An earlier version appeared in *Pyrotechnica IX* (1984).

The Physics, Chemistry and Perception
of Colored Flames

Part II

K. L. Kosanke

4.0 The Chemistry of Colored Flames

4.1 A Summary of General Chemistry for Colored Flame Production

This paper is intended to benefit readers who do not enjoy a thorough understanding of chemistry. Thus, before dealing with more advanced topics, a discussion of some aspects of general chemistry may be of benefit. Any reader with an understanding of chemical symbols and the Periodic Table, chemical formulas and IUPAC nomenclature, chemical equations, the idea of reversibility and Le Châtelier's Principle, stoichiometry and mole weights should skip ahead to section 4.2.

4.1.1 Chemical Symbols and the Periodic Table

The ancient Greeks believed that all material substances were composed of four basic elements: water, air, earth and fire. This idea, however wrong, showed profound insight. Their theory of basic elements recognized the fact that there are not millions of different fundamental substances, but rather these millions of substances are just different combinations of a few basic elements. This concept, basic elements in different combinations, is what got the whole idea of chemistry started; if you knew the basic elements and how to combine them, you could make anything you wanted.

Eventually, when the scientific method replaced philosophic rationalizing as the manner of conducting research, it became apparent that the Greeks' four elements didn't suffice, and the search was on for the real chemical elements. By the mid-nineteenth century, most of the elements had been discovered, named and given a shorthand chemical symbol. The name and chemical symbol for those elements most often encountered in pyrotechnics are listed in Table 1. (The utility of these chemical symbols will become increasingly clear as we continue working through this chemistry section.)

Early on, it was observed that there were groups of chemical elements that had similar physical and chemical properties. For example, one group of elements were all soft metals, an-

Table 1. Element Names and Atomic Symbols Commonly Used in Pyrotechnics.

Element Name	Atomic Symbol
Aluminum	Al
Antimony	Sb
Arsenic	As
Barium	Ba
Calcium	Ca
Chlorine	Cl
Copper	Cu
Hydrogen	H
Iron	Fe
Lead	Pb
Magnesium	Mg
Mercury	Hg
Nitrogen	N
Oxygen	O
Phosphorus	P
Potassium	K
Silicon	Si
Sodium	Na
Strontium	Sr
Sulfur	S
Titanium	Ti
Zinc	Zn

other group were all gases. Also all members of a group combined with elements of other groups in the same proportion, making compounds that again had similar properties. One of the groups, called alkali metals, consists of lithium, sodium, potassium, rubidium, cesium and francium. If you know something about the chemistry of ONE of these elements, you also know a little about the chemistry of ALL the others. For example, you probably know that sodium combines readily with chlorine to make common table salt, sodium chloride. Because lithium and potassium are members of the same group of elements, you can be reasonably certain that both lithium and potassium combine with chlorine to make lithium chloride and potassium chloride. You can also be reasonably certain that both lithium chloride and potassium chloride will have properties similar to sodium chloride, i.e., all will taste salty, all will be soluble in water and all will form crystals with similar appearance, hardness, and melting points, etc.

Chlorine, too, is a member of a chemical group, called halogens, consisting of fluorine, chlorine, bromine, iodine and astatine. With this information and your knowledge of sodium chloride, you can be rather confident about the existence of sodium fluoride, sodium bromide, potassium fluoride, etc., and you will know something about the properties of these compounds.

A knowledge of chemical groups combined with only a little other chemical knowledge gives you great predictive powers. A knowledge of sodium and chlorine, and the way they combine allows you to speculate on the existence, manner of combining and properties of a large number of compounds, in this case 30 (six alkali metals times five halogens).

It was realized very early in the systematic study of chemistry that the organization of chemical elements into relatively few groups would allow a great simplification of the subject. If all chemical elements could be organized in this fashion, and you learned the way the groups interact with one another, then you could speculate about tens of thousands of possible reactions. This would be a very great simplification indeed.

In 1869 Mendeleyev successfully organized all the chemical elements known at the time into a table (in order of increasing mass of the elements), in which the elements fell into the known groups. In fact, he was so successful that he was able to predict the existence of several then unknown elements because of unfilled positions in his table of elements. With only slight modification, Mendeleyev's arrangement of chemical elements has become known as the Periodic Table of Elements. It is called "Periodic" Table because, in a listing of chemical elements in order of increasing mass, chemical and physical properties repeat periodically. In essence, what Mendeleyev did was to lay out the elements from left to right, as they increased in mass. Each time elements seemed to be repeating properties of earlier elements, he started a new row. Thus the elements lithium, sodium and potassium all came to fall in the same column, because they all behaved similarly.

Today we understand the underlying reason why the Periodic Table appears as it does and why the properties of the elements repeat themselves. The reason is related to the way electrons arrange themselves about the nucleus of the different chemical elements. A discussion of these different electron arrangements and why they exist might be interesting to a few readers, but is beyond the scope of this paper.

Before leaving the subject of the Periodic Table, it is appropriate to spend a little more time to make it a useful tool. Below is a summary of what has already been said about the Periodic Table and some of the additional information contained in it. (A copy of the Periodic Table is included at the end of this article.)

(A) Each vertical column is representative of a chemical group of elements, with generally similar properties. This includes "physical" properties like melting points, metallic or non-metallic character, crystal structure, etc., as well as "chemical" properties such as tendency to combine with other elements, the relative proportions in which they combine, etc.

(B) Molecules formed by combining different elements of the same two groups will generally have similar physical properties. Thus, sodium chloride, lithium bromide and po-

tassium fluoride, etc., all are crystalline in nature, all are water soluble and all have rather high melting points.

(C) Some of the information contained in the Periodic Table of Elements is:

(1) Group number: The number of each chemical group, IA to VIIIA, is printed above the top chemical element in each vertical column.

(2) Chemical symbol: The shorthand symbol for each of the chemical elements is printed in the center of the square for that element. Also in each square is the name of the element.

(3) Atomic number: In the upper left hand corner of each square the element's atomic number is printed. This is the number of protons in the nucleus of each atom of that particular chemical element. It also equals the number of electrons orbiting each neutral atom of that chemical element.

(4) Atomic weight: The atomic weight for each element is printed in the upper right hand corner of each box. Atomic weights are proportional to the weight of one atom of that chemical element.

4.1.2 Chemical Formulas and IUPAC Nomenclature

Using the chemical symbols from the Periodic Table, a systematic chemical shorthand has been developed to describe combinations of chemical elements forming molecules. Use of that shorthand will simplify our discussions as well as shorten this paper significantly. For chemical elements in their natural atomic state, the shorthand notation is just to use the chemical symbol, instead of writing out the full chemical name. Thus, the symbol Na is used in place of the name sodium; Cl is used for chlorine, etc.

In the case of chlorine, the symbol Cl means chlorine atoms; however, chlorine is a diatomic gas under normal conditions. Diatomic means that chlorine molecules consist of pairs of chlorine atoms bound to each other. Instead of writing this as ClCl, it is written Cl_2. The subscript 2 means that two atoms of chlorine have combined to form a diatomic molecule. All gaseous elements, except those in group VIIIA, normally exist as diatomic molecules. Some examples are hydrogen (H_2), oxygen (O_2), and nitrogen (N_2).

In general, numeric subscripts are used to indicate when a molecule is composed of more than one atom of the same element. Another familiar molecule is water, H_2O. Here two atoms of hydrogen and one atom of oxygen are bound together to form a single molecule.

A chemical formula is the shorthand method of describing the type and number of atoms in a compound (molecule). Above, H_2O, Cl_2, O_2, etc., are all chemical formulas.

In order to avoid possible confusion, let me point out that sometimes when people talk about chemical formulas, they are really talking about something quite different. Sometimes recipes are mistakenly called chemical formulas. When someone tells you to mix one part water and one part dirt to make mud, they may be giving the formula for making mud, they have not given you the chemical formula for mud. There is quite a difference, the former is a recipe and the latter is the EXACT way in which atoms combine to form compounds.

At the beginning of this section, I said that elements in their "normal" atomic state are described by using their chemical symbol. This is true, but I should have been more specific and said "in their normal atomic state under standard thermodynamic conditions". Standard thermodynamic conditions are 25 °C and one (1) atmosphere pressure. (This should not be confused with standard temperature and pressure (STP) which is 0 °C and one atmosphere pressure.) The reason to be more specific is that by changing temperature and pressure, the normal state of elements and molecules changes. At 25 °C copper is a solid, above 1100 °C, it is a liquid, and above 2600 °C, it is a gas. When something is in some state other than its standard state, it is indicated by the use of (g), (l) and (s) as subscripts. The parentheses are normally used and g, l and s indicate gases, liquids and solids, respectively. Thus $Cu_{(l)}$ indicates we mean liquid copper and $Cu_{(g)}$ indicates gaseous copper. Sometimes, in order to make a point or to avoid possible confusion, even an element in its normal room temperature state will have its

state designated using these same symbols. It is not necessary to write $Cu_{(s)}$, but it is OK.

Another thing it is necessary to indicate in a chemical formula is whether something is electrically charged, i.e., whether it is a neutral atom or molecule, or an ion (charged). This is accomplished using a superscript plus or minus after the chemical symbol or formula. For example, Cl^- indicates a chlorine ion with a charge of minus one; Na^+ indicates a sodium ion with a plus one charge. If the charge of the ion is more than plus or minus one, a numeral is added before the sign. Thus Ca^{2+} indicates a calcium ion with two units of positive charge. Remember from the brief discussion of ionization (in Part I of this paper) that positive ions result when atoms or molecules LOSE one or more of the electrons that orbit them. Similarly, negative ions result when atoms or molecules GAIN one or more orbiting electrons. When writing formulas for ions, it is necessary to use the superscript plus or minus. Atoms don't normally exist as ions, so when writing about neutral atoms or molecules, it is not necessary to indicate their neutrality; however, sometimes to avoid possible confusion, a superscript 0 is used. For example, the chemical symbol Cu^0 indicates neutral copper atoms.

Sometimes neutral atoms or molecules have an electronic structure that makes them unusually reactive. When this happens, they are usually called "free radicals" and are indicated using a superscript dot (in place of the zero), e.g., $Cl^{\cdot}$ or $OH^{\cdot}$. Because free radicals are so reactive, they usually are not found at room temperature, where they quickly combine with other atoms or molecules. However, in pyrotechnic flames, free radicals abound.

The final topic in this section is IUPAC nomenclature. When the International Union of Pure and Applied Chemists (IUPAC) was formed, one of the first tasks undertaken was to standardize the method of naming chemical compounds. Below is a short discussion of some rules of nomenclature.

(A) Molecules composed of a metal and a non-metal, have the metal named first followed by a slightly modified non-metal name. The metal name is pronounced just as it would be for a metal powder. For example, Na in NaF is "sodium", Cu in CuCl is "copper". The non-metal name has its ending changed to "ide". Thus fluorine in NaF is "fluoride", chlorine in CuCl is "chloride" and oxygen in FeO is "oxide".

When a metal, like copper, is capable of combining in different proportions with the same non-metal elements, like chlorine, it is necessary to be able to distinguish between the different chemical forms. This is accomplished by adding a Roman numeral in parentheses between the metal and non-metal name. The Roman numeral indicates the "valence state" of the metal. (The concept of valence is beyond the scope of this paper; suffice it to say that a metal's valence state determines the ratio in which it will combine with other elements.) Gone are the frequently confusing names for copper such as "cuprous" and "cupric" in the names of CuCl and $CuCl_2$, respectively. In the new naming system, CuCl is copper(I) chloride, $CuCl_2$ is copper(II) chloride. When a metal has only a single valence state possible, it is not necessary to include the Roman numeral. Thus NaF is just sodium fluoride.

(B) There are several groups of atoms that stick together rather well and often act as if they were just a single element when forming compounds. These ionic functional groups have each been given their own names. Some of these encountered in pyrotechnics are: $(NO_3)^-$, nitrate; $(ClO_4)^-$, perchlorate; and $(NH_4)^+$, ammonium (see Table 2 for a more complete list). Some compounds containing these functional groupings are: $NaNO_3$, sodium nitrate; $KClO_3$, potassium chlorate; $CuSO_4$, copper (II) sulfate; and NH_4ClO_4, ammonium perchlorate.

(C) Complex natural organic molecules continue to be called by their historical names. Sometimes this is because the IUPAC name is very long and complicated; other times, this is because the natural substance is not a single compound, but several compounds in a variable mixture. Thus names like shellac, red gum (accroides), and gum Arabic are proper to use.

Table 2. Names and Formulas of Functional Ionic Groups Frequently Found in Pyrotechnics.

Group Name	Chemical Formula
Ammonium	NH_4^+
Carbonate	CO_3^{2-}
Chlorate	ClO_3^-
Hydrogen carbonate (bicarbonate)	HCO_3^-
Nitrate	NO_3^-
Oxalate	$C_2O_4^{2-}$
Perchlorate	ClO_4^-
Sulfate	SO_4^{2-}

Occasionally in this paper the prefix "mono" will be used in a chemical name, to indicate that the single atom is present in the compound. This is done to avoid possible confusion. For example, at normal temperatures, strontium always combines with chlorine in the ratio of 1 to 2 to form the solid $SrCl_{2(s)}$. Thus the proper name for the compound is simply strontium chloride. However, when $SrCl_2$. is vaporized, the stable molecule is $SrCl_{(g)}$. To avoid confusion, $SrCl_{(g)}$ will be called strontium monochloride.

The rules of nomenclature given thus far are a long way from being complete; however, they should help avoid confusion. As a further aid, you can refer to Table 3, which lists a number of the more common chemical names and formulas which are important in a discussion of the chemistry of colored light production.

4.1.3 Chemical Equations

Chemical equations describe chemical reactions, i.e., the way chemicals react to form new chemicals. Instead of telling you that hydrogen and oxygen can combine to form water, it can be done using a chemical equation:

$$2 H_2 + O_2 \rightarrow 2H_2O \qquad (1)$$

In addition to being shorter and easier to use, it also gives more information. It tells the relative numbers of atoms and/or molecules involved in the reaction, i.e., two molecules of hydrogen combine with one molecule of oxygen to form two molecules of water. The numeral 2 in front of H_2 and H_2O indicates that 2

Table 3. Names and Formulas of Chemicals Commonly Used to Produce Colored Flames.

Oxidizers	
Ammonium perchlorate	NH_4ClO_4
Barium chlorate[x]	$Ba(ClO_3)_2$
Barium nitrate[x]	$Ba(NO_3)_2$
Potassium chlorate	$KClO_3$
Potassium nitrate	KNO_3
Potassium perchlorate	$KClO_4$
Sodium nitrate[x]	$NaNO_3$
Strontium nitrate[x]	$Sr(NO_3)_2$
Fuels	
Aluminum	Al
Carbon[*]	C
Magnesium	Mg
Magnalium[xx]	Mg/Al
Red gum (accroides)	Complex
Shellac	Complex
Color Agents[**]	
Barium sulfate	$BaSO_4$
Calcium carbonate	$CaCO_2$
Calcium sulfate	$CaSO_4$
Copper acetoarsenite	$(CuO)_3As_3O_3 \cdot Cu(C_3H_3O_2)_3$
Copper(II) carbonate, basic	$CuCO_3 \cdot Cu(OH)_2$
Copper(II) chloride	$CuCl_2$
Copper metal	Cu
Copper(II) oxide	CuO
Copper sulfate	$CuSO_4$
Sodium hydrogen carbonate	$NaHCO_3$
Sodium oxalate	$Na_2C_2O_4$
Strontium carbonate	$SrCO_3$
Strontium sulfate	$SrSO_4$

Notes:

x These oxidizers also act as color agents.

* Charcoal has the composition 82% C, 13% O, 3% H, and 2% Ash (from Shimizu, 1981).

** Under high temperature conditions such as in strobe star burning, many of these color agents can also act as oxidizers.

xx Magnalium is an alloy of magnesium and aluminum, most often in near equal proportions.

molecules are involved in the reaction. The arrow in a chemical equation should be read as "reacts to form". The starting chemicals are called the REACTANTS, and the chemicals produced are called the PRODUCTS. In the water equation, H_2 and O_2 are the reactants and H_2O is the product.

To be a proper chemical equation, it must be balanced, just as a mathematical equation must be balanced. In chemical reactions, elements are immutable; they are neither created nor destroyed. Thus there must be an equal number of each type of atom on both sides of the arrow. If I had written the equation

$$H_2 + O_2 \rightarrow H_2O \qquad (2)$$

it would be incorrect, since it is not balanced. There are two atoms of hydrogen on each side of the equation, but the left side has two atoms of oxygen while the right side only has one. Note that Equation 1 is balanced.

Sometimes, for emphasis, chemical equations will indicate whether heat energy is consumed or generated during a chemical reaction. This could have been indicated in Equation 1 by listing heat as one of the products,

$$2\,H_2 + O_2 \rightarrow 2\,H_2O + Heat \qquad (3)$$

An example from pyrotechnics, complete combustion, where an oxidizer (potassium perchlorate) and a fuel (carbon, i.e., charcoal) combine completely to generate reaction products plus heat, is

$$KClO_4 + 2\,C \rightarrow KCl + 2\,CO_2 + Heat \qquad (4)$$
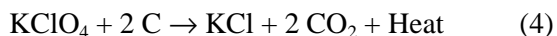
In order for molecules in a pyrotechnic flame to emit their characteristic band spectra, they must first be vaporized; this requires heat energy. Copper(I) chloride, CuCl, has the potential to be a powerful emitter of violet light if it has been vaporized. The chemical equation showing this vaporization is
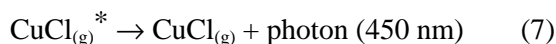
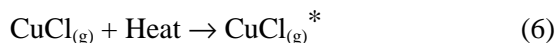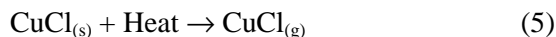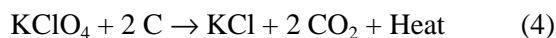$$CuCl_{(s)} + Heat \rightarrow CuCl_{(g)} \qquad (5)$$
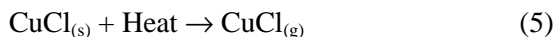
Another thing that can be shown in a chemical equation, to aid in clarity, is when an atom or molecule is in an excited electronic state, capable of emitting a light photon upon de-excitation. This is usually indicated using a superscript asterisk. Decay from an excited state with the emission of a photon can be indicated

by listing the light photon as one of the reaction products. Equations 6 and 7 are examples using CuCl:

$$CuCl_{(g)} + Heat \rightarrow CuCl_{(g)}{}^* \qquad (6)$$

$$CuCl_{(g)}{}^* \rightarrow CuCl_{(g)} + photon\ (450\ nm) \qquad (7)$$
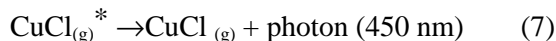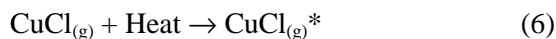
Equation 7 also indicates the wavelength of the emitted photon in nanometers (nm).

As an example of how chemical equations are a useful shorthand, consider the set of equations given above. They represent one possibility for generating violet light. In longhand, the process would be described as: "One molecule of potassium perchlorate reacts with two atoms of carbon to generate one molecule of potassium chloride, two molecules of carbon dioxide and heat. Copper(I) chloride, which is also present in the composition, consumes heat energy and is vaporized; it then consumes additional heat energy and becomes electronically excited. Finally, the excited molecule of copper(I) chloride de-excites generating a violet light photon of wavelength 450 nm." In the more explicit shorthand of chemical equations this becomes, simply:

$$KClO_4 + 2\,C \rightarrow KCl + 2\,CO_2 + Heat \qquad (4)$$

$$CuCl_{(s)} + Heat \rightarrow CuCl_{(g)} \qquad (5)$$

$$CuCl_{(g)} + Heat \rightarrow CuCl_{(g)}{}^* \qquad (6)$$

$$CuCl_{(g)}{}^* \rightarrow CuCl_{(g)} + photon\ (450\ nm) \qquad (7)$$

### 4.1.4 Chemical Reversibility and Le Châtelier's Principle

All chemical reactions are reversible to some extent. Thus, if two elements combine to make a compound, this compound has some tendency to decompose back into the two original elements. For reactions involving only a change of state, the idea of reversibility seems natural. For example,

$$H_2O_{(s)} + Heat \rightarrow H_2O_{(l)} \qquad (8)$$
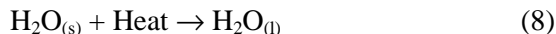
It is an everyday observation that the reverse reaction also takes place, i.e.:

$$H_2O_{(l)} \rightarrow H_2O_{(s)} + Heat \qquad (9)$$
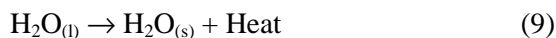
A convenient way to point out that this reaction is reversible, is to use a double-headed arrow in the equation

$$H_2O_{(s)} + \text{Heat} \leftrightarrow H_2O_{(l)} \qquad (10)$$
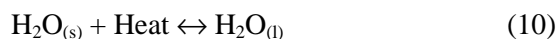
For most other reactions, the idea of reversibility may be hard to accept. Remember the example of potassium perchlorate reacting with carbon,

$$KClO_4 + 2\,C \rightarrow KCl + 2\,CO_2 + \text{Heat} \qquad (4)$$
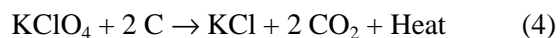
It seems inconsistent with common experience to suggest there is a tendency for the reaction products to recombine again to make potassium perchlorate and charcoal. In fact there IS a tendency to do just that, even if the tendency is very slight at room temperature and atmospheric pressure. At high temperatures and pressures, the tendency for the reverse action to occur is increased, though still not great.

As a consequence of chemical reactions always having some tendency to go in both directions, they never go 100% to completion. Some of the reactants are always left over at the end, because some of the products have reacted in a reverse direction to remake some of the reactants. The final amount of reactants and products depends on the relative tendencies for the forward and reverse reactions to occur. If the tendency for the forward reaction to occur is much greater, then almost all the reactants will be consumed. On the other hand, if the reverse reaction has a much greater tendency to occur, then very little of the starting material will be consumed.

Later in this paper when discussing colored flame production, it will be important to understand the concept of chemical reversibility and something closely related called Le Châtelier's Principle. Le Châtelier's Principle states that when stress is applied to a chemical system in equilibrium, the system will react in such a manner as to relieve that stress. In Equation 4, I said there was a very slight tendency for the reverse reaction to occur, but when the pressure was raised, the tendency of the reverse reaction to occur became greater. This is can be thought of as Le Châtelier's Principle in action. Note that the only gas involved is CO_2, one of the products. If we increase the pressure, the only way to relieve the stress of added pressure is for some of the gaseous product to recombine to form the more compact $KClO_4$ and carbon, and this is just what happens. Another way to apply stress to a chemical reaction is to increase the amount of one of the reactants or products. If more of one of the reactants is added, the reaction progresses to the right, using up more of the other reactants and making more of the products. If more charcoal is added, some of the left over $KClO_4$ will react with it to generate more of the reaction products. If you add some of one of the reaction products the reaction is pushed to the left, using up some of the other products to remake more of the reactants. Note in Equation 4 that heat energy is one of the products of the reaction. Thus if we apply stress to the reaction by raising the temperature (by adding heat), we would expect that stress would be relieved by some of the reaction products recombining, consuming heat energy, and remaking more of the reactants. This is just what does happen.

The reason it is important to understand Le Châtelier's Principle when attempting to generate good colored flames is that it gives us a way to shift chemical reactions so that they produce more desirable light generating species in colored flames, or so that they produce less undesirable light generating species.
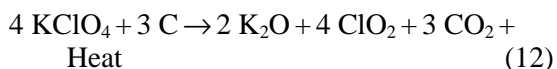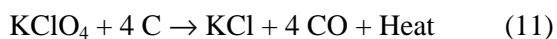
4.1.5 Stoichiometry and Mole Weights

Stoichiometry (pronounced sto-i-key-om'-a-tree) is the detailed study of the ratio in which atoms and molecules combine to form other molecules. Whenever we write a chemical equation that is properly balanced (and expresses reality), it is an exercise in stoichiometry. Equation 4 for the complete combustion of carbon using potassium perchlorate,

$$KClO_4 + 2\,C \rightarrow KCl + 2\,CO_2 + \text{Heat} \qquad (4)$$
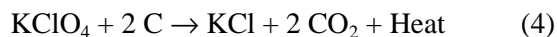
is an exact description of one of the ways in which potassium perchlorate and carbon react in a pyrotechnic flame to produce heat. It tells you exactly how many atoms of carbon combine with one molecule of potassium perchlorate. If this were the only way for the reaction to proceed, it would be a relatively simple matter to design pyro-reactions on paper that worked perfectly in practice. Knowing that two atoms of carbon were consumed for each molecule of potassium perchlorate, you could (knowing about molecular weights) calculate the exact weight of potassium perchlorate and carbon to use in a pyro-formulation. Unfortunately,

Equation 4 is only one of the possible ways for the reaction to proceed. Two more equally legitimate possibilities are:

$$KClO_4 + 4\,C \rightarrow KCl + 4\,CO + Heat \qquad (11)$$

$$4\,KClO_4 + 3\,C \rightarrow 2\,K_2O + 4\,ClO_2 + 3\,CO_2 + Heat \qquad (12)$$

Equation 11 suggests that the proper ratio is four carbon atoms to one potassium perchlorate molecule, not two to one as in Equation 4. Equation 12 suggests that carbon and potassium perchlorate will react three to four. In practice, when formulating, how can you be certain which of the three ratios to use? In fact, none of the ratios are exactly correct. EACH of the reactions occurs and is correct in a stoichiometric sense. The problem is that ALL THREE equations (and others) take place to some extent at the same time in the flame reaction. It's not that stoichiometry doesn't work; it's just that flame reactions are too complex to be represented completely by a single chemical equation. To add to the complexity, the extent to which the various flame reactions occur depend on such additional things as: grain size of the chemicals, degree of compaction of the material, type and amount of color agents and other chemicals added to the formulation, pressure, velocity at which the composition is moving through air (i.e., flame temperature). It is just not possible to write a single equation, no matter how long and complex, that will precisely describe chemical reactions in a typical pyrotechnic flame under all conditions.

In spite of this, stoichiometry can be a great help in developing pyro-chemical formulations. It can provide very good, although only approximate, starting points for amounts of chemicals to use. In addition, stoichiometry can tell you almost exactly how to make substitutions in your formulations.

Stoichiometry (balanced chemical equations) tells in what proportions atoms and molecules react. However, in your pyro-lab, you don't work with individual atoms; you work with grams, ounces or pounds. What is needed to know is how many ounces of this combine with how many ounces of that. The concept of "molecular weights" will let you work with amounts by weight instead of numbers of atoms. To explain molecular weights, it is necessary to de-

fine a new unit, a "mole". A mole is a number, a very big number; it is equal to 602 thousand billion billion atoms (6.02×10^{23} atoms). This large number is the number of hydrogen atoms in a single gram of atomic hydrogen. Instead of talking about 6.02×10^{23} atoms of hydrogen, one can simply call it a mole of hydrogen. The unit "mole" is used in just the same way as the unit "dozen"; just think of a mole as a "super dozen". In your kitchen you make recipes using individual eggs, but an army cook works in dozens of eggs. Similarly in your pyro-lab, you need to think in terms of moles (super dozens) of atoms.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \qquad (1)$$

Equation 1, gave the ratio of hydrogen and oxygen molecules that combine to make water. It told you that two molecules of hydrogen combine with one molecule of oxygen to make two molecules of water. However, it is also true that two dozen hydrogen molecules combine with one dozen oxygen molecules, or that two moles of hydrogen molecules combine with one mole of oxygen molecules. If you want to make water, and want to use precisely the right amount of hydrogen and oxygen, you still need to know how much a mole of hydrogen and a mole of oxygen weigh. Remember from the discussion of the Periodic Table, that one type of information contained on it are atomic weights (the number in the upper right corner of the box for each element). The atomic weight is the weight of one mole of that element in grams. Thus one mole of atomic hydrogen (H) very nearly weighs one gram. However, because hydrogen is a diatomic gas (H_2), the molecular weight of a mole will be twice its atomic weight, or 2 grams per mole of molecules. Similarly for oxygen, with an atomic weight of 16, one mole of molecular oxygen (O_2) weighs 32 grams. From Equation 1 you know that 2 moles of H_2 combines with one mole of O_2. Thus 4 grams of hydrogen gas (2 moles $\times$ 2 grams/mole) combine with 32 grams of oxygen gas (1 mole $\times$ 32 grams/mole).

Since the metric system is not in general use in the US, many people don't formulate using grams as a unit of mass. Well, the above information is still useful and it's not necessary to convert units of weight. The above information indicates that 4 parts by weight hydrogen com-

bine with 32 parts by weight oxygen to make water. The unit of weight can be anything convenient: grams, grains, ounces, pounds, kilos, tons, etc.

As a more relevant example demonstrating molecular weights, consider a problem from pyrotechnics. Suppose you wished to substitute metallic copper powder for copper(II) oxide in a blue star formulation. It is relatively safe to assume that it is only the amount of copper that is important and that the presence of oxide ions has only minor effect on flame color. The first thing needed to be established is how much copper is in copper(II) oxide, CuO. The molecular weight of CuO is 79 grams/mole (63 grams/mole for copper + 16 grams/mole for oxygen). The fraction of copper in copper(II) oxide is 63/79 or about 4/5. Thus every five grams of copper(II) oxide contributes four grams of copper. If the blue formulation called for ten parts copper(II) oxide, you should begin by using eight parts of copper metal (10 parts × 4/5).

4.2 Pyrochemical Flames for Color Production

4.2.1 Definition and Function of Flames in Color Production

The most important characteristic one uses to determine whether something is a flame is the emission of light. Other characteristics such as flickering, giving off heat and apparent chemical nature are far less important. The emission of light is in fact the best criterion to use. It is important to point out that in Figure 42 (a drawing of a typical flame) the principal difference between point B (just inside the flame envelope) and point C (just outside the flame) is that the molecules at point B are emitting visible light and those at point C are not. For the most part, the same kinds of molecules are present at both points, and the temperature at point C is only a little lower than at point B.

Even though the temperature difference between B and C is small, it is sufficient to account for the molecules at point B emitting light while those at point C are not. Remember that energy is required for excitation of electrons from their ground states to excited states, and that light is given off when those electrons fall
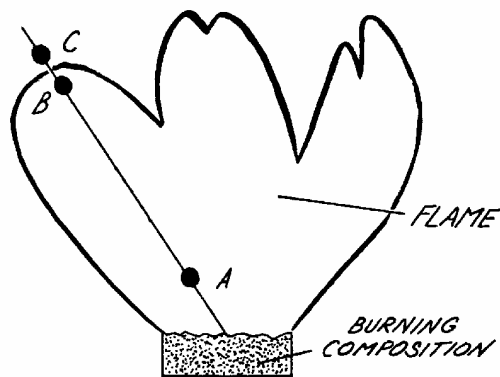

Figure 42. Typical pyrotechnic flame.

back to lower energy states. If the temperature at some point is high enough to cause electron excitations, then the molecules at that point can give off light. At the same point, if the temperature falls lower, such that there is no longer sufficient energy for electronic excitation, no light is given off. Figure 43 is a graph of expected temperatures along the line in Figure 42 on which points A, B and C fall. Included in Figure 43 is a line meant to correspond to the approximate flame temperature necessary for the production of light from the molecules present. At point A, the temperature is well above that value, at point B the temperature is slightly above that value, and at point C, slightly below. The molecular species that are present at point B are also present at point C. As far as light
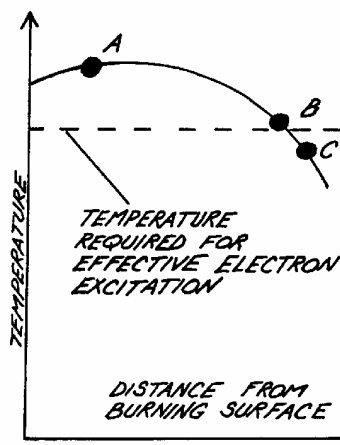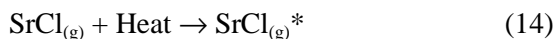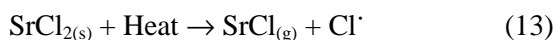

Figure 43. Flame temperature as a function of distance from burning surface.

generation is concerned, the only important difference is temperature and that difference is not great.

Thus an appropriate definition of a flame is that region surrounding a source of chemically generated heat energy where the temperature is sufficient for the emission of visible light.

In the generation of color in pyrotechnics, the flame serves two functions. The first is to supply the heat energy necessary to vaporize the chemical color agent. (Remember only vaporized atoms and molecules can be sources of useful flame color. Solid particles and liquid droplets emit undesirable continuous spectra.) The second function is to supply the heat energy necessary to excite electrons in the color agent in preparation for their decay and consequent emission of light. Using chemical equations for a strontium red flame, the process can be represented as:

$$SrCl_{2(s)} + Heat \rightarrow SrCl_{(g)} + Cl^{\cdot} \qquad (13)$$

$$SrCl_{(g)} + Heat \rightarrow SrCl_{(g)}^* \qquad (14)$$

$$SrCl_{(g)}^* \rightarrow SrCl_{(g)} + photon\ (630\ nm) \qquad (15)$$

4.2.2 The Source of Energy in a Flame

The energy for colored light production is the result of combustion. The general formula for combustion is:

Oxidizer + Fuel →

Combustion Products + Heat   (16)

As a starting point in this discussion, it is worth considering how the heat energy of combustion is generated and why different fuels and oxidizers generate differing amounts. When atoms come together to form molecules, chemical bonds form between the atoms. These chemical bonds hold the atoms together as a molecule, and are the result of electronic forces caused by either a transfer or a sharing of electrons between atoms. It requires energy to break chemical bonds and energy is given off when new chemical bonds form. The stronger the bonds, the more energy is required to break them and the more energy is given off upon their formation. The strength of the chemical bond depends on the type and number of atoms forming the molecule.

During a chemical reaction, chemical bonds are broken and new ones are formed. If heat is to be produced during a chemical reaction, then, on the average, the chemical bonds formed must be stronger than those broken. This is the case with combustion, oxidizers and fuels have chemical bonds that are weak when compared with chemical bonds of the reaction products. When various fuels and oxidizers are used, different numbers of bonds will be broken and formed between different kinds of atoms. Thus it should be expected that varying amounts of energy will be produced in these different combustion reactions. The energy released by some common oxidizers reacting with carbon (charcoal) to produce carbon dioxide (CO_2) is listed in Table 4. Here, the unit kcal (kilocalorie) is used as a measure of the heat produced in the reaction.

In Table 4, note that potassium perchlorate and not potassium chlorate produces the greater amount of heat energy. This is typically true for $KClO_4$ and is not an isolated result caused by using carbon as the fuel. For the most part, it is the result of $KClO_4$ containing one additional oxygen atom per molecule in comparison with $KClO_3$. The additional oxygen atom is available to form a strong bond with a carbon atom, thereby releasing more energy. The result is that $KClO_4$ is the more potent generator of heat energy. This may seem to contradict your experience. You may have observed that formulations using $KClO_3$ are often easier to ignite and

Table 4. Energy Released by Some Common Oxidizers.

Oxidizer	Energy Released	
	kcal/mol	kcal/g
$KClO_4$	189	1.4
$KClO_3$	146	1.2
$Sr(NO_3)_2$	146	0.7
$Ba(NO_3)_2$	131	0.5
KNO_3	42	0.4

Note: In each case the fuel is charcoal and it is oxidized to CO_2. The results were calculated using data published in Shidlovskiy (1964, p. 24) and Douda (1964, p. 46).
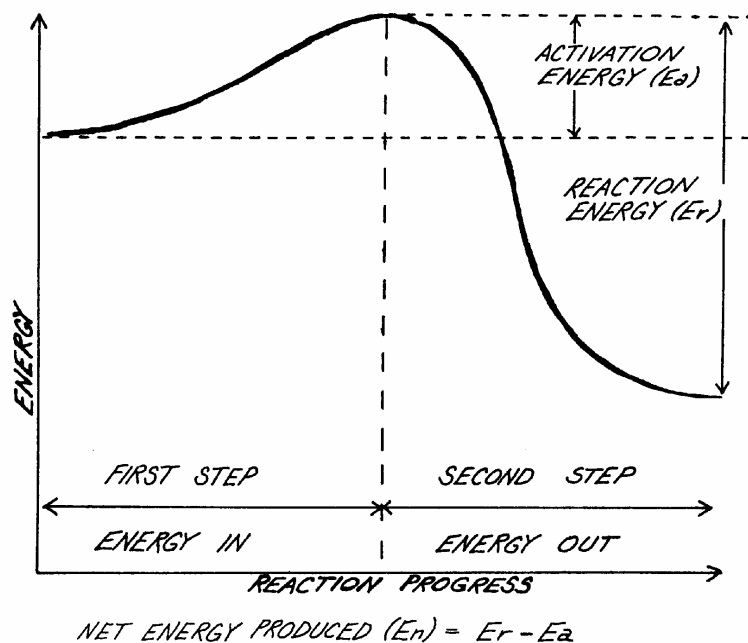
Figure 44. *Generalized chemical energy level diagram.*

more resistant to being extinguished when moving at high velocities through the air than are formulations using $KClO_4$. These observations are accurate (Shimizu, 1981, p. 23) but are not the results of $KClO_3$ being the better heat producer. This will be discussed below.

Even though a formulation has the ability to generate heat energy, it usually requires an input of energy to begin the process. For example, before a star gives off energy in the combustion process, it is necessary to add heat energy (i.e., to light it). Chemical reactions can usually be broken into these two parts with respect to energy production. It is possible to think of the first step as when old chemical bonds are being broken. This requires energy, called activation energy in Figure 44. In a very real sense, this is an energy barrier that must be surmounted before the reaction can begin. Similarly, the second step can be thought of as when new chemical bonds are being formed. This liberates energy. In terms of the amounts of energy involved, the two steps are mostly unrelated. The activation energy can be large or small and has little effect on the amount of energy produced by the reaction. In Figure 44 the difference between the activation energy (energy in) and the reaction energy (energy out) is the net energy generated by the reaction. The energies in Table 4 correspond to the net energy generated in Figure 44.

Activation energy is a measure of how difficult it is to initiate a reaction. If the activation energy is large, the reaction is difficult to get started, and is also difficult to keep going. If the activation energy is small, the reaction is easily started and kept going. If the activation energy is zero, the reaction will start spontaneously. Formulations containing potassium chlorate have rather low activation energy barriers to surmount. This has the desirable effect of making these formulations easy to light and they tend to stay lit when moving at high velocities. However, this low energy barrier is also the reason $KClO_3$ formulations are rather friction and shock sensitive. Similar formulations containing potassium perchlorate have a higher activation energy barrier, but also produce more energy during the reaction. Figure 45 shows chemical energy level diagrams for typical formulations containing $KClO_3$ and $KClO_4$.
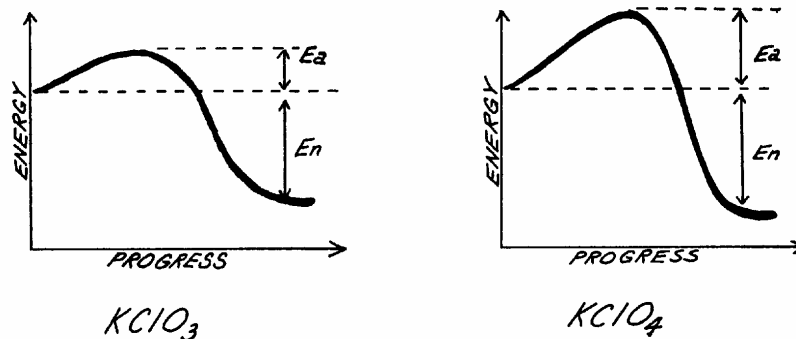
Figure 45. Comparison of KClO₃ and KClO₄ formulations.

4.2.3 Flame Temperature in Color Production

For the most part, the flame temperatures produced are a function of the amount of energy released in a chemical reaction. The more energy released during a fixed period of time, the higher the flame temperature. Thus, in Table 5, which is a compilation of flame temperatures taken from Shimizu (1976, p. 74), the order of flame temperatures produced by the different oxidizers should and generally does follow the same order as the amounts of energy produced when reacted with carbon (listed in Table 4).

The amount of energy produced in combustion, and therefore flame temperature, also depends on the fuel chosen. Table 6 is a listing of flame temperatures observed for some non-metal fuels reacting with $KClO_4$, NH_4ClO_4 and $Ba(ClO_3)_2$.

Flame temperature has important ramifications in the production of intensely colored flames. Recall that the characteristic most different between points just inside and just outside a flame was that molecules at one point emit light and those at the other point do not. The type and number of molecules at both points are similar; the difference is that inside the flame the temperature is still high enough for visible light production and outside, it is not. For the most part, at temperatures above that which is required for colored light production, the higher the temperature, the greater the amount of light produced. In addition, the relationship between temperature and light produc-

tion is non-linear; a small change in temperature causes a large change in light production. Thus one of the criteria for intensely colored flames is high flame temperature. Another criterion is to have a high concentration of the color generating molecules (atoms) in the flame. Unfortunately, as more color agent is added to a colored flame formulation, more energy must

Table 5. Maximum Flame Temperatures of Oxidizers with Shellac (Data from Shimizu, 1976, p. 74).

Oxidizer	%	Fuel	%	Flame Temp. (°C)
$KClO_4$	74	Shellac	16	2247
NH_4ClO_4	76	Shellac	14	2207
$KClO_3$	77	Shellac	13	2177
KNO_3	72	Shellac	18	1697

Note: All mixtures contained 10% $Na_2C_2O_4$.

Table 6. Flame Temperatures, in Degrees Celsius, of Oxidizers with Various Fuels (Data from Shimizu, 1976, p. 74).

Fuel	$KClO_4$	NH_4ClO_4	$Ba(ClO_3)_2$
Pine pitch	2465	2238	2177
Colophony	2322	2092	2237
Shellac	2245	2198	2032
Woodmeal	2057	2025	1688

Note: All mixtures contained 10% $Na_2C_2O_4$, necessary to measure flame temperature.

be used to vaporize it. The consumption of this energy lowers flame temperature, lowering light output. Thus a compromise must be struck, as shown in Figure 46, between too little color agent and too low a flame temperature. Obviously fuel/oxidizer combinations that produce high flame temperatures have the advantage of being able to accommodate greater amounts of color agents and are thus capable of producing more vividly colored flames.

Some fuel/oxidizer combinations produce flame temperatures so low as to be virtually useless for the production of colored flames. For example, the only intense color that can be produced using KNO_3 and non-metal fuels is yellow.

One way to partially overcome the loss of energy taken to vaporize the color agent is to use a color agent that is itself an oxidizer. For example, using $KClO_4$ and red gum as the primary source of thermal energy, considerably more strontium can be added to the formulation, without seriously lowering flame temperature, in the form of $Sr(NO_3)_2$ than $SrCO_3$. This is because $Sr(NO_3)_2$ can itself react with red gum to produce additional heat energy.

Another way to increase the amount of color agent in a formulation without lowering flame temperature to a point too low for good color production, is to start with a fuel/oxidizer combination that is capable of producing very high flame temperatures. This can be accomplished using a metal fuel: aluminum, magnalium or magnesium. A comparison of Tables 5 and 6 with Table 7 demonstrates the ability of magnesium to significantly increase flame temperature. In terms of maintaining color purity, mag-

Table 7. Metal fuel flame temperatures (data from Shimizu, 1976, p. 76).

Oxidizer	Flame Temp (°C)	Magnesium %
$KClO_4$	2987	45
KNO_3	2552	60
$Sr(NO_3)_2$	2902	45
$Ba(NO_3)_2$	2717	45

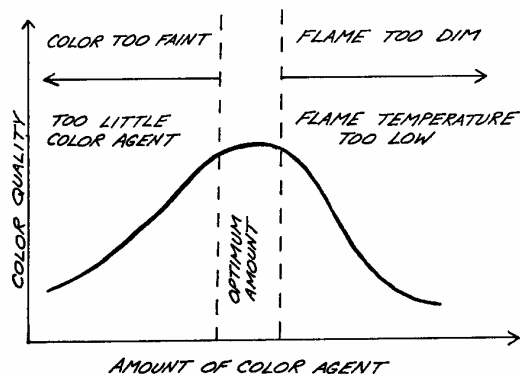Note: All mixtures contained either 10% PVC or 10% shellac.

Figure 46. Optimum amount of color.

nesium is the best choice, followed next by magnalium, and then by aluminum. This is because when aluminum is burned, aluminum oxide, a source of white light, is formed. This reduces the purity of the colored flame produced.

Fuel and oxidizer combinations capable of producing high temperatures are important for producing intensely colored flames. However, the very highest flame temperatures are not usually the best. The chemical species responsible for generating intensely colored pyrotechnic flames are almost always molecules. At very high temperatures, these desirable light producing molecules decompose. This is a double-barreled problem; not only does decomposition result in a loss of desirable light emitters, but the products of decomposition are almost always undesirable light sources. This can result in a serious loss of color purity in the flame.

4.3 Color Production in Flames

4.3.1 Desirable Color Generating Chemical Species

Table 8 is a list of the metals commonly used to produce colored pyrotechnic flames. Also included are the chemical species actually responsible for the color. Note that in all cases except sodium, it is molecular compounds (not atoms) that are the color generating species. For example, the red color generating species are SrOH and SrCl. Strontium atoms not only don't produce red light, they interfere with the production of intensely colored red flames; stron-

Table 8. List of Metals Commonly Used to Generate Colored Pyrotechnic Flames (Basic Data from Douda, 1964).

Metal	Color	Color Generating Species	Approximate (equivalent) Wavelength (nm)
Strontium	Red	SrCl	630
	Red-orange	SrOH	610
Barium	Green	BaCl	520
	Green	BaOH	weak emitter
Copper	Violet-blue	CuCl	450
	Green	CuOH	540
Calcium	Orange	CaOH	600
	Red-orange	CaCl	610
Sodium	Yellow	Na^0 (atoms)	589

Note: In general, any of the halogens (group VIIA) can be substituted for chlorine in the metal monochlorides.

Table 9. List of Metals Rarely Used to Produce Colored Pyrotechnic Flames (Basic Data from Douda, 1964).

Metal	Color	Color Generating Species	Approximate (equivalent) Wavelength (nm)
Lithium	Red	Li^0	650
Rubidium	Red	Rb^0	630
Cesium	Blue	Cs^0	460
Boron	Green	BO_2	530
Thallium	Green	Tl^0	530

NOTE: $Cl^\cdot$ and $OH^\cdot$ are not stable chemical species at room temperature; however, they can be formed and are stable at flame temperatures.

Unfortunately, these reactions are not the only possibilities in a strontium flame. Figure 47 is an attempt to summarize the most important flame reactions for strontium. To some extent all of the reactions in Figure 47 take place. The problem is that strontium monochloride (SrCl) and strontium monohydroxide (SrOH) are the only chemical species that generate good quality red light. The light generating properties of all the others are more or less detrimental (see Table 10).

Because of the production of chemical species that seriously reduce color quality, and in order to optimize the production of useful species, it is necessary to control the reactions taking place in flames.

tium atoms emit a mixture of blue and violet light.

Table 9 is a listing of some other, rarely used, metals that can be used to produce colored pyrotechnic flames. The reason these metals are not used is their generally high cost and technical limitations.

4.3.2 Typical Flame Reactions and Detrimental Color Generating Species

It rarely occurs that color agents added to a formulation are the color generating species listed in Table 8. For example, the source of strontium is usually $SrCO_3$ or $Sr(NO_3)_2$. Thus it is usually necessary to form the color generating molecules in the flame itself. In general, the mechanism is first to break apart the color agent. Then, by providing a source of the proper non-metal atoms or atom groups, allow the desired chemical species to form. For strontium a simplified version of this can be represented as:
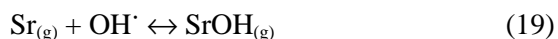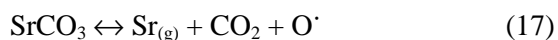
$$SrCO_3 \leftrightarrow Sr_{(g)} + CO_2 + O^\cdot \qquad (17)$$

$$Sr_{(g)} + Cl^\cdot \leftrightarrow SrCl_{(g)} \qquad (18)$$

$$Sr_{(g)} + OH^\cdot \leftrightarrow SrOH_{(g)} \qquad (19)$$

Table 10. Partial Listing of Chemical Species, Present in Strontium Red Flames, That Have Undesirable Light Generating Properties.

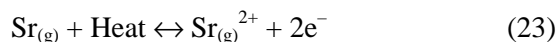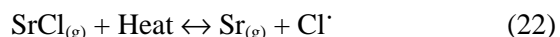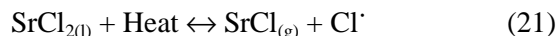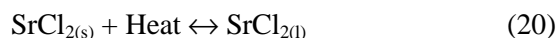| Chemical Species	Detrimental Effect
$SrCl_{(l)}$ or $_{(S)}$	strong continuous spectrum
SrO	blue-violet color
Sr^+	violet color and continuous spectrum from ion recombinations
$SrO_{(s)}$	orange color
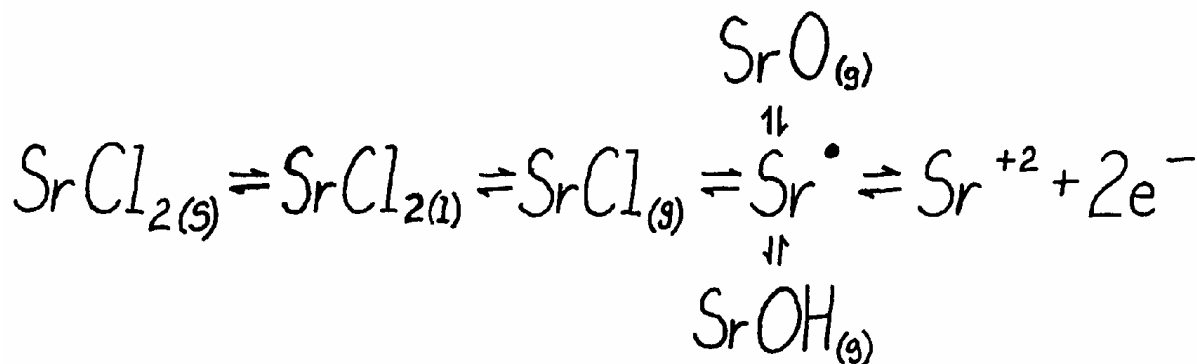
Figure 47. A representation of some of the possible reactions for strontium in a flame (taken from Douda, 1964). NOTE: In order to simplify the figure, some reactants and products are not explicitly shown.

4.3.3 Control of Flame Chemistry

As discussed earlier, all chemical reactions are reversible; none go 100% to completion. Thus to some extent all those chemical species shown in Figure 47 will be present in a strontium red flame. However, it is possible to preferentially form more of the desirable color emitting species if Le Châtelier's Principle is cleverly used, i.e., when the proper stresses are applied to the chemical system.

In Figure 47, each step moving to the right requires the input of energy. It is as though heat energy was one of the chemical reactants. This is shown in Equations 20 to 23:

$$SrCl_{2(s)} + Heat \leftrightarrow SrCl_{2(l)} \tag{20}$$

$$SrCl_{2(l)} + Heat \leftrightarrow SrCl_{(g)} + Cl^{\cdot} \tag{21}$$

$$SrCl_{(g)} + Heat \leftrightarrow Sr_{(g)} + Cl^{\cdot} \tag{22}$$

$$Sr_{(g)} + Heat \leftrightarrow Sr_{(g)}^{2+} + 2e^{-} \tag{23}$$

Flame temperature is an approximate measure of heat energy available in a flame, thus you can appreciate the importance of flame temperature. It is $SrCl_{(g)}$ that we wish to have present in the flame, not $SrCl_{2(s)}$ or $SrCl_{2(l)}$. If flame temperature falls too low, this is equivalent to removing heat (one of the reactants). This is a stress on the reacting system. The stress is relieved by some of the $SrCl_{(g)}$ combining with $Cl^{\cdot}$, condensing as liquid $SrCl_2$ droplets. With the loss of $SrCl_{(g)}$, the red color generating molecule, the purity of the red flame is reduced. On the other hand, if the temperature rises too high, more of

the $SrCl_{(g)}$ decomposes into $Sr_{(g)}$ and $Cl^{\cdot}$, again reducing color purity. This high temperature problem is unfortunate because the brightness of a colored flame increases significantly with relatively minor increases in temperature. Thus it would be desirable to have the flame temperature as high as possible.

One way to allow a higher flame temperature, without a loss of $SrCl_{(g)}$ by decomposition, is to balance the stress caused by adding heat, by adding more of one of the products, $Cl^{\cdot}$ for example. One benefit of using $KClO_3$ or $KClO_4$ as the oxidizer in this type of colored flame production is their ability to contribute some $Cl^{\cdot}$ to the flame. Substantially greater amounts of $Cl^{\cdot}$ (or HCl which is equivalent) can be added using most any chlorine-rich compound that does not interfere in some way with other aspects of flame chemistry. Among the important properties of these chlorine donors are: a high percentage of chlorine, a low heat of decomposition, and the ability to decompose under conditions present in flames. Table 11 lists a number of chlorine donors commonly used in fireworks and their percentage of chlorine. Other properties to take into consideration when selecting a chlorine donor are toxicity, cost, the ability to act as a fuel, and the ability to consume excess oxygen in a flame.

It is worth mentioning that any halogen (i.e., group VIIA element) can be used in place of chlorine. Strontium fluoride, SrBr and SrI are all useful emitters of red light. However, shifts

Table 11. Percent Chlorine of Common Chlorine Donors.

Name	Formula	Chlorine %
Hexachlorobenzene	C_6Cl_6	74
Benzene hexachloride	$C_6H_6Cl_6$	73
Parlon (poly, 2-methyl 1,3 butadiene)	$(C_5H_6Cl_4)_n$	68
Calomel (mercury(I) chloride)	Hg_2Cl_2	15
Chlorowax	variable	40–70
PVC (polyvinyl chloride)	C_2H_3Cl	57

of dominant wave lengths occur, compared to SrCl, as the result of differing atomic weights and bond strengths.

Another chemical species responsible for strontium red light production is $SrOH_{(g)}$. Strontium monohydroxide is not as desirable a color emitter as $SrCl_{(g)}$ because it emits orangish-red light. However, if conditions in the flame are such as to favor SrOH formation, this too would be good. The best way to achieve production of SrOH is to provide a generous supply of hydroxyl radicals (OH·). This happens automatically whenever hydrocarbons are present in a color formulation, which is most of the time. Organic resin fuels, most organic chlorine donors and dextrin are all hydrocarbons. When a hydrocarbon reacts with a source of oxygen, water vapor is one of the reaction products. At the temperature of a pyrotechnic flame, some of the water vapor breaks down into H· and OH· radicals. The process is shown in Equations 24 and 25 for the simplest hydrocarbon, methane (CH_4).

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O_{(g)} + Heat \qquad (24)$$

$$H_2O_{(g)} + Heat \leftrightarrow H· + OH· \qquad (25)$$
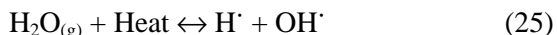
It is worth noting that B. Douda (private communication) reports only having observed SrOH in relatively low temperature flames, never when metal fuels were used. He conjectures that SrOH is unstable at high temperature.

Chlorine donors and hydrocarbons aid in the production of useful red color emitters based on strontium. As such it is appropriate to consider both of them "color enhancers" for strontium

reds. Much of the same is true for barium greens, copper blues and calcium oranges. This is true because in each case the useful color emitters are monochlorides and monohydroxides (see Table 8).

In cases such as sodium yellows or lithium reds, chlorine donors and hydrocarbons do not act as color enhancers. In these cases, it is neutral metal atoms (Na^0 and Li^0) that are the desirable color generating species. Sodium and lithium monochlorides and monohydroxides are undesirable light emitting species. Thus the addition of chlorine donors or unnecessary hydrocarbons do not enhance the color, they weaken it by consuming desirable species and generating undesirable species. This is not much of a problem for sodium yellow, because sodium is an unusually powerful color emitter and the weakening will not be noticeable. However, for the weaker lithium reds, these so-called color enhancers must be avoided.

I still need to discuss what can be done to further limit production of the undesirable species, Sr^{2+} and $SrO_{(g)}$. I intentionally said "further limit" because those things mentioned above that foster increased production of SrCl and SrOH also help limit production of Sr^{2+} and SrO. This is because all four are competitors for Sr^0 in the flame. The more SrCl and SrOH made, the less Sr^0 is available to form strontium ions or oxide.

One way to limit strontium ionization,

$$Sr^0 + Heat \leftrightarrow Sr^{2+} + 2e^- \qquad (26)$$
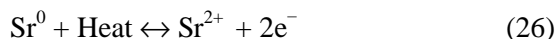
is to stress the reaction in the reverse direction. This could be done by removing heat energy from the flame, but remember this has the undesirable effect of lowering flame temperature, thereby reducing light output. A better way is to provide a source of free electrons, one of the reaction products. Although this may sound difficult, it is not. In fact you normally provide for this, without realizing it. The introduction of any easily ionizable metal into the flame will supply electrons to the flame. If the metal ionizes more easily than strontium, the electrons thus generated will act to suppress strontium ionization. One such metal is potassium, which may already be present in the flame, if for example $KClO_4$ or $KClO_3$ is used as oxidizer in the color formulation. Because of their ability

Table 12. First Ionization Energies of Metals Usable for Light Generation (From Data Presented in Sargent-Welch's Periodic Table Catalog S18806).

Metal	First Ionization Energy (kcal/mole)
Copper	178
Calcium	141
Strontium	131
Barium	120
Sodium	119
Potassium	100

to suppress other undesirable ionization in flames, metals such as potassium are sometimes referred to as "ionization buffers". See Table 12 for a listing of ionization energies for potassium and metals commonly used for colored light generation.

Probably the best way to limit formation of SrO in flames is to limit, as much as practical, the presence of oxygen radicals in the flame. Obviously the first thing to do to accomplish this is *not* to use an excess of oxidizer in the formulation. (Another good reason to do this is that slightly fuel rich flames tend to have larger flame envelopes.) However, even fuel rich flames will pick up additional oxygen from the air, leading to the formation of oxides in the flame tips. For strontium this is not that noticeable, because the formation of SrO produces orange flame tips. On the other hand, in barium greens, this produces yellow flame tips and in copper blues produces pink flame tips. The objectionable production of oxides in flame tips can sometimes be reduced by the use of secondary, slow-reacting fuels that consume the excess oxygen. T. Fish (Fish, 1981) recently discussed this for formulations in which magnesium was the primary (more active) fuel. In that work Fish coined the descriptive term "flame deoxidizing agent" for hexamine (hexamethylenetetramine), his choice as the secondary fuel.

4.4 Colored Pyrochemical Flames

4.4.1 Red, Green and Orange Flames

In the production of intensely colored flames, using strontium for red and barium for green, exactly the same chemical principles apply. In the discussion above, where strontium was used as the example, barium can be substituted in nearly every sentence and chemical equation where strontium appears. The same is almost true for calcium used to produce orange flames, except that CaOH is the preferred orange color emitting species and not CaCl (see Table 8).

A look at the Periodic Table of elements suggests why the interchangeability of Sr, Ba and Ca in the above discussion should not be a surprise. Calcium, strontium and barium are all group IIA elements, and should be expected to follow the same general chemistry.

4.4.2 Blue Flames

The standard blue flame is produced using copper. In general, everything that has been said about strontium red flames also applies to copper blue flames. Only a couple of additional points are worth discussing. For strontium reds, both the monochloride and the monohydroxide emit useful colored light. This is not the case for copper blues. The principal emission bands for CuCl fall in the purplish-blue portion of the spectrum. However, those of CuOH fall mostly in the green portion of the spectrum. Thus for effective blue flames, it is even more important to include a generous source of chlorine. However, the presence of a small amount of CuOH in the flame is useful because its green emissions add to the purplish-blue emissions of CuCl to produce a high purity blue light. This color addition is shown on a chromaticity diagram in Figure 48. (For information on scales, wave lengths and colors for the chromaticity diagram, see Figure 31 from Part I of this paper.)

Because of the suspected loss of CuCl by decomposition at relatively low temperatures, it is probably true that temperatures of blue flames cannot be allowed to range as high as strontium reds. However, some of the notions about low flame temperatures have been improperly stated. For example, a reason often expressed for using stearine in blue formulations is that it lowers
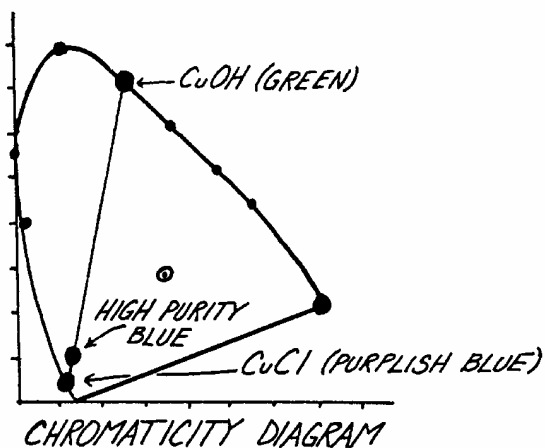
Figure 48. The addition of CuOH and CuCl emissions in the proper proportion to produce high purity blue light.

flame temperatures. This does not make much sense; a more effective way to lower flame temperature would be to add more copper color agent and/or chlorine donor. Perhaps the beneficial effect of stearine results more from its acting as a flame deoxidizing agent.

4.4.3 Yellow Flames

Yellow is generally thought to be the easiest flame color to produce. The addition of almost any source of sodium will suffice. This is because essentially no attention has to be given to flame temperature, color enhancers, or flame deoxidizing agents, etc. Flame temperatures too low to allow intense production of the other colors can still produce good yellow color. On the other hand, very high flame temperature is not really a problem either. For other color flames, high flame temperatures can result in the loss of desirable color generating species by decomposition. For sodium yellows, it is sodium atoms that are the color generating species; thus there are no molecules to decompose. Ionization will still occur at high flame temperatures, but sodium is so powerful a color source, that this is not much of a problem. Again because it is sodium atoms that emit yellow light, color enhancers are not necessary. Even the formation of oxides at flame tips does not weaken the strong yellow flame color.

There are two factors, however, that make the production of good yellow flames less than trivial. The first is the tendency for double decomposition reactions to occur between water soluble sodium color agents and the oxidizer, when water soluble binders are used. An example of such a double decomposition reaction is:

$$KNO_3 + NaHCO_3 \leftrightarrow NaNO_3 + KHCO_3 \quad (27)$$

The problem here is production of $NaNO_3$ which is hygroscopic, i.e., tends to pick up moisture from the air. This can result in drying problems, ignition problems and possibly additional decomposition problems with other ingredients because of the retained moisture.

The other area for concern with sodium yellow flames is the use of magnesium or magnalium in the formulation. Again, if the sodium color agent is water soluble and the composition is dampened with water, there is a probability that undesirable reactions will occur, producing potentially dangerous amounts of heat in the mixture. The solution is the same for both problems; either eliminate the use of water soluble binders or use water insoluble sodium color agents. Two such insoluble substances are sodium aluminum fluoride (cryolite) and sodium aluminosulfosilicate (ultramarine), the latter of which requires rather high flame temperatures to be effective.

4.4.4 Purple Flames

In Part I of this paper, the difficulty of producing intensely purple colored flames was discussed. The reason is restated again in the chromaticity diagram in Figure 48, intensely purple colored flames are those whose additive spectral colors produce color points in the shaded region of the chromaticity diagram. The lower the color point falls in the shaded region, the more intensely colored the flame appears. The only way to produce colors in this region is to combine spectral colors from opposite ends of the spectrum (i.e., purple itself is not a "spectral" color). It is commonly believed that high purity purple can result from combining red and blue light. This is not really true, red and violet (purplish-blue) light are the necessary ingredients. Remember from the discussion above that the formation of a small amount of CuOH (green) is useful, tempering the purplish-blue

light of CuCl and producing a high purity blue flame (color point A in Figure 49). Similarly, the production of both SrOH (red-orange) along with the preferred SrCl (red) still produces an effective red flame (but with its color point shifted from color point B to C). When these colors (points A and C) are added in the approximate ratio of 4:1, a relatively low purity purple flame results (color point D).

If the formation of CuOH and SrOH had not occurred, color points E and B (corresponding to CuCl and SrCl respectively) would have resulted. When these colors are added in the approximate ratio of 4:1, a relatively high purity purple flame results (color point F). Thus the key to production of high purity purple flames is to foster the production of CuCl and SrCl and limit the production of CuOH and SrOH. This can be accomplished by using fuels and chlorine donors that do not contain hydrogen atoms. Metal powders and carbon are possible fuels. Hexachlorobenzene (C_6Cl_6) and mercury(I) chloride (Hg_2Cl_2) are possible chlorine donors. Organic binders (hydrocarbons), like dextrin and red gum, should be avoided. For a binder, it might be possible to use hexachlorobenzene, which is soluble in benzene. (Note that benzene is a carcinogen.) B. Douda (private communication) has suggested that high flame temperatures may also aid in the production of good quality purple flame. This is because he believes CuCl and SrCl (the desired color sources) are more stable than the hydroxides at high temperatures.

Acknowledgments

I wish to gratefully acknowledge the comments and suggestions of R. M. Winokur and other members of the Pyrotechnica staff, and especially the technical comments of B. E. Douda and his colleagues at the US Naval Weapons Support Center (Crane, IN).
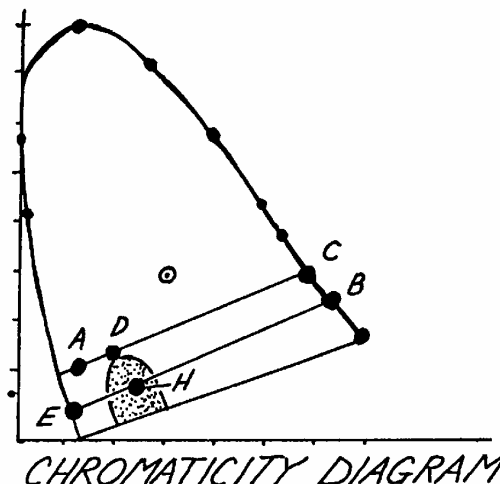

Figure 49. Why a good purple is still tough, but not impossible.

References Cited in Part II

B. E. Douda, *Theory of Colored Flame Production*, RDTN No. 71, US Naval Ammunition Depot, Crane, Indiana, AD-A951815, 1964.

T. Fish, "Green and Other Colored Flame Metal Fuel Compositions Using Parlon", Issue VII, *Pyrotechnica: Occasional Papers in Pyrotechnics* (1981).

A. A. Shidlovskiy, *Fundamentals of Pyrotechnics.* Translated from *Osnovy Pirotekhniki* (1964). Picatinny Arsenal, AD-462474, 1965.

T. Shimizu, *Feuerwerk von physikalischem Standpunkt aus*, Hower Verlag, 1976.

T. Shimizu, *Fireworks from a Physical Standpoint.* Part I. Pyrotechnica Publications, 1982.

END OF PART II