

Prediction of Flame Temperatures, Part 1: Low Temperature Reactions

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ABSTRACT

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

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

Introduction

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

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

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

Method

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

Once ΔH_r is known, a correlation between ΔH_r and flame temperature (T) could be investigated. This was done for 38 reactions with flame temperatures that were published by Shimizu.^[5,6] The results are shown in Figure 1. The heat of reaction was calculated per 100 grams since molar quantities cannot be used for mixtures of many different molecules of different

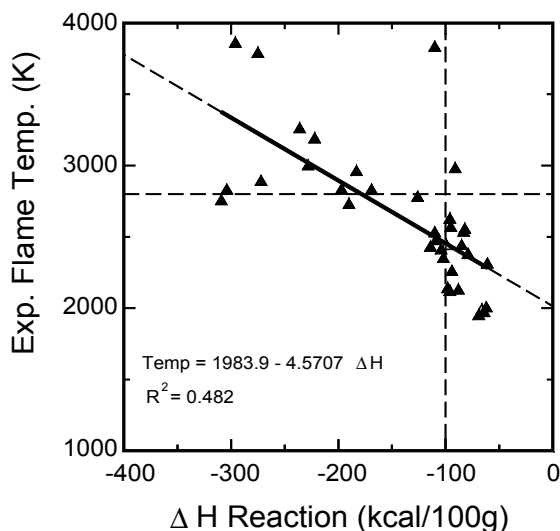


Figure 1. Attempted correlation of ΔH_r with flame temperature.

molecular weights. It can be seen that there is a definite trend to the correlation, but the correlation is not good (correlation coefficient, $R^2 = 0.482$). There are some particularly disturbing features of this graph. For example, reactions with $\Delta H_r = -100$ kcal/100 g $\pm 10\%$ show flame temperatures ranging from 2100 to 3800 K, and reactions that show a flame temperature of about 2800 K come from reactions with ΔH_r ranging from -125 to -300 kcal/100 g. Examination of the points furthest from the line showed that some exhibited the well known temperature lowering effect of organic additives to a magnesium fuel; that is the reactions with a high ΔH_r (~ 300 kcal/100 g) but low flame temperatures (~ 2800 K) contained both magnesium and an organic fuel. However, some “simple” reactions, such as 50:50 mixtures of either barium nitrate or potassium perchlorate ($\text{Ba}(\text{NO}_3)_2$ or KClO_4) and magnesium (Mg) also showed surprising behavior. The two had similar flame temperatures (~ 3800 K), but their ΔH_r differed by almost 200 kcal/100 g. Thus, this simplistic method was deemed to be nearly useless.

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

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

Temp (K)	KCl	K ₂ CO ₃	CO ₂	H ₂ O	O ₂	Na ₂ O	C	H ₂	N ₂	HCl	Cl ₂
300	12.26	20.50	8.89	8.03	7.02	17.45	2.05	6.89	6.69	6.96	8.12
500	13.08	22.50	10.67	8.41	7.43	19.43	3.49	6.99	7.07	7.00	8.62
700	13.86	24.23	11.84	8.95	7.88	21.40	4.44	7.03	7.35	7.16	8.82
900	15.03	26.16	12.66	9.54	8.21	23.38	4.97	7.15	7.67	7.42	8.92
1100	17.2	28.09	13.24	10.15	8.44	25.35	5.30	7.30	7.94	7.69	8.98
1300	17.59	30.02	13.65	10.72	8.60	27.00	5.52	7.49	8.16	7.93	9.03
1500	17.59	31.97	13.95	11.23	8.74	27.03	5.66	7.72	8.33	8.14	9.07
1700	17.59	33.91	14.17	11.67	8.86	27.06	5.76	7.92	8.46	8.31	9.10
1900	9.29	35.87	14.35	12.05	8.97	27.07	5.83	8.11	8.56	8.44	9.13
2100	9.33	36.80	14.49	12.37	9.08	27.10	5.99	8.28	8.64	8.56	9.17
2300	9.37	36.80	14.60	12.63	9.19	27.11	5.94	8.43	8.70	8.66	9.20
2500	9.41	36.80	14.69	12.86	9.30	15.01	5.97	8.58	8.76	8.74	9.24
2700	9.45		14.77	13.06	9.40	15.01	6.01	8.70	8.80	8.81	9.29
2900	9.52		14.84	13.23	9.50	15.01	6.04	8.81	8.84	8.87	9.36
3100	9.56		14.84	13.37	9.60	15.01	6.07	8.91	8.87	8.92	9.40
3300	9.60		14.95	13.50	9.68	15.24	6.10	9.01	8.90	8.97	9.46
3500	9.64		15.00	13.62	9.72		6.13	9.11	8.94	9.04	9.52
3700	9.68		15.05	13.72	9.84		6.16	9.20	8.95	9.09	9.57
3900	9.72		15.09	13.81	9.90		6.20	9.29	8.98	9.11	9.62
4100	9.72		15.14	13.89	9.96		6.23	9.38	9.00	9.13	9.66

capacity of different bodies is not the same. It takes more heat to warm 1 mole of CO₂ by 1 °C than it takes to warm 1 mole of N₂ (8.87 versus 6.96 calories/degree mole). That is because heat is related to motion, and the molecules of carbon dioxide (CO₂) are substantially heavier than the molecules of nitrogen (N₂). Compare two hypothetical reactions which each yield -10.0 kcal. If one reaction gives 1 mole of CO₂ as a product, then the rise in temperature of the gas will be 10.0/0.0087 = 1140°. A similar reaction that yields 1 mole of N₂ will experience a rise in temperature of 10.0/0.0069 = 1440°. Thus, one of the things that will have to be taken into account is the molar quantities and heat capacity of the gaseous and solid products produced in any pyrotechnic reaction.

In addition, the heat capacity of a material is not constant with changing temperature. As a body becomes hotter it generally takes more heat to warm that body by a given temperature difference. For example, it takes 8.87 calories to warm 1 mole of CO₂ by 1 °C at room temperature, but at pyrotechnic temperatures (2500 K) it requires 14.69 calories for the same effect. Thus, to accurately calculate the temperatures of pyro-

technic flames, the changing values of C_p must also be accounted for. The values of C_p used in this study are listed in Table 1. Most of these values were taken from the JANAF tables.^[3] Others were obtained using the formulas for calculating C_p given in the *CRC Handbook*.^[4] In addition to C_p , the phase transition temperatures, heats of transition, or changes in molecular structure are given^[3,4] in Table 2. Where a molecule breaks into two fragments (e.g., Na₂O → NaO + Na) the value for C_p is taken as the sum of the heat capacities for the fragments.

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

Change	Temp. (K)	Heat (kcal/mol)
KCl _(s) → KCl _(l)	1044	+6.28
KCl _(l) → KCl _(g)	1700	+28.7
K ₂ CO _{3(s)} → K ₂ CO _{3(l)}	1170	+7.80
K ₂ CO _{3(l)} → K ₂ O + CO ₂	2100	+106
Na ₂ O _(s) → Na ₂ O _(l)	1193	+10
Na ₂ O _(l) → NaO _(g) + Na _(g)	2250	+108
Cl _{2(g)} → 2Cl _(g)	2100	+30

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

Surprisingly all of the phase transitions *except* that of the vaporization of water had to be taken into account. If the loss of heat due to heat of vaporization (ΔH_{vap}) of water ($\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$) was included in the stepwise temperature calculations, all of the flame temperatures were predicted to be too low by an amount corresponding to $\Delta H_{\text{vap}}(\text{H}_2\text{O})$. This probably reflects the fact that the reaction actually doesn't occur at 298 K, but at an elevated temperature above the boiling point of water. Warming a fuel to a temperature above 373 K (100 °C) requires less heat input than warming and boiling the same amount of water. Liquid water contains a network of strong hydrogen bonds, and the boiling of water requires a large amount of heat to break these hydrogen bonds. Since these hydrogen bonds do not exist in a fuel, no heat is needed to break such hydrogen bonds when raising the temperature of a fuel past 373 K. If the fuel then burns above this temperature, the product water formed will already be in a gaseous state. The fact that other transitions such as the melting of potassium chloride ($\text{KCl}_{(s)} \rightarrow \text{KCl}_{(l)}$) had to be taken into account may reflect the fact that the crystal forces holding potassium chlorate (KClO_3) together are roughly the same as those holding KCl together, so the same answer is obtained no

matter if we calculate ΔH_{vap} for KClO_3 or for KCl. Thus, the calculations still work in spite of the simplifying assumption that the heat of reaction warms a KCl product rather than KClO_3 starting material.

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

This calculation can be simplified slightly by using heats of decomposition which give known products. For example, there is no need to calculate ΔH_f for the decomposition of potassium chlorate ($\text{KClO}_3 \rightarrow \text{K} + \text{Cl} + 3/2 \text{O}_2$) and then recalculate the ΔH_f for potassium chloride ($\text{K} + \text{Cl} \rightarrow \text{KCl}$). Instead one may take the shortcut of adding the heat payback of forming KCl (-104.4 kcal/mol) to the heat cost of decomposing KClO_3 (-95.1 kcal/mol) to find that one actually obtains -10.6 kcal/mol when KClO_3 decomposes. This fact can be experimentally verified by placing a small amount of pure KClO_3 on an anvil and striking it with a hammer. It is possible to get the sample to decompose without a fuel. This is one reason KClO_3 is such a useful yet sensitive and potentially dangerous oxidizer. The ΔH_f and heat of decomposition (ΔH_{decomp}) values used for this study are listed in Table 3.^[1,4,8]

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

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

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

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

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

In this study three numbers were calculated using different methods: (A) The “most stable first” method, in which the reactants that gave the most stable products scavenged all of the oxygen first, followed by the second most stable, etc., until all of the oxygen was consumed. The assumption behind this method is that the product molecules and fragments are in dynamic equilibrium at the reaction temperature,

and react to give a predominance of the most stable products. (B) The “balanced” method, in which all of the reactant molecules were consumed proportional to their concentrations in the reaction. (C) The “hydrogen first” method, in which the hydrogen was consumed first, then the carbon, etc. The basic assumption behind the hydrogen-first method is based on the fact that when a reactant molecule approaches an organic fuel molecule, the hydrogens are the most accessible atoms on the fuel. All three methods were used, and were then judged on their ability to predict the flame temperatures. One method was clearly superior, as shown below.

In addition, one has to be careful to consider possible “secondary” reactions. The accepted mode of decomposition^[1b] for KNO_3 is to give potassium oxide (K_2O), N_2 , and O_2 . However, calculations for ΔH_r for black powder based on these products gave values that were from 22 to 35 kcal/100 g too low compared to the experimental measurement. However, the discrepancy was due to the fact that the experiments were performed in a sealed bomb immersed in a water bath, which held the initial products in close

proximity. As the mixture released its heat to the bomb bath, this allowed the K_2O to combine with the CO_2 releasing additional heat. By adding in the ΔH_r contribution of the reaction of K_2O with CO_2 we were able to obtain a theoretical value of -62.8 kcal/100 g, as compared to the experimental value^[1c] of -66 kcal/100 g.

Results

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

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

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

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

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

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

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

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

Cmpd	KCl		CO ₂		H ₂ O		Na ₂ O		C		H ₂		ΔH
Moles	0.57		1.13		0		0.074		0.1		1.08		
Temp	C _p	ΔH	C _p	ΔH	C _p	ΔH	C _p	ΔH	C _p	ΔH	C _p	ΔH	Rem.:
300	12.26		8.89		8.03		17.45		2.05		6.89		
500	13.08	1.39	10.67	2.00	8.41	0.00	19.43	0.25	3.49	0.04	6.99	1.48	75.87
700	13.86	1.49	11.84	2.41	8.95	0.00	21.4	0.28	4.44	0.06	7.03	1.50	70.16
900	15.03	1.58	12.66	2.67	9.54	0.00	23.38	0.31	4.97	0.08	7.15	1.51	63.92
1100	17.2	5.29	13.24	2.86	10.15	0.00	25.35	1.08	5.3	0.09	7.3	1.54	53.04
1300	17.59	1.96	13.65	2.99	10.72	0.00	27.00	0.37	5.52	0.10	7.49	1.57	46.03
1500	17.59	2.00	13.95	3.08	11.23	0.00	27.03	0.39	5.66	0.11	7.72	1.61	38.81
1700	17.59	18.30	14.17	3.15	11.67	0.00	27.06	0.39	5.76	0.11	7.92	1.66	15.11
1900	9.29	1.05	14.35	3.20	12.05	0.00	27.07	0.39	5.83	0.11	8.11	1.71	8.628
2100	9.33	1.05	14.49	3.24	12.37	0.00	27.10	0.39	5.99	0.11	8.28	1.75	2.058
2300	9.37	1.06	14.6	3.27	12.63	0.00	27.11	0.39	5.94	0.11	8.43	1.78	-4.587
2500	9.41	1.06	14.69	3.29	12.86	0.00	15.01	8.98	5.97	0.11	8.58	1.82	-19.87
2700	9.45	1.07	14.77	3.31	13.06	0.00	15.01	0.22	6.01	0.11	8.7	1.85	-26.46
2900	9.49	1.07	14.84	3.33	13.23	0.00	15.01	0.22	6.04	0.12	8.81	1.87	-33.10
3100	9.52	1.08	14.84	3.35	13.37	0.00	15.01	0.22	6.07	0.12	8.91	1.90	-39.78

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

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

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

Figure 37 of Reference 5 gives flame temperature as a function of the composition of four mixtures of potassium chlorate and shellac, and of the distance along the flame. Figure 2 of this paper is taken from that figure, but has been modified to give temperatures in K. The agreement of the estimated temperature (2160 K) and the temperature one cm from the burning surface (2190 K) is very good. Note that the curve for 70% KClO₃ starts at about 2190 K, then rises to

about 2260 K, and then declines. This can be explained in the following fashion: Since this is a fuel rich mixture, the flame contains substantial amounts of hydrogen and some carbon. As these reactants travel away from the source of the flame, oxygen from the surrounding air dif-

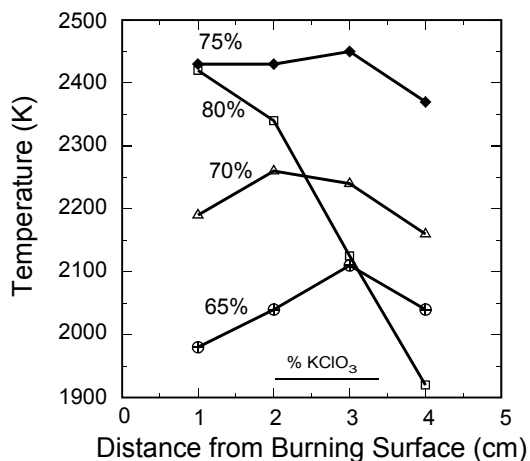


Figure 2. Flame temperature as a function of distance from the burning surface, for a mixture of n% potassium chlorate, 90-n% shellac, and 10% sodium oxalate (after Shimizu).

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

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

The values for 15 reactions containing varying amounts of KClO_3 , KClO_4 , KNO_3 or NH_4ClO_4 with shellac (and with 10% $\text{Na}_2\text{C}_2\text{O}_4$ added for the line reversal method) are reported in Table 5 and shown in Figure 3. The small average error seems to indicate that there is no systematic error in the method. The absolute error is 2% ($46^\circ/2200 \text{ K}$), which is probably within the unreported errors in the experimental methods (for example, the combination of the weighing errors for the compositions tested and the errors in the temperature measurements may well be 2%).

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

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

Average Error, absolute value: 46°

Average Error, signed: $+4.1^\circ$

Estimated Temperatures for ammonium perchlorate taken from Table 6.

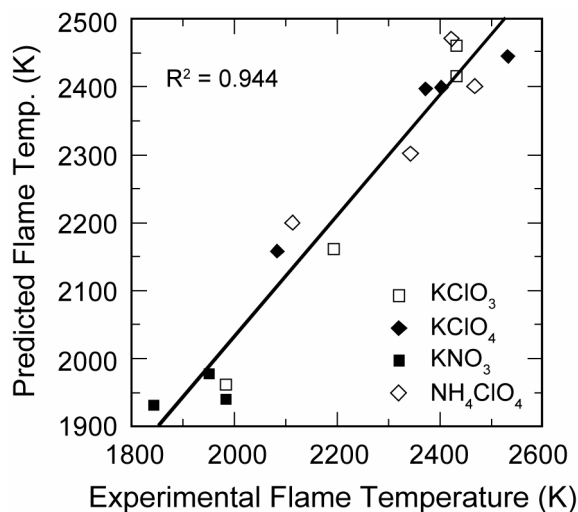
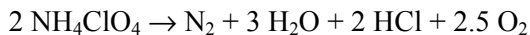


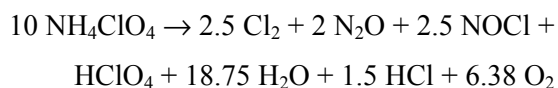
Figure 3. Predicted versus experimental flame temperatures for 15 different mixtures of oxidizer, shellac, and 10% sodium oxalate.

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



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

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



The combination of the lower heat of decomposition and the reduced amount of oxygen available gave an overall ΔH_r which is too low. The effect of the low value of ΔH_r was exacerbated by the increased amount of water formed, since water has a high C_p on a per-gram basis. The estimated flame temperature for an 80% NH_4ClO_4 / shellac/ $\text{Na}_2\text{C}_2\text{O}_4$ flame based on this decomposition scheme was 2283 K, compared to the experimental value of 2423 K. The predicted temperatures were also too low for the reactions containing 75, 70, and 65 percent of

NH_4ClO_4 . Unfortunately, the original paper cited by Conkling was not available at our library, and so some assumptions about the reaction scheme above were made. It seems reasonable to assume that the perchloric acid (HClO_4) was formed *via* incomplete decomposition, since the re-formation of perchloric acid from a mixture of hot radicals of chlorine, hydrogen, and oxygen is entropically very unfavorable. It should be reasonable to assume that given a longer reaction time (or hotter temperature) that the perchloric acid (HClO_4) would not survive the reaction. In addition, it was felt that the N_2O and NOCl had probably formed either through the condensation of intermediate radicals (NO and Cl) or as side product of the quenching of an incomplete reaction (e.g., N_2O).

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

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

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

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

() = Difference with experimental temperature

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

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

Conclusion

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

Acknowledgments

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