

# Thermochemical Calculations for Potassium Ferrate(VI), $K_2FeO_4$ , as a Green Oxidizer in Pyrotechnic Formulations

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**Abstract:** This paper documents the first-time assessment of a novel oxidizer, potassium ferrate(VI), as an alternative to perchlorate and hazardous metal-containing oxidizers in energetic formulations, using thermochemical calculations. Calculations were performed for several different types of pyrotechnic formulations using the NASA Chemical Equilibria with Applications (NASA-CEA) program. Formulations used in devices including smokes, illuminants, signals, igniters, delays, and flashes were evaluated to determine the feasibility of using potassium ferrate(VI) as an alternative oxidizer. The calculated adiabatic flame temperatures and

equilibrium combustion products for the proposed formulations were compared to those of common baseline formulations for different pyrotechnic applications to determine the likelihood of functional success of potassium ferrate(VI)-based formulations. Based on these initial data, it is highly probable that formulations incorporating potassium ferrate(VI) will result in reactive compositions for a variety of pyrotechnic applications. This material could address environmental concerns about perchlorate and heavy metal contamination by offering an environmentally-friendly alternative oxidizer.

**Keywords:** Potassium Ferrate(VI) • Iron • Potassium • NASA-CEA • Oxidizers

## 1 Introduction

Many pyrotechnic compositions contain oxidizers that are not environmentally friendly, such as perchlorates and those containing heavy metals. Replacement of perchlorate oxidizers in military munitions has been an area of strong emphasis over the past two decades [1–3]. In addition to the perchlorate oxidizer issue, the problems with heavy metals in pyrotechnic formulations have also raised concern. In many cases heavy metal oxidizers are still being used in pyrotechnic formulations and still pose detrimental environmental and health effects [4]. Barium chromate has two major health and environmental impacts due to its barium and chromium (VI) content. The use of boron carbide and high nitrogen compounds as alternatives to oxidizers containing perchlorate and heavy metals has recently been reported [5–8].

Potassium ferrate(VI) is not a new material [9]. Its application as an oxidizer, though, is relatively new. It recently has been hailed as a “green” super oxidizer in the treatment of wastewater [10,11]. Recent advances in the synthesis of potassium ferrate(VI) have made its use more feasible in applications such as wastewater treatment. Potassium ferrate(VI) has also been studied for use in developing ‘super-iron’ batteries [12,13].

Potassium ferrate(VI) (CAS # 13718-66-6) has the following formula,  $K_2FeO_4$  and is a paramagnetic salt. This iron compound has an unusually high oxidation state, +6, in comparison to more familiar iron compounds in the oxidation state +2 or +3 ( $Fe^{2+}$  or  $Fe^{3+}$ ). Owing to its high oxidation state,  $Fe^{VI}O_4^{2-}$  serves as a powerful oxidizing agent.

As a dry solid,  $K_2FeO_4$  is stable but it decomposes with evolution of  $O_2$  in neutral water. In acidic (low pH) conditions, the decomposition is rapid and if using this oxidizer in energetic formulations, care must be taken to work with non-acidic conditions.

Potassium ferrate(VI) is considered a very good candidate for use as an oxidizer due to its “super-oxidative” characteristics as well as its “green” by-products. The by-product, rust ( $Fe_2O_3$ ), is non-toxic, stable, and non-corrosive. In contrast, some related oxidants such as chromate are considered environmentally hazardous. Many of the contaminants in wastewater can be removed by  $Fe^{VI}$  in seconds to minutes with formation of non-hazardous products.  $Fe^{VI}$  is also a disinfectant, antifoulant, and coagulant, and therefore a promising multi-purpose wastewater treatment chemical.  $K_2FeO_4$  is also a selective oxidant for a large number of organic compounds with  $Fe^{III}$  as a by-product.  $Fe^{VI}$  therefore has a role in cleaner (‘greener’) technology for organic synthesis.

The use of potassium ferrate(VI) as an oxidizer in energetic formulations has for the most been overlooked; although in 2009, Battelle Memorial Institute developed a thermite patent [14]. This paper reports the first assess-

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ment of potassium ferrate(VI) as a possible alternative to oxidizers containing perchlorates, heavy metals, and chromium for use in pyrotechnics.

## 2 Computational Method

The main goal of this study was to determine the utility of potassium ferrate(VI) as a pyrotechnic oxidizer. Therefore, baseline compositions covering a wide variety of pyrotechnic applications were selected for the study. These baselines were selected from the literature or are related to compositions used in fielded items. Additional 'exploratory' baselines were identified to include formulations with a range of different oxidizers (potassium chlorate, potassium perchlorate, barium chromate). These were chosen to determine the suitability of potassium ferrate(VI) as a replacement oxidizer. Formulations with a range of different fuels (sugar, magnesium, boron, aluminum, tungsten) were chosen to determine their predicted reactivity with potassium ferrate(VI).

The NASA-CEA code [15] was used to predict combustion products and adiabatic reaction temperatures for the formulations. These parameters provide an indication of how a formulation might perform for a particular application. For example, a delay composition relies on solid combustion products to reliably and repeatably transfer energy to another material at a tightly controlled rate. A colored smoke composition relies on cool gaseous combustion products to sublime and transport colored dye into an extended cloud for signaling. Analysis of the predicted combustion products and temperatures for the replacement formulations can give insight into potential applications to which the formulation may be suited.

NASA-CEA code can be run in several different modes, depending on the information desired. For this study, the enthalpy and pressure were assumed to be constant (hp mode,  $P=0.1$  MPa). The reactants, weight percentages thereof, and enthalpies of formation for species not included in the thermal database were input to the program. The enthalpy of formation for potassium ferrate(VI) was estimated from the enthalpies of dipotassium and ferrate ions [16]. Based on the elemental species contained in the reactants, the program will identify all possible products from the thermal database, then iteratively solve for the percentage of products and reaction temperature at chemical equilibrium; in other words, the change in Gibbs free energy for the system will equal zero, assuming that the sum of the enthalpies of the products at the reaction temperature is equal to the sum of the enthalpies of the reactants at the input condition (in this case, 298.15 K).

In many cases the code was run iteratively to determine the stoichiometric weight percentages for a set of ingredients. The stoichiometries for the exploratory baseline formulations were determined iteratively using the NASA-CEA code, such that excess fuel or oxidizer was eliminated in

the list of products. Formulations containing potassium ferrate(VI) as a replacement for the oxidizer in the baseline formulations were created either by directly replacing the oxidizer with ferrate without adjusting percentages, or by iteratively determining balanced stoichiometries using the NASA-CEA code.

The predicted product species are limited only to those contained in the database. The products are those expected at equilibrium, which is most likely not achieved in a dynamic combustion situation. The output temperature is the maximum that could be attained assuming that all energy evolved from the reaction is transferred into the products, with no loss of heat to the surroundings by convection, conduction, or radiation. These results do not give information about reaction rates, how easily the material is ignited, or whether combustion can be sustained. They do, however, give an approximation of the maximum reaction temperature that can be attained, the dominant reaction pathway, and the phase of the reaction products.

Another limitation of the NASA-CEA code is its inability to sometimes handle mixtures that are far from stoichiometric. This occurs particularly when the temperature at which the calculation is attempting to converge is near the temperature at which a phase change occurs for one of the products. For a fuel-rich case, oxygen may be added to the reactants to enable more of the fuel to react. This will boost the adiabatic reaction temperature to an artificially high level. The amount of oxygen included in such a case is the minimum amount required for convergence. The amount is reported as a percentage in excess of the other reactants, which total 100%.

## 3 Results and Discussion

The results of all analyses will be presented by composition type to facilitate discussion. In each of the subsequent sections, a Table will present the baseline and replacement formulations, predicted reaction temperatures, distribution of reaction products and their phases.

### 3.1 Colored Smoke Base Compositions

The smoke base compositions are given in Table 1. These formulations are fuel-rich and in practice will also contain an organic dye, which is sublimed to form smoke, and a coolant, which acts to reduce the reaction temperature and slow the burn rate. For these calculations no dye was included, since the NASA-CEA code will predict complete combustion for organic dyes. This would yield products including carbon oxides, water and nitrogen oxides, and the reallocation of energy to combust the dye would reduce the predicted reaction temperature significantly. Therefore, only fuels and oxidizers are included in the formulations to compare their predicted reaction temperatures and products.

**Table 1.** Colored smoke base compositions.

Replacement	wt-%	Products	Phase	wt-%	Baseline	wt-%	Products	Phase	wt-%
Mix A		CO	g	9.487	Mix B [17]		CO	g	23.905
$K_2FeO_4^a$	75	CO <sub>2</sub>	g	7.013	KClO <sub>3</sub> <sup>c</sup>	59	CO <sub>2</sub>	g	25.698
$C_{12}H_{22}O_{11}^b$	25	H <sub>2</sub>	g	1.012	$C_{12}H_{22}O_{11}^b$	41	HCl	g	0.784
		H <sub>2</sub> O	g	5.420			H <sub>2</sub>	g	0.631
<i>T</i> [K]		KOH	g	0.037	<i>T</i> [K]		H <sub>2</sub> O	g	17.762
1173		Fe	s	9.249	2006		K	g	0.330
		Fe <sub>947</sub> O	s	15.489			KCl	g	29.858
Fraction condensed		K <sub>2</sub> CO <sub>3</sub>	s	18.630	Fraction condensed		KOH	g	0.737
0.77		K <sub>2</sub> CO <sub>3</sub>	l	33.660	0.00		K <sub>2</sub> Cl <sub>2</sub>	g	0.281
		trace		0.004			OH	g	0.010
							trace		0.005

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = -1027.98\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -2223.13\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = -391.77\text{ kJ mol}^{-1}$ .

The baseline formulation (Mix B [17]) contains the main fuel (sucrose) and oxidizer (potassium chlorate) used in colored smoke formulations. The predicted reaction temperature for Mix B is 2006 K, and all products are gaseous. In practice, the temperature can be lowered to 900 to 1100 K by adjusting the amount of binder and cooling agents (sodium hydrogen carbonate, for example) added to ensure that the dye will sublime rather than combust.

The replacement formulation (Mix A) is an oxidizer rich mixture of potassium ferrate(VI) and sucrose. The predicted reaction temperature of 1173 K is much cooler, and a significant fraction of the products are condensed species. Because a fairly cool temperature is predicted, a coolant may not be required for smoke formulations containing potassi-

um ferrate(VI). This could be an added benefit to the replacement by potassium ferrate(VI). However, the large fraction of condensed species might be unfavorable for smoke cloud formation, as gaseous products may more efficiently transport the volatilized dye into the air.

### 3.2 Illuminant Compositions

The illuminant compositions are given in Table 2. The baseline formulation (Mix E [18]) contains the fuel (magnesium) and oxidizer (sodium nitrate) used in standard illuminating rounds. It has a high reaction temperature (> 3100 K) and a single condensed product, molten magnesium oxide. Mix C contains magnesium and potassium ferrate(VI). It is pre-

**Table 2.** Illuminant compositions.

Replacements	wt-%	Products	Phase	wt-%	Baseline	wt-%	Products	Phase	wt-%
Mix C		Fe	g	0.508	Mix E [18]		Mg	g	14.286
Mg <sup>a</sup>	25	FeO	g	0.463	Mg <sup>a</sup>	53	MgO	g	5.409
$K_2FeO_4^b$	75	K	g	28.346	NaNO <sub>3</sub> <sup>d</sup>	47	NO	g	0.258
		KO	g	1.681			N <sub>2</sub>	g	7.623
<i>T</i> [K]		K <sub>2</sub>	g	0.045	<i>T</i> [K]		Na	g	12.654
2793		K <sub>2</sub> O	g	0.037	3171		NaO	g	0.088
		Mg	g	0.097			O	g	0.458
Fraction condensed		MgO	g	0.126	Fraction condensed		O <sub>2</sub>	g	0.427
0.68		O	g	0.134	0.59		MgO	l	58.784
		O <sub>2</sub>	g	0.996			trace		0.012
		Fe <sub>947</sub> O	l	26.397					
		MgO	s	41.171					
Mix D		CO	g	10.318					
Mg <sup>a</sup>	40	Fe	g	0.025					
$K_2FeO_4^b$	45	H <sub>2</sub>	g	0.969					
$C_{12}H_{22}O_{11}^c$	15	K	g	17.712					
		KH	g	0.032					
<i>T</i> [K]		K <sub>2</sub>	g	0.024					
1962		Mg	g	15.143					
		C	s	1.884					
Fraction condensed		Fe	l	12.664					
0.56		MgO	s	41.213					
		trace		0.016					

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -1027.98\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = -2223.13\text{ kJ mol}^{-1}$ ; <sup>d</sup> $\Delta H_f(298.15\text{ K}) = -467.44\text{ kJ mol}^{-1}$ .

**Table 3.** Ignition compositions.

Replacement	wt-%	Products	Phase	wt-%	Baseline	wt-%	Products	Phase	wt-%
Mix F		BO	g	0.283	Mix G [19]		BO	g	1.574
B <sup>a</sup>	15	BO <sub>2</sub>	g	2.268	B <sup>a</sup>	22.2	BO <sub>2</sub>	g	0.010
K <sub>2</sub> FeO <sub>4</sub> <sup>b</sup>	85	B <sub>2</sub> O <sub>2</sub>	g	0.305	KNO <sub>3</sub> <sup>d</sup>	77.8	B <sub>2</sub> O <sub>2</sub>	g	34.022
O <sub>2</sub> <sup>c</sup>	15 <sup>f</sup>	B <sub>2</sub> O <sub>3</sub>	g	13.669			B <sub>2</sub> O <sub>3</sub>	g	1.523
		Fe	g	10.613			K	g	12.202
T [K]		FeO	g	0.648	T [K]		KBO <sub>2</sub>	g	37.456
2763		K	g	0.294	2558		N <sub>2</sub>	g	7.639
		KBO <sub>2</sub>	g	60.523			BN	s	5.562
Fraction condensed		O	g	0.011	Fraction condensed		trace		0.011
0.11		Fe	l	4.243	0.06				
		Fe <sub>947</sub> O	l	7.137	Mix H		BCl	g	0.420
		trace		0.006	B <sup>a</sup>	22	BCl <sub>2</sub>	g	0.048
					KClO <sub>4</sub> <sup>e</sup>	78	BO	g	10.075
							BOCl	g	6.417
							BO <sub>2</sub>	g	0.509
					T [K]		B <sub>2</sub> O <sub>2</sub>	g	32.650
					3070		B <sub>2</sub> O <sub>3</sub>	g	6.978
							Cl	g	2.084
					Fraction condensed		K	g	2.227
					0.00		KBO <sub>2</sub>	g	9.440
							KCl	g	29.120
							K <sub>2</sub> Cl <sub>2</sub>	g	0.012
							trace		0.020

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -1027.98\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>d</sup> $\Delta H_f(298.15\text{ K}) = -494.47\text{ kJ mol}^{-1}$ ; <sup>e</sup> $\Delta H_f(298.15\text{ K}) = -433.42\text{ kJ mol}^{-1}$ ; <sup>f</sup> oxygen was included in the composition so that the simulation would converge.

dicted to have a somewhat lower combustion temperature (approx. 2800 K) and an additional condensed product of iron(II) oxide. Both of these mixtures are fuel-rich. Based on temperatures and condensed species, Mix C may be a feasible illuminant, as magnesium burns brightly.

Mix D is oxidizer-rich with a blend of magnesium and sucrose fuels. Sucrose was added to the mixture with the intent of reducing the reaction temperature and, in practice, slowing the reaction rate. The shift in stoichiometry should further these effects. Indeed the predicted reaction temperature is reduced significantly (1962 K). The fraction of condensed products is close to that of the baseline Mix E, with species of particulate carbon, molten iron and magnesium oxide predicted. Mix D is not as attractive a candidate for an illuminant application.

### 3.3 Ignition Compositions

The common igniter composition, boron-potassium nitrate (B-KNO<sub>3</sub>) [19] was included in the replacement study, as shown in Table 3. This composition (Mix G) has a predicted combustion temperature of 2558 K, and a very small fraction (0.06) of particulate boron nitride as a product. In order for this simulation to run, an additional amount of oxygen had to be added as a reactant.

The replacement mix with boron and potassium ferrate(VI) (Mix F) has a higher reaction temperature (2763 K) than Mix G and a higher fraction (0.11) of partially oxidized molten

iron as its condensed product. These characteristics would make it a good igniter.

As potassium perchlorate is one of the oxidizers we are interested in replacing with potassium ferrate(VI), its behavior with boron was also investigated. Mix H is a stoichiometric mixture with a predicted combustion temperature of 3070 K and no condensed products. Mix F has a combustion temperature 300 degrees lower than Mix H and small fraction of condensed products. In general, boron with potassium ferrate(VI) will burn cooler than boron with potassium perchlorate, but hotter than boron with potassium nitrate.

### 3.4 Boron Delay Compositions

A common boron delay formulation is listed in Table 4. Mix J [20] is a slightly fuel rich mixture of boron and barium chromate. It has a predicted reaction temperature near 2100 K, and a high condensed fraction (0.71), comprised mainly of molten boric oxide and solid barium oxide and chromium. Two ferrate-containing compositions were simulated. Mix F (Table 3) is an oxidizer-rich mixture of boron and potassium ferrate(VI), with a predicted reaction temperature of 2756 K and a condensed fraction of only 0.11. This is significantly hotter and has a much higher fraction of gaseous products than the baseline. For this reason Mix F may not function well as a delay.

Mix I is fuel-rich and contains poly(vinyl chloride) (PVC) in addition to boron and potassium ferrate(IV). Oxygen was included in this simulation to obtain convergence. In both

**Table 4.** Boron delay compositions.

Replacements	wt-%	Products	Phase	wt-%	Baselines	wt-%	Products	Phase	wt-%
Mix I		BO	g	0.098	Mix J [20]		BO	g	0.017
B <sup>a</sup>	22	B <sub>2</sub> O <sub>2</sub>	g	12.327	B <sup>a</sup>	10	B <sub>2</sub> O <sub>2</sub>	g	5.899
K <sub>2</sub> FeO <sub>4</sub> <sup>b</sup>	73	B <sub>2</sub> O <sub>3</sub>	g	0.923	BaCrO <sub>4</sub> <sup>e</sup>	90	B <sub>2</sub> O <sub>3</sub>	g	1.109
C <sub>2</sub> H <sub>3</sub> Cl <sup>c</sup>	5	CO	g	4.074	O <sub>2</sub> <sup>d</sup>	3 <sup>f</sup>	Ba	g	0.207
O <sub>2</sub> <sup>d</sup>	10 <sup>f</sup>	Fe	g	0.127			BaO	g	0.021
		FeCl <sub>3</sub>	g	3.928	T [K]		Cr	g	0.026
T [K]		HBO	g	2.586	2116		B	s	0.132
2156		HBO <sub>2</sub>	g	0.070			B <sub>2</sub> O <sub>3</sub>	l	22.045
		H <sub>2</sub>	g	0.123	Fraction condensed		BaO	s	52.635
Fraction condensed		K	g	3.448	0.71		Cr	s	17.910
0.25		KBO <sub>2</sub>	g	47.657					
		B	s	7.390					
		Fe	l	17.234					
		trace		0.014					

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -1027.98\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = -96.09\text{ kJ mol}^{-1}$ ; <sup>d</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>e</sup> $\Delta H_f(298.15\text{ K}) = -1447.38\text{ kJ mol}^{-1}$ ; <sup>f</sup> oxygen was included in the composition so that the simulation would converge.

cases where potassium ferrate(VI) was substituted for barium chromate, more gaseous products are predicted than for the baseline. The addition of PVC did cool the temperature to near that of the baseline but still yielded a low percentage of condensed products. In addition, the chlorine in the PVC reacts to form FeCl<sub>3</sub>, which is highly corrosive and, as such, is an undesirable product.

### 3.5 Tungsten Delay Compositions

Mix L [21] is a common delay formulation containing tungsten fuel, barium chromate and potassium perchlorate oxidizers, and VAAR (vinyl acetate alkyl resin) binder, as shown in Table 5. This is fuel-rich and has a predicted combustion

temperature of 1602 K and a condensed product fraction of 0.88. Tungsten with potassium ferrate(VI) (Mix K) is a stoichiometric mixture with a predicted combustion temperature of 1375 K and all condensed products. Oxygen (16%) had to be included in the simulation for convergence. Mix K may be a feasible replacement for a delay application.

### 3.6 Flash Compositions

Both magnesium and aluminum when combined with potassium perchlorate react with a very energetic flash and report. Mix N [22] in Table 6 is a slightly fuel-rich flash composition. It contains more aluminum fuel than a typical oxidizer-rich flash composition would. Its predicted reaction

**Table 5.** Tungsten delay compositions.

Replacements	wt-%	Products	Phase	wt-%	Baseline	wt-%	Products	Phase	wt-%
Mix K		O <sub>2</sub>	g	0.030	Mix L [21]		BaCl <sub>2</sub>	g	0.175
W <sup>a</sup>	31.7	Fe <sub>2</sub> O <sub>3</sub>	s	23.617	W <sup>a</sup>	48	Ba(OH) <sub>2</sub>	g	0.019
K <sub>2</sub> FeO <sub>4</sub> <sup>b</sup>	68.3	KO <sub>2</sub>	l	42.059	BaCrO <sub>4</sub> <sup>d</sup>	38.4	CO	g	2.599
O <sub>2</sub> <sup>c</sup>	16 <sup>g</sup>	WO <sub>3</sub>	s	34.294	KClO <sub>4</sub> <sup>e</sup>	9.6	CO <sub>2</sub>	g	2.225
					C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> <sup>f</sup>	4	HCl	g	0.010
T [K]							H <sub>2</sub>	g	0.116
1375					T [K]		H <sub>2</sub> O	g	1.708
					1602		K	g	0.022
Fraction condensed					Fraction condensed		KCl	g	4.271
1.00					0.88		KOH	g	0.092
							K <sub>2</sub> Cl <sub>2</sub>	g	0.731
							(WO <sub>3</sub> ) <sub>3</sub>	g	0.016
							BaCO <sub>3</sub>	s	8.107
							BaCl <sub>2</sub>	l	0.024
							BaO	s	16.779
							Cr <sub>2</sub> O <sub>3</sub>	s	11.520
							W	s	27.320
							WO <sub>2</sub>	s	24.257
							trace		0.008

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -1027.98\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>d</sup> $\Delta H_f(298.15\text{ K}) = -1447.38\text{ kJ mol}^{-1}$ ; <sup>e</sup> $\Delta H_f(298.15\text{ K}) = -433.42\text{ kJ mol}^{-1}$ ; <sup>f</sup> $\Delta H_f(298.15\text{ K}) = -640.61\text{ kJ mol}^{-1}$ ; <sup>g</sup> oxygen was included so that the simulation would converge.

**Table 6.** Flash compositions.

Replacement	wt-%	Products	Phase	wt-%	Baseline	wt-%	Products	Phase	wt-%
Mix M		Al	g	0.017	Mix N [22]		Al	g	3.486
Al <sup>a</sup>	26.65	Al <sub>2</sub> O	g	0.021	Al <sup>a</sup>	40	AlCl	g	8.337
K <sub>2</sub> FeO <sub>4</sub> <sup>b</sup>	73.35	Fe	g	11.593	KClO <sub>4</sub> <sup>c</sup>	60	AlCl <sub>2</sub>	g	0.051
		FeO	g	0.087			AlO	g	7.494
T [K]		K	g	28.912	T [K]		AlOCl	g	0.742
2823		KO	g	0.015	3802		AlO <sub>2</sub>	g	0.206
		K <sub>2</sub>	g	0.039			Al <sub>2</sub> O	g	7.244
Fraction condensed		Al <sub>2</sub> O <sub>3</sub>	l	50.281	Fraction condensed		Al <sub>2</sub> O <sub>2</sub>	g	2.739
0.59		Fe	l	9.023	0.39		Al <sub>2</sub> O <sub>3</sub>	g	0.019
		trace		0.011			Cl	g	4.084
							K	g	9.923
							KCl	g	12.947
							KO	g	0.306
							O	g	2.852
							O <sub>2</sub>	g	0.779
							Al <sub>2</sub> O <sub>3</sub>	l	38.779
							trace		0.012

<sup>a</sup> $\Delta H_f(298.15\text{ K}) = 0\text{ kJ mol}^{-1}$ ; <sup>b</sup> $\Delta H_f(298.15\text{ K}) = -1447.38\text{ kJ mol}^{-1}$ ; <sup>c</sup> $\Delta H_f(298.15\text{ K}) = -433.42\text{ kJ mol}^{-1}$ .

temperature is 3802 K, the highest predicted in this study. Its only condensed product is alumina. Mix M is a stoichiometric mix of aluminum and potassium ferrate(VI). Its predicted reaction temperature is 1000 K lower, with nearly 60% condensed products. Mix C (Table 2), which contains magnesium and potassium ferrate(VI), has a similar predicted temperature and condensed products. The predicted temperature is also close to the predicted temperature for boron and ferrate (Mix F, Table 3). In general, when perchlorate is replaced with ferrate, temperature is reduced and more condensed species are formed. This reduction in temperature may not be favorable for use as a flash composition.

## 4 Conclusions and Future Work

Thermochemical calculations indicated that potassium ferrate(VI) may be a feasible alternative oxidizer. Flame temperatures and combustion products were comparable to baseline formulations in several, but not all cases. This material may be a viable oxidizer for smokes, illuminants, igniters, and tungsten-based delays. It is noted that in all cases where potassium ferrate was directly substituted for potassium perchlorate, the temperature predicted was significantly lower (300 K–1000 K). For this reason potassium ferrate(VI) may not be a suitable drop-in replacement for potassium perchlorate.

Potassium ferrate(VI) is environmentally friendly because it contains no heavy metals, chlorides, or other halogen impurities. Its ultimate reaction by-product is rust (Fe<sub>2</sub>O<sub>3</sub>). This species is used as a pyrotechnic oxidizer itself, so it may provide a secondary reaction or catalytic effect. This could further oxidize the combustion products to much more environmentally-friendly chemical species.

Potassium ferrate(VI) is a strong oxidizer, and in the presence of moisture, may degrade and oxidize materials it is in contact with, particularly organics. Initial studies indicate that ferrate is stable at ambient humidity conditions. Further study is needed to determine its stability and compatibility at elevated temperatures and humidity.

Based on these initial data, it is highly probable that formulations incorporating potassium ferrate(VI) will result in reactive compositions that will ignite and sustain combustion. Because a single set of percentages was used to perform calculations, formulation adjustments will be needed to obtain required temperature and reaction rates in practice. A set of formulations has been identified for further study and characterization, including combustion testing.

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