Introductory Chemistry for Pyrotechnists, Part 1: Atoms, Molecules, and Their Interactions

Wesley D. Smith
Department of Chemistry, Ricks College, Rexburg, ID 83460, USA

ABSTRACT

This is the first in a series of tutorials that introduce the concepts of chemistry to practicing pyrotechnists. It begins with the fundamental ideas of atoms and molecules. The reactions of these entities, together with their symbols, their nomenclature, their stoichiometry, and their energetics, are then described with pyrotechnic examples.

Keywords: chemistry, atomic theory, chemical formulas, chemical equations, stoichiometry, energetics, nomenclature

Introduction

If you're building fireworks without a rudimentary understanding of chemistry, you're hindering yourself. You may well be able to fabricate numerous and wonderful pyrotechnic devices. You might have read books, watched videos, and taken courses on all aspects of fireworks construction. You may even have served apprenticeships with the masters of pyrotechnics. But with little chemistry, by and large, all you know is *how* to do it. If you ever wanted to improve a formulation or to create a novel and original effect—and what pyrotechnist hasn't?—you'd have to go beyond the scope of your reference works and outside the experience of your mentors. And lacking chemical insight, you could only do that by accident, by hunch, or by trial and error. Any such approach would be hazardous at least and tedious at best.

On the other hand, if you understood a surprisingly small number of fundamental chemical concepts, you'd know *why* many fireworks phenomena work as they do. You'd possess the background to channel your creative efforts in safer, more efficient directions. And you'd have the credentials to exonerate yourself with your mother, who always told you, "Never touch that stuff unless you know exactly what you are doing!"

So, why haven't you studied more chemistry? It's probably because you've never found a chemist who would talk to you on your level. You're a fireworks person. Your IQ has the normal three digits, not four, not two. You don't want to be snowed or patronized. And you're practical. You don't want a treatise on the whole breadth of chemical science. You just want to know and understand what applies to pyrotechnics. If that's the kind of introductory chemistry you've been seeking, then this series of articles is for you.

Chemical Thinking

Interestingly, to begin thinking chemically, you don't need to get all formal and scientific. Instead, you simply have to use your imagination.

It's easy to visualize something that's within your own experience. For example, take a sheet of aluminum foil. Tear off a corner. Examine the removed scrap. Isn't it still aluminum? Of course. The tearing action hasn't changed it into some new substance. With a razor blade, pare off a minute flake. That shaving, too, is still aluminum. You can envision all this.

What's great about imagination is that you can also venture out beyond your experience. In your mind's eye, go on creating ever–smaller fragments of the aluminum foil. You can picture yourself viewing and manipulating those pieces at whatever sub-microscopic level you wish, can't you? What would you get if you kept doing this forever? Would each of the new flecks continue to be aluminum? Chemists would say, "No, they wouldn't!" According to them, the process would lead to some tiniest–possible particle of aluminum, which, if subdivided further, would become something different.

Actually that idea isn't as far-fetched as it first sounds. Liken the aluminum foil to a big sheet of postage stamps. As long as you tear off pieces along the perforations, you are just creating smaller sheets of stamps. But when you come to the smallest–possible "sheet"—a single stamp—you can't go any further; if you tear *it* up, it no longer works for postage.

To chemists, any sample of aluminum is a huge number of minuscule particles which are all essentially identical to each other. Each chemist has in mind something analogous to a skyscraping stack of acre-sized postage-stamp sheets that has shrunk to the dimensions of the sample. Can you see the same preposterous spectacle in your own imagination? If so, you are thinking chemically.

Atoms

The primary, "postage–stamp" particle of aluminum is called an aluminum *atom*. An atom is the smallest unit of an element that retains its properties. You have never experienced any one of these on an individual basis because they are so incredibly minute. Take, for example, one of the tiniest bits of aluminum that you *have* encountered: a lone 5-micron minigrain of German dark aluminum. This speck, though barely visible, contains a whopping quadrillion aluminum atoms (10^{15} or 1,000,000,000,000,000 atoms, give or take a few hundred trillion)! Your personal computer, at top speed (100 MHz), would take nearly four months to count them. But if you can conceive of aluminum atoms as single entities, then you have begun to grasp the most fundamental chemical concept.

This concept, the atomic theory, says that *every* element, not just aluminum, is composed of atoms. Just as postage stamps vary in size and denomination, so do the atoms of other elements like sulfur, carbon, or magnesium. All atoms of a particular element are alike, but they differ from the atoms of any other element. Imagine the frantic behavior of the aluminum atoms in a salute mix as it explodes. If you ignite separate samples of the same flash powder, the new aluminum atoms are going to behave identically, right? But if you replace the aluminum with, say, zinc, you know that something different is going to happen. That's because zinc atoms are not the same as aluminum atoms, and, on ignition, they are going to do their own frantic thing.

There are just over a hundred different elements, and, thus, there are only that many different kinds of atoms. Each element (and atom) has a name and a chemical symbol. And each is characterized by its own unique behavior. Those most commonly found in pyrotechnics are listed in Table 1.

Table 1. Elements Commonly Used in Pyrotechnics.

Name	Symbol	Typical Valence State*	Atomic Weight
Aluminum	Al	+3	26.98
Antimony	Sb	+3	121.75
Arsenic	As	+3	74.92
Barium	Ba	+2	137.33
Bromine	Br	–1	79.90
Calcium	Ca	+2	40.08
Carbon	C	+4	12.01
Chlorine	Cl	–1	35.45
Chromium	Cr	+3	52.00
Copper	Cu	+2	63.55
Hydrogen	H	+1	1.01
Iodine	I	–1	126.90
Iron	Fe	+3	55.85
Lead	Pb	+4	207.2
Lithium	Li	+1	6.94
Magnesium	Mg	+2	24.30
Manganese	Mn	+2	54.94
Mercury	Hg	+2	200.59
Nitrogen	N	–3	14.01
Oxygen	O	–2	16.00
Phosphorus	P	–3	30.97
Potassium	K	+1	39.10
Silicon	Si	+4	28.09
Sodium	Na	+1	22.99
Strontium	Sr	+2	87.62
Sulfur	S	–2	32.06
Titanium	Ti	+4	47.90
Zinc	Zn	+2	65.38

* Most elements have other valence states, but these are the ones most likely to be found.

Molecules

It's the interaction of atoms that causes pyrotechnic effects. But the interaction has to be *chemical*.

Take, for example, the classic model-rocket fuel, zinc and sulfur. When the two elements are mixed, they both retain their properties. They interact only on a physical basis. If you vibrated the loose mixture, the heavier zinc dust would sink to the bottom, and the lighter sulfur powder would float to the top. You'd see a yellow layer separate from the grayish mass, and you'd verify that the two elements had kept their characteristic colors. If you added acid, the zinc would produce bubbles of hydrogen gas, just as if it were alone. If you heated the mixture, the sulfur would melt into a smelly, brown syrup at about 120 °C, as if no zinc were around. Right to the end of the countdown, neither element would lose its identity no matter how intimately the two were intermingled in the casing. (This is a desirable attribute for a well-behaved rocket.)

But on ignition, the fireworks happen. The elements interact chemically, and something new takes their place. Instead of yellow or gray substances, you now have an abundance of white ashes—not off-white, not pale yellowish-gray, but bridal-gown *white*. Its color is so deep and intense that the residue was once used widely as an artist's pigment. Further, if you tested it, no part of the ash would form bubbles with the strongest of acids nor would any of it melt even at temperatures of many hundreds of degrees. It is nothing at all like the zinc or the sulfur you started with. Yet, remarkably, chemical analysis would show that the new material contained both. The white product is not a new kind of mixture of elemental zinc and elemental sulfur, rather it is a *compound* of the two. A compound is a substance composed of two or more elements that are united chemically in fixed proportions.

Now imagine how this process takes place on the atomic level. Like the individual bits of German dark aluminum, the tiny specks of zinc dust in the mixture are each collections of billions upon billions of atoms. So are each of the pieces of sulfur powder. Even at the tiniest mesh sizes and with the most intimate of mixing, these conglomerations of atoms can come in contact with each other only at a few places on their surfaces. (See Figure 1, Top.)

And, at room temperature, there is little likelihood that many zinc and sulfur atoms can get together. The rocket fuel simply lies dormant in its casing. But when the fuse is lit, fire comes to the mixture. The sulfur nearest to the fuse melts and oozes around the solid zinc. (See Figure 1, Bottom.) Now there is much more physical contact between much more energetic zinc and sulfur atoms. And chemistry happens. Zinc and sulfur atoms begin to pair off and bind together. The result of each union is a *molecule* with, in this case, two atoms tightly connected with a chemical bond. Furthermore, each molecule finds itself with less chemical potential energy (energy in storage) than the unbound atoms from which it was formed. The excess potential energy takes kinetic form as heat and light, and a chemical reaction has taken place. The energy quickly spreads throughout the mixture, initiat-

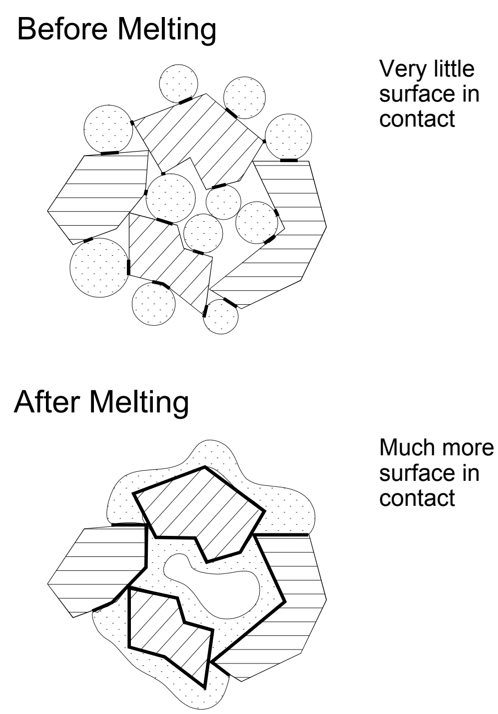

Figure 1. An illustration of the greatly increased contact with the melting of one component of a mixture.

ing more combinings of zinc and sulfur, releasing more chemical potential energy, and producing more heat and light. In a flash (literally), nearly all the zinc and sulfur atoms are united into molecules, and the rocket flies. This little description is the springboard into a number of chemical concepts that need elaboration. Among them are the symbolic representation of molecules, the naming of molecules, the symbolic representation of chemical reactions, the proportions in which substances react, and energy considerations. The balance of this article is devoted to their explanations.

Formulas

As the rocket fuel is burned, one atom of zinc, Zn, combines with one atom of sulfur, S. The *formula* of the resulting compound is written as ZnS, a combination of the elements' symbols. Other simple compounds, such as table salt, which is made from the elements sodium, Na, and chlorine, Cl, are written similarly, NaCl. But most compounds are not straightforward, one-to-one combinations. Water and carbon dioxide are surely the most familiar of these. The formula for a water molecule, having two hydrogen atoms and one oxygen atom, is, of course, H_2O. Carbon dioxide, having one carbon and two oxygens, is CO_2. In general, a chemical formula shows the symbol for each element in the compound followed by a subscript indicating how many atoms of that element are in the molecule. The absence of a subscript is understood to mean 1. Thus a molecule of antimony trisulfide, Sb_2S_3, is a combination of two antimony atoms and three sulfur atoms.

Why is water H_2O and not HO_2 or just HO? Each element has a typical combining capacity or *valence state*. This is either a positive or negative integer, and it represents the bonding behavior of its atoms. Table 1 lists the most likely valence state for each element. The handy thing about an element's valence state is that it tells you the subscript on the *other* element in a compound.

Here's how you use it. First, note that two elements combine only when they have valence states of opposite sign. Second, simply criss-cross the valence states to get the subscripts in the formula. Find in the Table 1, for example, that hydrogen is +1 and oxygen is –2. Once you notice that the signs are opposite, you don't need them any longer. Criss-crossing just the numbers, you would get H_2O_1. But don't show any subscripts that are 1; instead write the well-known formula as H_2O. [Can you see why HO_2 or HO won't work? Verify, by this method, that antimony trisulfide should indeed be Sb_2S_3.] There is one other wrinkle in this process that needs to be ironed out. Try carbon (+4) and oxygen (–2). The result, C_2O_4, is not the formula of carbon dioxide. So the third rule is this: whenever both subscripts can be divided by the same number, do it. Thus, divide the 2 and the 4 by two to get the correct formula, CO_2. [That is how you would predict the formula, ZnS, right? Try it.]

This criss-cross trick is designed for compounds that contain only two different elements. If there are three or more elements, things become messy. However, certain combinations of atoms, called functional groups, often stay together as units in multi-element compounds. They can be treated as above. Table 2 is a listing of common functional groups in pyrotechnic and explosive compositions. Criss-crossing their valence states works just as if they were

Table 2. Common Functional Groups.

Name	*Formula*	*Valence State*
Ammonium	NH_4	+1
Azide	N_3	–1
Benzoate	$C_7H_5O_2$	–1
Bicarbonate	HCO_3	–1
Carbonate	CO_3	–2
Chlorate	ClO_3	–1
Dichromate	Cr_2O_7	–2
Fulminate	CNO	–1
Nitrate	NO_3	–1
Oxalate	C_2O_4	–2
Perchlorate	ClO_4	–1
Peroxide	O_2	–2
Picrate	$C_6H_2N_3O_7$	–1
Salicylate	$C_7H_5O_3$	–1
Sulfate	SO_4	–2
Styphnate	$C_6HN_3O_8$	–2

single elements. For example, barium chlorate, a possible ingredient for green stars, would be $Ba_1(ClO_3)_2$ or just $Ba(ClO_3)_2$. Note that the parentheses are necessary here; without them—$BaClO_{32}$—you'd be giving the silly impression that the molecule contained thirty-two oxygen atoms. Ammonium nitrate, part of the Oklahoma City explosive, would come out $(NH_4)_1(NO_3)_1$, or NH_4NO_3. Parentheses are not needed whenever the subscript is 1. [What would be the formulas of potassium dichromate and ammonium oxalate? Who would have believed that, after reading these few pages, you would be jotting down such jargon as $K_2Cr_2O_7$ and $(NH_4)_2C_2O_4$?]

Names of Compounds

Chemists have thick manuals itemizing the current set of rules for giving any compound a unique and systematic name. But you don't have to know the gory details in order to make sense of most names. Generally a compound has a two-word name. The first word is the name of the element (or functional group) with the positive valence state. The second word names the one with the negative valence state. Sometimes various official prefixes (e.g., di- and tri-), suffixes (e.g., -ide), and/or roman numerals (e.g., IV) are thrown in to avoid ambiguity, but grasping their exact purpose won't add much to your understanding at this point. The only additional information you may need is the ability to recognize a few common leftovers from an out-dated system (e.g., cuprous and cupric refer to copper; ferrous and ferric mean iron). Otherwise, look up in a technical dictionary any names you can't translate (e.g., orpiment and Paris green).

Chemical Equations

You've just been reading whole paragraphs that describe the reaction between zinc and sulfur to give zinc sulfide. Much of that description could be summarized symbolically by a *chemical equation*:

$$Zn + S \rightarrow ZnS$$

Here the plus sign is read as "and," and the arrow is read as "reacts to give or to yield." The elements in the original mix, which disappear in the course of the reaction, are called *reactants*. That which appears in their place is called the *product(s)*.

Most reactions are not this simple. Take, for example, the burning of potassium chlorate with lampblack carbon to give potassium chloride and carbon dioxide. Written in shorthand form, it becomes

$$KClO_3 + C \rightarrow KCl + CO_2$$

The three oxygen atoms, originally attached to the chlorine atom of the potassium chlorate, leave, and two of them connect themselves to the carbon atom. Somewhere in the process, if you believe this notation, an oxygen atom gets lost. That just can't happen in chemistry. Molecules can fall apart, and molecules can form. But every atom that you start with in the reactants has to be there in the products. That's a law of nature. Therefore, the notation must be mistaken. What's needed here is a *balanced* chemical equation, one that follows this conservation-of-atoms law:

$$2\ KClO_3 + 3\ C \rightarrow 2\ KCl + 3\ CO_2$$

Now, both in the reactants and in the products, there are two potassium atoms, two chlorine atoms, six oxygen atoms, and three carbon atoms. These fundamental ingredients are conserved; they have only redistributed themselves into different molecules.

Examples of balanced chemical equations include the thermite reaction,

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$$

the decomposition of nitroglycerin (an understatement if there ever was one),

$$4\ C_3H_5N_3O_9 \rightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

and one of the reactions in the space shuttle's solid rocket boosters

$$6\ NH_4ClO_4 + 10\ Al \rightarrow 3\ N_2 + 9\ H_2O + 6\ HCl + 5\ Al_2O_3$$

This last equation, though balanced, is too simplistic a representation of the overall launch-vehicle reaction. (This is because of other materials, such as binders, mixed with the ammonium perchlorate and aluminum.) The reaction in the shuttle's main engines, however, is considerably less complex:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

Stoichiometry

With a balanced equation as a description of a chemical reaction, you are able to *count* precisely the number of atoms of each element involved. In fireworks formulations, however, you *weigh* the substances. *Stoichiometry* (a word whose Greek roots mean the measurement of components) is the conversion between these two processes.

In the model-rocket fuel, one atom of zinc reacts with one atom of sulfur. To formulate the fuel properly, then, you want to mix equal numbers of atoms. That does *not* mean mixing equal weights of each. Zinc atoms do not weigh the same as sulfur atoms. (Remember the postage stamps of different sizes and denominations?) What you need are the parts by weight that contain the same number of atoms. This is given by each element's *atomic weight*. If the atomic weight is expressed in grams, the amount of the element is called a *mole*. According to Table 1, the atomic weights of zinc and sulfur are 65.4 and 32.1, respectively. Thus, you would mix 65.4 parts zinc and 32.1 parts sulfur, by weight—approximately 2 grams or ounces or pounds of zinc to every 1 of sulfur—to make the rocket fuel. If you are interested in percentages, which means you want all the parts by weight to add up to 100, you have to do some calculations. The weight of zinc, divided by the total weight of all components, times 100%, gives you the number you want,

$$\frac{65.4}{(65.4+32.1)} \times 100\% = 67.1\%$$

Similarly, you can obtain 32.9% for sulfur.

For reactants that are compounds instead of just elements, you need a way to find the parts by weight that give equal numbers of molecules. You want the compound's *formula weight*, or the sum of the atomic weights of each atom in the molecule. For potassium nitrate, KNO_3, the formula weight is the sum of 1(39.1), for the one potassium atom, plus 1(14.0), for the single nitrogen atom, plus 3(16.0), for the three oxygen atoms, giving a total of 101.1. Similarly, for barium perchlorate, $Ba(ClO_4)_2$, the formula weight is

$$1(137.3) + 2[1(35.5) + 4(16.0)] = 336.3$$

Put all this together for the first step in the Senko-Hanabi reaction of black powder.

$$2\ KNO_3 + 3\ C + S \rightarrow K_2S + 3\ CO_2 + N_2$$

What proportions of each reactant should be mixed according to this equation? Will it come out to be the classic 75-15-10 proportions? For 2 molecules of KNO_3, the parts by weight are 2(101.1) = 202.2; for 3 atoms of carbon, they are 3(12.0) = 36.0; and for one atom of sulfur, they are 1(32.1) = 32.1. So, in parts by weight, the ratio of the mixture should be 202.2 to 36.0 to 32.1. The total weight is the sum of these, or 270.3, and the percentages come out to be 74.8% potassium nitrate to 13.3% carbon to 11.9% sulfur. These aren't quite equal to the venerable black powder proportions; the mixture is slightly sulfur-rich. Apparently this helps promote the beautiful branching sparks of the Senko-Hanabi effect.

The challenge of the stoichiometric approach to pyrotechnic formulation is to obtain a plausible chemical equation. There's no problem identifying what reactants are involved, but it may be difficult to discern what some or all of the products should be. Studies have shown, for example, that when black powder burns, it does not produce just the three products shown above. Rather it yields dozens of products. It happens that these three are the most abundant of the products, but a more complete equation may imply slightly different proportions of the reactants. Nevertheless, a balanced equation, whether you discover it in a reference text or you create it as best you can alone, is still a better first approximation to the ideal composition than any random conglomeration.

Energy in Pyrotechnics

The whole point of formulating pyrotechnic mixtures is to produce kinetic energy, especially in the form of sound and light. Since such energy cannot be created out of nothingness (that's another law of nature), it has to be extracted from the chemical potential energy already existing in molecules.

The nitrate and perchlorate compounds commonly found in pyrotechnic compositions are examples of substances that contain large stores of chemical potential energy. The ash and gas that result from their ignition are compounds of considerably lower potential energy. The difference is released as the kinetic energy of the pyrotechnic effect: sparks, flame, and/or noise.

In order to get the reaction going, however, the ingredients must be supplied with an amount of initiating or *activation energy*. That's because the reactant atoms and molecules have to be propelled against one another with enough force to break some of the existing chemical bonds. Only as a result of such collisions can the new chemical bonds of the product molecules be formed. For example, in the chlorate-lampblack reaction above, the oxygen atoms first have to be torn away from the chlorine atoms in potassium chlorate—that is, activation energy must be provided—before they can combine with the carbon atoms. But the resulting carbon dioxide molecules have so much less chemical potential energy than the reactant molecules that all the invested activation energy and considerably more gets returned as kinetic energy.

You can visualize this on the diagram in Figure 2. As the pictured reaction, a generalized pyrotechnic process, progresses from left to right, it first has to climb an energy hump (the activation energy). Once over the top, however, it coasts back down to its original level, recovering the energy it has just expended. Then it continues to drop to the energy level of the products, releasing the heat (or other kinetic energy) of reaction.

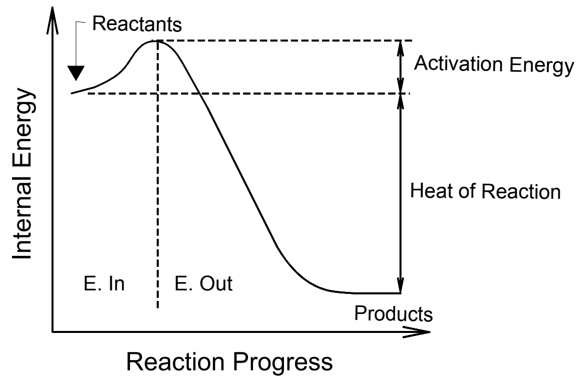

Figure 2. An illustration of activation energy and heat of reaction for a chemical reaction.

The activation energy hump acts as a barrier to reaction. And because different compositions have different-sized activation energy restraints, they differ in their ease of ignition. Some of the humps are small, making the reaction mixture sensitive to accidental ignition. Chlorate-sulfur mixtures and nitroglycerin are examples of energetic materials with dangerously low activation energy barriers. Relatively tiny amounts of initial energy, from static electricity, minor impact, or slight friction, for instance, can be enough to set them off. Other formulations, like thermite mixtures, have inconveniently high activation energy barriers and are difficult to ignite. Good pyrotechnic compositions, like black powder, have "Goldilocks" activation energies: not too high, not too low, but just right.

The Foundation of It All

Being able to imagine how atoms, molecules, and energy interact puts you well on the way to understanding the full chemistry of fireworks. What remains for future parts of this series are just deeper examinations of these fundamental principles.