by subjective assessment, the more promising compositions were filled into test devices and fired. The relative noise, light and smoke emissions were evaluated using instrumental techniques.

Alternative Reactants

The factors which most determine the characteristics required of the reactants for an effective impulse noise-producing pyrotechnic composition are the reaction rate achievable under pressure and the resulting temperature of the products. This tends to limit the choices to high energy reactants such as oxidants which include the alkali metal perchlorates and nitrates of potassium and barium, and the metal fuels including aluminium, magnesium, titanium and zirconium. Certain carbonaceous fuels including tetranitrocarbazole and carbon (gunpowder) have been used in noise simulators but these tend to produce large volumes of smoke.

From the operational safety aspect, the reduction of smoke emission is certainly important as is the maintenance of noise emissions within the specified noise limit criteria,[5] but the intense luminous emission from metal powder photoflash compositions can also cause operational problems including the temporary loss of vision.

The cost factor is also important in the selection of alternative reactants because practice simulators tend to be used in large numbers and hence need to be relatively inexpensive items. This would normally tend to eliminate the use of exotic (and expensive) fuels like titanium and zirconium in devices of this type unless there were significant advantages to be gained. For example the inclusion of titanium is known to increase the light output but also increases the smoke emissions.[6] It has been generally accepted that obscuration effect observed in many pyrotechnic reactions is related to the type and particle dimensions of the reaction products, particularly the metallic oxide (MgO, Al_2O_3, etc.) formed.[7] It was thus decided to investigate several carbonaceous materials, hexamine and nitrocellulose, as possible fuels and compare their performance with magnesium and aluminium.

There is probably more scope to vary the choice of oxidant. They can also contribute to the formation of particulate reaction products (smoke) and in the case of barium, the smoke tends to be toxic. It was therefore decided to investigate the use of the ammonium salts of nitrate, picrate and perchlorate (the reaction products of which are largely gaseous) and compare their performance with compositions containing potassium perchlorate.

Initial Assessment of Candidate Compositions

The study was concentrated in two main areas.

- analysis of the effects of impulse noise, light and smoke output by varying the fuel/oxidant ratio of the more conventional ingredients of photoflash compositions (aluminium and magnesium as the fuel and ammonium or potassium perchlorate as the oxidant) and,
- investigation of the effect of substituting several novel fuels or oxidants in compositions by measuring the relative impulse noise, light and smoke emissions.

The preliminary assessment of the compositions was conducted using test charges designed to contain 1.0 g of each composition. These were fixed into a jig located in an open field and fired electrically. The complete list of the systems considered in the initial assessment can be seen in Table 1. Four experienced pyrotechnicians were located at the positions marked on the layout shown in Figure 1. Each provided a subjective assessment of the emissions from each charge on a scale of 1 to 10 (1 indicating the lowest output). The compositions judged to be clearly inferior with respect to noise emission were eliminated from further study. The more promising compositions were subjected to a series of comparative assessments for light, noise and smoke output.

Table 1. Compositions Used in Initial Screening Assessment.

Composition		Noise	Flash	Smoke	Comments
1	$Mg/KClO_4$/Acaroid (40/59/1)	10	10	10	AMRL (X) 206
2	Mg/NH_4ClO_4 (50/50)	>10	10	10	
3	Mg/NH_4ClO_4 (40/60)	10	10	10	Fuel-deficient
4	Mg/NH_4ClO_4 (55/45)	>10	10	10	Fuel-rich
5	Mg/NH_4NO_3 (48/52)	8	6	7	Unstable, NH_3 evolved
6	Mg/NH_4Picrate (50/50)	4	9	9	Low noise
7	$Al/KClO_4$/Aerosil (40/59/1)	10	10	9	AMRL (X) 210
8	Al/NH_4ClO_4 (46/54)	8	8	9	
9	Al/NH_4ClO_4 (40/60)	10	9	7	Fuel-deficient
10	Al/NH_4ClO_4 (50/50)	10	>10	10	Fuel-rich
11	Al/NH_4NO_3 (40/60)	—	—	—	Did not function
12	Al/NH_4Picrate (50/50)	—	—	—	Did not function
13	Hexamine/$KClO_4$ (15/85)	6	1	4	“sharp” report
14	Hexamine/$KClO_4$ (30/70)	7	1	6	“sharp” report

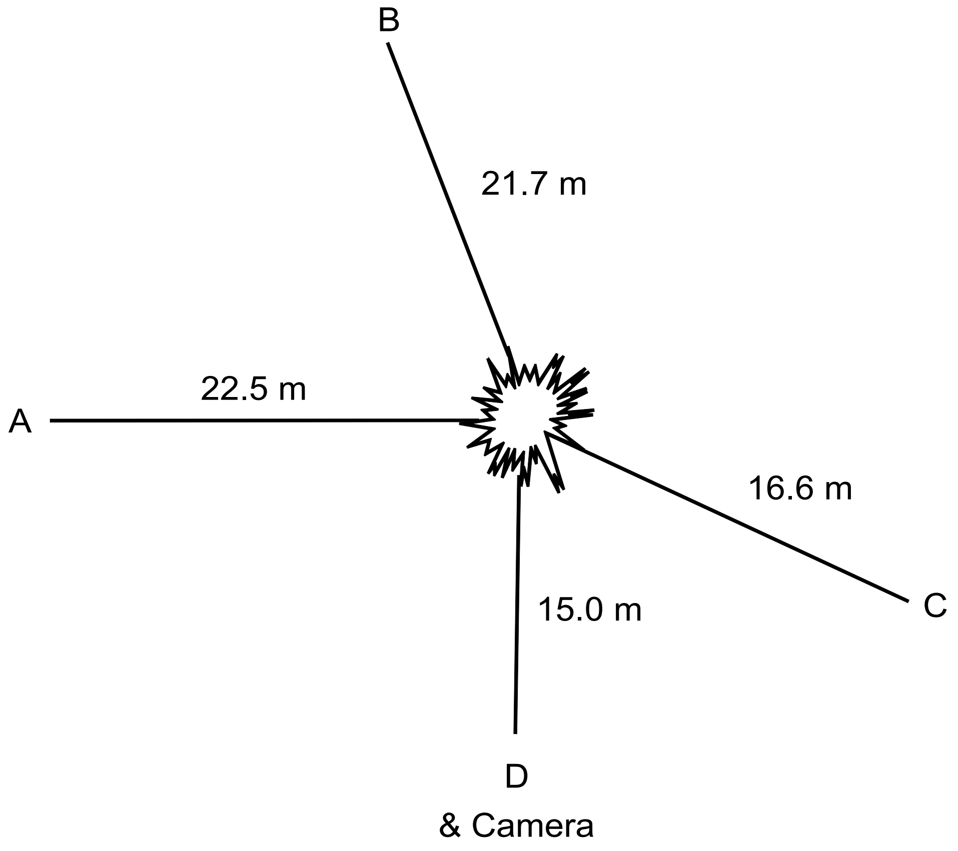

Figure 1. Sketch indicating observer positions.

Table 2. Noise Level Outputs (1 g Sample).

	Composition	Peak Pressure (kPa)	Positive Phase Duration(μs)	Impulse (kPa·s)
1	Hexamine/KClO$_4$ (15/85)	3.8	309	0.001
2	Hexamine/KClO$_4$ (30/70	4.9$^{(1)}$	226	0.001
3	Al/NH$_4$ClO$_4$ (50/50)	>9.6$^{(1)}$	458	0.002
4	Al/NH$_4$ClO$_4$ (40/60)	10.0	411	0.002
5	Al/NH$_4$ClO$_4$(37/63)	7.5	365	0.001
6	Al/KClO$_4$/Aerosil (40/59/1)	13.0	344	0.002
7	Mg/KClO$_4$/Acaroid(40/59/1)	8.7	400	0.002

(1) Only one reliable result because of fragments hitting the waveform plate.

Noise Output

Pressure gauges were mounted in the centre of two large baffle plates positioned one metre off the ground. The pressure signals were recorded on a IQ400 DSO tape recorder, later downloaded to a PC and analysed by a specially developed software package, Blast, developed at AMRL. From this, the peak pressure, positive phase duration and the impulse were determined for each sample and listed in Table 2. A typical pressure-time profile can be seen in Figure 2.

Light Output

The light emission was measured by a Spectra-Pritchard Tele-Photometer (rise time 10 μs) at a distance of 5.75 m. Calibration was conducted in the illuminance mode with a NML quartz halogen 2856 K intensity standard as the source. The voltage output of the telephotometer was recorded on a HP 400 MHz digital storage oscilloscope. Typical results of the light output measurements are listed in Table 3 and a typical light emission-time profile can be seen in Figure 3.

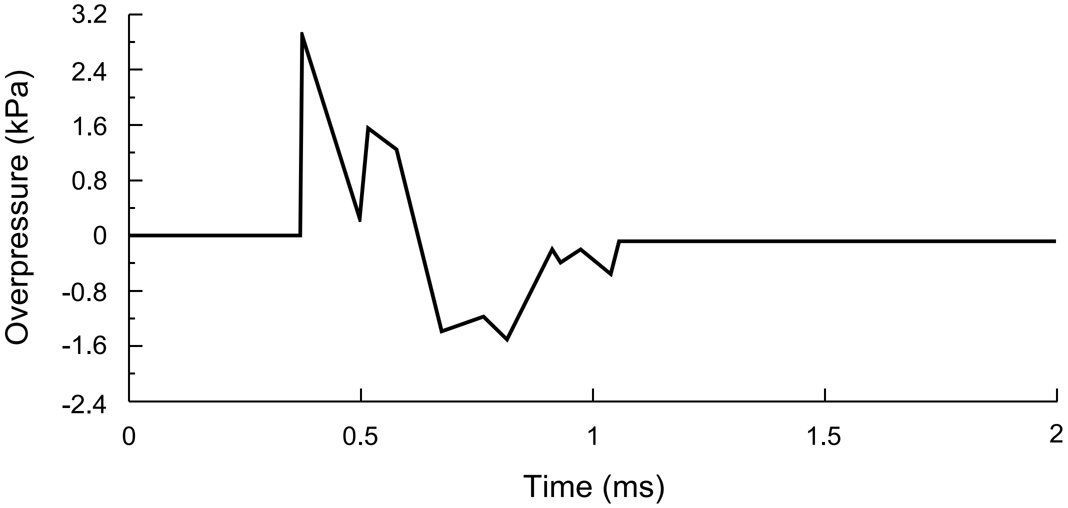

Figure 2. Pressure-time profile for hexamine/potassium perchlorate (15/85).

Table 3. Light Output of Cardboard-Cased Compositions (1 g Payload).

	Composition	Max. Intensity (cd)	Pulse Duration (ms)	Light Output (cds)
1	Hexamine/$KClO_4$ (30/70)	2.2×10^2	0.33	0.12
2	Hexamine/ $KClO_4$ (15/85)	8.3×10^1	0.13	0.05
3	Hexamine/NH_4ClO_4 (30/70)	7.2×10^1	0.40	0.02
4	Al/ NH_4ClO_4 (50/50)	8.3×10^5	2.5	2.1×10^3
5	Al/ NH_4ClO_4 (40/60)	5.3×10^5	(a)	N/A
6	Al/ NH_4ClO_4 (30/70)	2.7×10^5	<1	8.0×10^2
7	Al/$KClO_4$/Aerosil (40/59/1)	4.5×10^6	0.9	N/A
8	Mg/$KClO_4$/Acaroid (40/59/1)	1.9×10^6	0.5	N/A

(a) Incomplete records of this event.

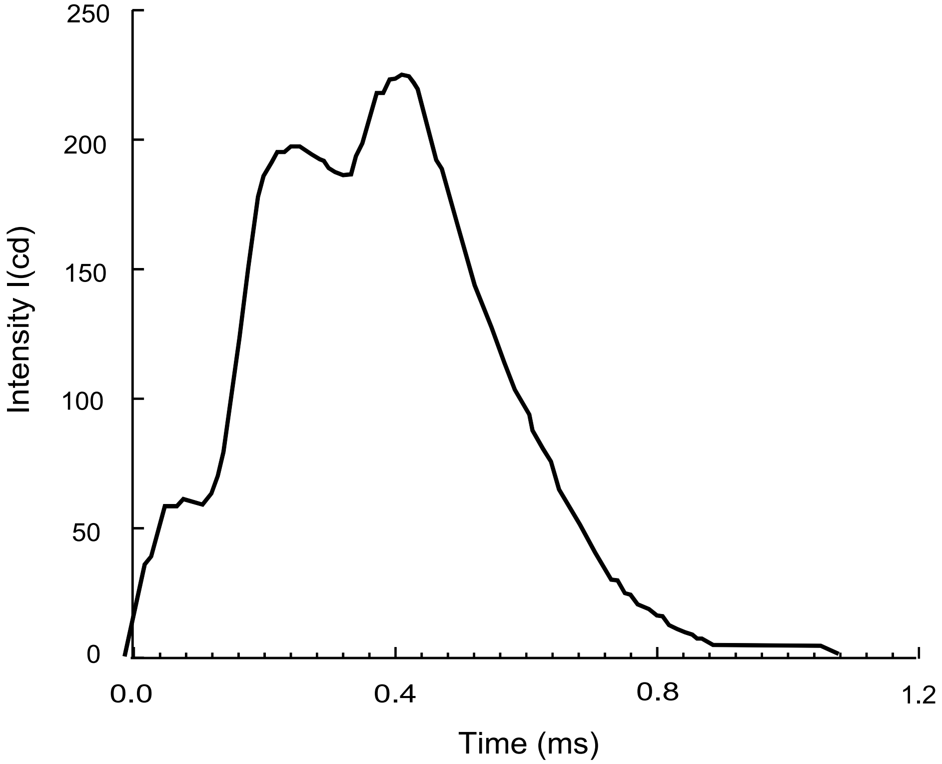

Figure 3. Light emission profile (intensity vs. time) for hexamine/potassium perchlorate (15/85).

Smoke Output

The obscuration effect of the reaction products was measured in the AMRL Smoke Chamber (Figure 4). The key features of the chamber are that it has an optical path length of 5.0 m and a total volume of 32.45 m^3. The smoke produced was allowed to circulate by the four fans situated in each corner of the chamber. The pyrotechnic systems were fired approximately 1 m above the floor of the chamber and the smoke produced from the reaction allowed to circulate for 5 minutes to achieve a uniform distribution. Loss of transmission (obscuration) was monitored with a He/Ne laser (0.6328 µm) over a prolonged period (up to 5 minutes). Obscuration data was determined for a number of

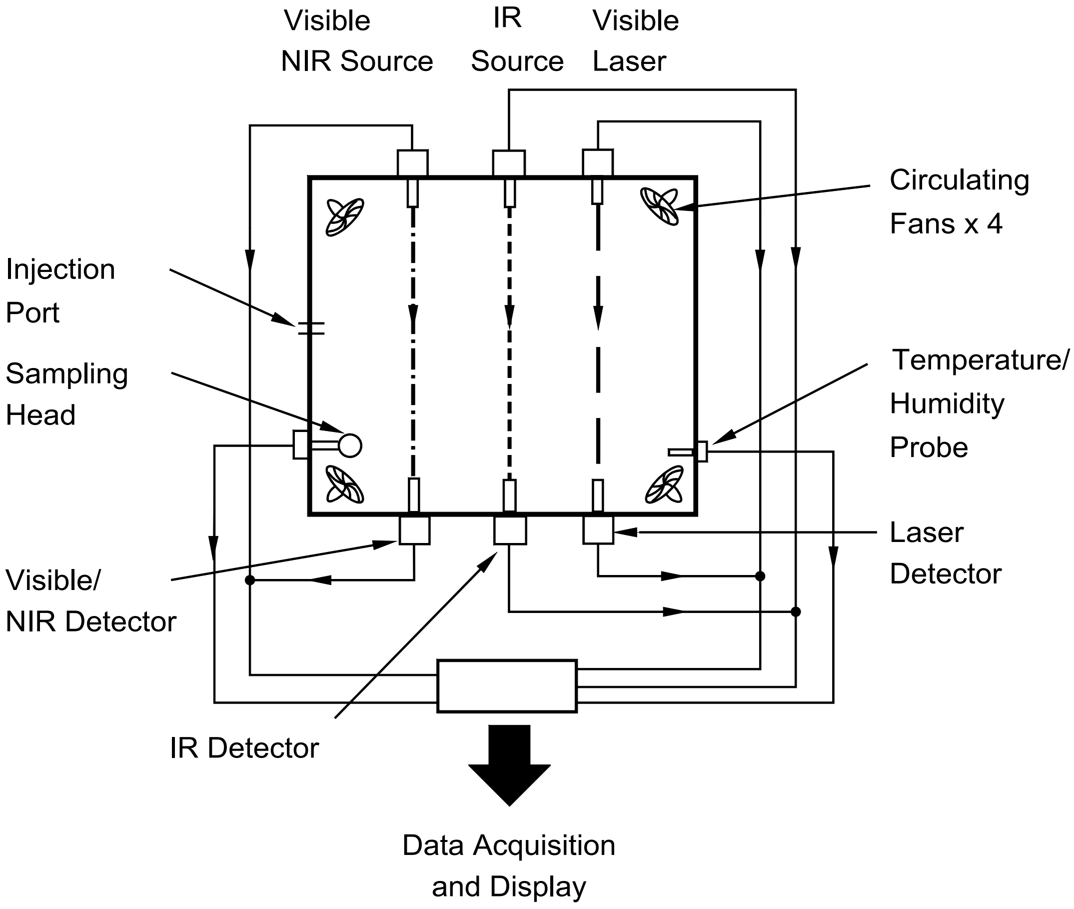

Figure 4. Schematic of the AMRL smoke chamber.

composition weights and the results for 6 g charges are shown in Figure 5.

Discussion

A survey was undertaken to study alternative fuels and oxidants that could be used in training simulators. The criteria used by the four observers was based on a relative light, noise output and smoke output. A low obscuration value was critical because it not only considered the amount of particulate matter produced but also provided an indication of the concentration of the reaction products which was important in any consideration of the possible harm that those products could cause if inhaled. This was, in effect, why serious consideration was given to such fuels as hexamine and oxidants such as nitrates and picrates because in the chemical reaction process a significant component of the reaction products are low toxic gases. Some examples are listed below:

nitrates → nitrogen

picrates, N/C, hexamine → nitrogen, CO_2

A study using the NASA-Lewis thermodynamic code has confirmed that these gases are in fact the predominant products (along with the metallic oxide) but there should be some concern that under particular fuel/oxidant ratios it is also possible to produce alternative and toxic gaseous products (e.g., oxides of nitrogen, carbon monoxide and hydrocarbons).[8] In the circumstance where the training simulator was to be used in a confined environment, this now becomes the predominant consideration.

An additional factor not able to be taken into account by the thermodynamic codes is that the fuel and oxidant may not be chemically com-

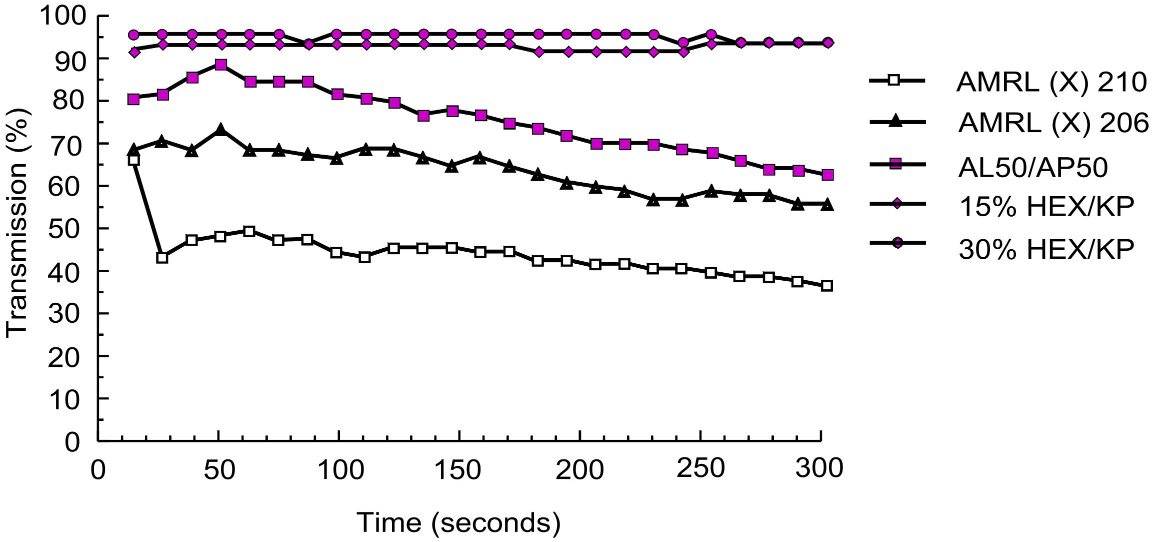

Figure 5. Smoke obscuration vs. time profiles for a range of compositions.

patible. An example was seen with the composition containing magnesium fuel and ammonium nitrate oxidant which was observed to release ammonia gas during mixing.

The most significant result can be seen in Figure 5. The more common photoflash compositions used in simulators are based on magnesium as the fuel and potassium perchlorate as the oxidant [AMRL (X) 206]. Replacement of the magnesium fuel with aluminium powder as the fuel [AMRL (X) 210] overcomes the fuel oxidation problem resulting in hydrogen evolution, but, as Figure 5 confirms, there is a significant increase in the amount of smoke produced.

However the graphs shown in Figure 5 also indicate that there is a significant decrease in the smoke output if ammonium perchlorate is used as the oxidant in place of potassium perchlorate. Traditionally ammonium perchlorate is not used widely in pyrotechnics, and there are several reasons for this. Firstly it tends to be hygroscopic, and hence its use would result possible reduction in service life. Secondly and perhaps more importantly, it is generally regarded as a more explosively hazardous component especially if the system is vulnerable to contamination or incompatibility. Recent studies in propellant technology have reported an improved processing capability and chemical and thermal stability using certain binders (e.g., 0.5% Aziridene) to coat the ammonium perchlorate.[9] Its use in pyrotechnic applications has yet to be explored. Even if improved stability and decreased explosive sensitiveness can be obtained by the coating of the ammonium perchlorate, in pyrotechnic applications there is a maximum loading of binder or diluent that can be added before the system no longer functions as designed. For example, in the development of composition, AMRL (X) 210, the flow properties were found to be considerably improved with the addition of 1% of Aerosil.[4] If the Aerosil content was raised above 3% it was observed that the pyrotechnic performance of the composition was degraded.[10]

As mentioned earlier, one of the complaints with aluminium-based photoflash composition has been that the light output has been sufficient to cause temporary flash blindness. This situation is not ideal for training simulators. Results obtained with aluminium/ammonium perchlorate composition indicate that there is no significant decrease in the light output when compared with AMRL (X) 210.

Conclusions

A preliminary study has been undertaken to investigate the use of alternative reactants in training simulator compositions. The main problems with the existing systems have been the rapid oxidation of the magnesium fuel and the increased light and smoke emissions of the aluminium-based compositions.

The initial findings have indicated that there are some advantages (lower smoke at similar noise output) by replacing the potassium perchlorate oxidant with ammonium perchlorate. There are a number of disadvantages associated with the use of ammonium perchlorate in pyrotechnic systems (moisture sensitivity, chemical instability and increased explosive sensitiveness) but more recent processing techniques have been developed (coating of the AP) which have helped to overcome many of those problems.

The results also indicated that the use of non-metallic fuels such as hexamine can certainly reduce the smoke output with only a relatively small reduction in noise output. As a result of this study, one of the outcomes may be to used separate fillings in noise and light simulators.

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