Introductory Chemistry for Pyrotechnists
Part 2: The Effect of Electrons

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ABSTRACT

This is the second in a series of tutorials that introduce the concepts of chemistry to practicing pyrotechnists. The behavior of electrons in atoms is given as the fundamental explanation for all pyrotechnic processes. The periodic arrangement of the elements in a table and their tendencies to unite in chemical bonds are attributed to electrons. Even the production of heat, light, sound, and color in fireworks are ascribed to electronic movements.

Keywords: chemistry, electrons, periodic table, chemical bonds, oxidation, reduction, colored flames.

Introduction

The early parts of this century brought a revolution in the way scientists thought of atoms (the subject of Part 1 of this series[1]). They found that atoms, long regarded as indivisible and featureless, were not the most fundamental ingredients of matter. They discovered, instead, that atoms themselves were composed of tiny components. Each atom consisted of a dense, central kernel, called a *nucleus*, seeming to contain a menagerie of exotic particles. That was surrounded by a swarm of different particles called *electrons*. In addition, scientists learned that none of these subatomic particles behaved as familiar, tangible pieces of matter did. Rather they acted strangely, seeming to follow their own *quantum mechanical* set of rules. Although this elaborate, new concept of the atom made things more complicated, it provided explanations for phenomena that had puzzled people for years. In particular, the idea of quantum mechanical atoms containing electrons answered a question that had been asked, off and on, for seven or eight centuries: "Why do fireworks work?"

The Quantum Picture of an Atom

Imagine that you have the ability to magnify atoms to outrageous sizes. Make one so large that is fills, a football stadium. What do you see? At first, you become aware of an annoying blurriness in your vision that you can't clear up, even in your mind's eye. (Quantum objects have a built-in uncertainty about them; you cannot simultaneously pin down their locations and their speeds.) Nevertheless, you see well enough to spot the nucleus, a pea-sized piece of matter writhing on the 50–yard line. And you make out the mosquito-like electrons, not so much as individuals, but as clouds pervading all the bleachers. The overwhelming impression you get from this stadium-sized atom is that it is mostly empty space; it contains very little matter for the volume it occupies. But the matter that does exist in it is dynamic.

As you approach the atom for a better look, you are assaulted by the enormous forces that are coursing through it. These forces arise, in part, from the electrical charges on the electrons and on the nucleus. The electrons carry a negative charge, and the nucleus exhibits an opposite, positive charge. But the forces are more than just electrical. They seem also to impose a certain order on the electrons. You notice that the electrons are segregated according to their energies. The slowest of them occupy the clouds nearest the nucleus, while the more energetic electrons inhabit the more distant clouds.

If you observed atoms of every element on this same huge scale, you would find that the behavior of electrons is quite orderly indeed. Each atom has a similar set of segregated electron clouds, called *shells* or *energy levels*. The electrons prefer to occupy the shells with the lowest energies. Only when those are filled to capacity do electrons move into upper energy levels. The capacities of the first four shells are 2, 8, 8, and 18.

Two quantum properties of these energy levels are important in fireworks. First, only those elements that happen to have exactly enough electrons to fill up the energy levels are stable and satisfied. (There are just six of these elements, helium with 2 electrons and neon with 10, for example. They are called the noble gases, and they hardly ever participate in chemical reactions.) The rest of the hundred-odd elements have partially-filled energy levels that make them chemically reactive. They will combine with other elements in order to obtain a more favorable configuration of electrons. All pyrotechnic effects are the visible or auditory result of such electron rearrangements. Second, the energy gap between one level and another is forbidden territory. Electrons may not take on any energy in that void. It's like a step ladder. You may stand on one rung or you may stand on another, but you cannot stand between rungs. If any electron is to change energy levels, it must absorb or give off the associated amount of energy all at once. No gradual build-ups or let-downs are allowed; it's the entire amount or nothing. Colored flames are the result of electrons jumping between shells and giving off energy in the form of visible light.

The rest of this paper will examine these two quantum effects in more detail.

The Periodic Chart of the Elements

By the time electrons were discovered, chemists, as a practical matter, had already organized the elements onto a chart that was rich in information. They found that if the elements were listed in a certain order, by rows, they would line up in columns of elements with similar chemical properties. This *periodic chart* of the elements is pictured in Figure 1.

When chemists connected the concept of electrons to this well-established arrangement, it was a watershed moment for science. Not only did electrons explain the particular order, but they also accounted for the periodic or cyclic repetition of properties. It turned out that the sequencing of elements, from left to right, was by their *atomic numbers*, the numbers of electrons in their neutral atoms. And the odd way of splitting them into rows of unequal length also became clear. The lengths of the first four rows were 2, 8, 8, and 18 the exact capacities of the electron energy levels. Furthermore, the elements lining up in the same columns each lacked the same number of electrons to fill their outermost shells.

The utility of this chart—with or without an electron explanation—comes from how near the symbols of different elements are to each other. You can expect many of the elements' properties (and that of their compounds) to vary gradually as you go from one box to the next. The most useful feature, however, is the way particular elements reside above or below each other in the columns. All the elements in the same column are regarded as belonging to a *chemical family*. Although each element is a unique individual, members of the same family are alike in many of their chemical properties. For example, their compounds will have analogous formulas. Sodium is in the same chemical family as potassium. Thus, if you know that potassium nitrate is KNO_3, then you also know that sodium nitrate is $NaNO_3$, not Na_2NO_3 or $Na(NO_3)_2$. You've seen titanium (Ti, element 22) salutes giving off brilliant white sparks along with their loud reports. Many pyrotechnists know that zirconium (Zr, element number 40) also emits white sparks in salute compositions. Since zirconium is a member of titanium's family on the periodic chart, such a similarity in behavior, though not inevitable, is not surprising either. [Could there be still another element that, when added to a salute, would produce similar sparks? Perhaps you can narrow down the possibilities on Figure 1 to a singularly likely candidate.]

Unfortunately, some important pyrotechnic properties of elements and compounds do not overtly follow periodic tendencies. The green flame color produced from barium compounds, for instance, is randomly different from the red of strontium compounds and the orange of calcium compounds even though all three elements are in the same chemical family. Sodium compounds are generally hygroscopic; they absorb unacceptable amounts of moisture from the air. However, potassium compounds are generally not. The periodic table cannot easily

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Te	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104														
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

Figure 1. A simple periodic table of the elements, giving their atomic numbers and symbols. The staircase dividing line separates metals and nonmetals.

be used to predict the flame color or the hygroscopic nature of substances.

Chemical Bonding

Every element on the chart, except the six noble gases in the far right column, is composed of atoms having electron shells that are only partially filled. That means that nearly all atoms have less-than-ideal numbers of electrons in their outermost energy level. In order to remedy this situation, atoms react with one another, and they form chemical bonds. A *chemical bond* is an arrangement between two atoms for the sharing or transfer of electrons. Whenever such bonding occurs, the resulting configuration of electrons is more favorable than those of the separate, unbonded atoms: the chemically bonded atoms have less chemical potential energy.

When each of the combining atoms already has nearly ideal numbers of electrons—that is, when neither lacks more than one or two from a completely filled shell—the atoms will share electrons. They form *covalent bonds*. For example, hydrogen lacks one electron from becoming like the noble gas helium, and oxygen wants two to become like neon. If a hydrogen atom obtains a share of one of oxygen's electrons, it has improved its electron configuration. But oxygen's need is not fulfilled with its share of hydrogen's single electron; it's still short one. Thus, two hydrogen atoms must combine with one oxygen atom to satisfy all participants. The resulting H_2O molecule is a more stable combination of hydrogen and oxygen than just HO. In fact, the combination is so stable that whenever hydrogen and oxygen participate in a pyrotechnic process, the end result is the production of water.

The types of elements that form covalent bonds with one another are the *nonmetals*, those elements to the right and above the stair-case dividing line on the periodic chart.

About 80% of the elements on the chart, however, are not even close to having enough electrons to fill their outermost electron levels. Generally, it would take four or more electrons to complete their shells. These elements are the *metals*, those to the left and below the dividing line on the chart. The metals, therefore, adopt a different strategy when they combine: they transfer electrons.

Magnesium metal, for example, would need to gain six electrons to become like the noble gas argon (element 18). But if it could lose just two, it would be like neon. Magnesium's outermost shell would then be empty, leaving the remaining electrons in filled shells. Magnesium atoms, in fact, find perfect fulfillment when they encounter atoms like oxygen. Each oxygen, you remember, is in need of two electrons while each magnesium is looking to jettison two. A transfer of two electrons satisfies them both. That's why all pyrotechnic effects involving magnesium produce MgO, which often glows brightly in the flame. In the exchange of electrons, oxygen takes on two extra negative charges. It becomes a charged atom, or ion, with a –2 electrical charge. The magnesium, now free of two electrons, but with the same nucleus as before, becomes an ion with a +2 electrical charge. (Two of the positively-charged protons in its nucleus no longer have electrons to balance them.) The magnesium ion and the oxygen ion attract each other because of their opposite charges, and MgO is held together with an *ionic* bond. [Determine from the periodic chart why the ionic combination of NaCl (table salt) is so common.]

Table 1 shows the electrical charges that atoms of the first 20 elements take when they have formed stable ions those with no partially-occupied energy levels. These ionic charges are identical to the typical valence states listed in Part 1 if this series of articles. [1] In other words, each atom's electronic structure determines its combining capacity. Whenever two elements combine in these common valence states, they become as stable as they can get, electron-wise. The resulting compounds, with atoms in these states, are generally found as the products of reactions rather than as the reactants (starting materials). [The valence states of all atoms in a neutral molecule must add up to zero. Verify that all the atoms in CO_2 and K_2S, two of the by-products of black powder combustion, are in their typical valence states and thus have stable electronic structures.]

Table 1. The Electronic Charges or Typical Valence States of the First 20 Elements.

Name	Formula	Charge
Hydrogen	H^+	+1
Helium	He^0	0
Lithium	Li^+	+1
Beryllium	Be^{2+}	+2
Boron	B^{3+}	+3
Carbon	C^{4+}	+4
Nitrogen	N^{3-}	–3
Oxygen	O^{2-}	–2
Fluorine	F^-	–1
Neon	Ne^0	0
Sodium	Na^+	+1
Magnesium	Mg^{2+}	+2
Aluminum	Al^{3+}	+3
Silicon	Si^{4+}	+4
Phosphorus	P^{3-}	–3
Sulfur	S^{2-}	–2
Chlorine	Cl^-	–1
Argon	Ar^0	0
Potassium	K^+	+1
Calcium	Ca^{2+}	+2

Table 2. Oxidizers Commonly Used in Pyrotechnics.

Name	Formula	Notes
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	Volcanoes
Ammonium perchlorate	NH_4ClO_4	
Barium chlorate	$Ba(ClO_3)_2$	Green Color Agent
Barium nitrate	$Ba(NO_3)_2$	Green Color Agent
Hexachloroethane	C_2Cl_6	Smoke
Iron oxide (red)	Fe_2O_3	Thermite
Lead oxide (red)	Pb_3O_4	Dragon Eggs
Potassium chlorate	$KClO_3$	
Potassium dichromate	$K_2Cr_2O_7$	Burn Catalyst/ Mg Coating
Potassium nitrate	KNO_3	
Potassium perchlorate	$KClO_4$	
Sodium nitrate	$NaNO_3$	Yellow Color Agent
Strontium nitrate	$Sr(NO_3)_2$	Red Color Agent

Oxidation and Reduction

Certain combinations of elements, however, cannot produce a maximally beneficial exchange of electrons. Two different metals like aluminum and magnesium, for example, may mix to form an alloy like magnalium, but they will not truly react with each other chemically. Other sets of elements, for the lack of better alternatives, will combine without achieving the stability of substances like H_2O or NaCl. For example, when oxygen and chlorine unite to form the perchlorate ion, ClO_4^-, they do so at chlorine's expense. Rather than being able to gain one electron and to obtain the favorable valence state of –1, the chlorine atom has to relinquish control of seven electrons to the oxygen atoms. Thus, if you allow oxygen to have its typical valence state of –2, then chlorine must take on a valence state of +7 [(+7) + 4(–2) = –1]. Although the perchlorate ion is energetically more stable than if chlorine and oxygen atoms remained uncombined under the same conditions, the chlorine atom in a perchlorate ion will seize any opportunity to improve its valence state and to give off more energy. The valence state of chlorine is highly electron-deficient.

Some elements find themselves in valence states with an excess of electrons. Lactose ($C_{12}H_{22}O_{11}$), for instance, contains carbon with a valence state of zero [12(0) + 22(+1) + 11(–2) = 0]. Carbon prefers a valence state of +4, where it has lost four electrons and has adopted the electronic structure of helium. Thus, in lactose, the valence state of carbon is electron-rich.

A substance whose atoms are in electron-deficient valence states is called an *oxidizer*. A compound or element with atoms in electron-rich valence states is called a *fuel*. Neither has an ideal number of electrons, and both have more chemical potential energy than they would like. Mixtures of oxidizers and fuels, therefore, are reactive combinations. In fact, all such mixtures can participate in *oxidation-reduction* reactions, in which electrons are transferred from one substance to another. Electron-flush fuels deliver their extra negative particles to the electron-starved oxidizers, and both transform their excess chemical potential energy to heat, light, or sound. In many such reactions, fireworks happen.

Tables 2 and 3 list the oxidizers and fuels most commonly used in pyrotechnics. [Consulting Tables 1 and 2, can you tell that the nitrogen in the nitrate oxidizers, having a valence state of +5, is electron-deficient? Likewise, can you see from Tables 1 and 3 that aluminum metal, with a valence state of 0, is an electron-rich fuel?]

Table 3. Fuels Commonly Used in Pyrotechnics.

Name	Formula	Notes
Aluminum	Al	
Antimony trisulfide	Sb_2S_3	
Charcoal	"C"	≈85% Carbon
Ferroaluminum	Fe/Al	Typical Alloy 35:65
Ferrotitanium	Fe/Ti	Typical Alloy 30:70
Graphite	C	
Hexamine	$C_6H_{12}N_4$	Hexamethylene tetramine
Iron	Fe	
Lactose	$C_{12}H_{22}O_{11}$	
Lamp black	C	
Magnesium	Mg	
Magnalium	Mg/Al	Typical Alloy 50:50
Silicon	Si	
Sodium benzoate	$NaC_7H_5O_2$	Whistles
Sodium salicylate	$NaC_7H_5O_3$	Whistles
Stearic acid	$C_{18}H_{36}O_2$	
Titanium	Ti	
Wood meal	Complex	Mostly Cellulose
Zinc	Zn	

Colored Flame

In pyrotechnic reactions, chemical potential energy is transformed into kinetic energy. This kinetic energy often appears as heat, when the atoms and molecules in a reaction are made to move faster. If the atoms and molecules are made to move fast enough, the energy appears as *incandescent radiation*, the increasingly brighter glow that is given off when objects are heated from red-hot to white-hot. All of these phenomena are explained by the atomic theory. But to understand how energy appears as colored flames, you must again look at electrons.

As you saw in the stadium-sized atom, electrons organize themselves by energy into shells. They prefer the lowest energy levels, and they leave the highest levels unoccupied. But you can change that. Call down a bolt of lightening that will increase the energy of some electrons. When the added energy is right, the electrons absorb it and move from their lower energy level to the higher one, forming an *excited* atom. This term has nothing to do with atomic emotions; it describes an atom with one or more electrons in a higher-than-usual energy level. Such excited atoms do not last long. As soon as the disturbing jolt of energy has passed, the exited electrons revert back to their original levels. But in doing so, they each can give off a photon, with an exact energy equal to the difference in the two levels (illustrated in Figure 2). If those photons have wavelengths in the range of 380 to 780 nanometers, they can be detected by your eyes, and you see colored light.

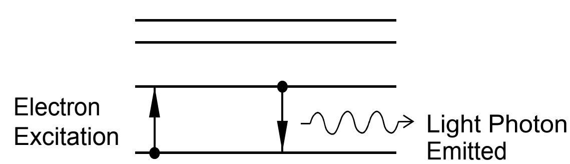

Figure 2. Diagram of atomic energy level showing electron excitation and photon emission.

For pyrotechnic formulations, you need two things to create colored flames. First, you must add an ingredient whose atoms or molecules have energy levels separated by the wavelength of color you are interested in. Table 4 lists a number of common color-producing agents. For

Table 4. Commonly Used Color Agents.

Name	Formula	Notes
Barium carbonate	$BaCO_3$	Green, Neutralizer
Barium sulfate	$BaSO_4$	Green
Calcium carbonate	$CaCO_3$	Reddish Orange
Calcium sulfate	$CaSO_4$	Reddish Orange
Copper (II) carbonate, basic	(I) $CuCO_3{\bullet}Cu(OH)_2$ (II) $2CuCO_3{\bullet}Cu(OH)_2$	Blue; commercially available material is usually a mixture of (I) and (II).
Copper (I) chloride	$CuCl$	Blue
Copper (II) oxide	CuO	Blue
Copper (II) oxychloride	$CuCl_2{\cdot}3Cu(OH)_2$	Blue
Cryolite	Na_3AlF_6	Yellow
Synthetic ultramarine (Sodium disilicate)	$Na_2S_2{\bullet}NaAlSi_2O_4$	Yellow
Sodium oxalate	$Na_2C_2O_4$	Yellow
Sodium sulfate	Na_2SO_4	Yellow
Strontium carbonate	$SrCO_3$	Red
Strontium sulfate	$SrSO_4$	Red

instance, atomic sodium in a flame emits photons that have a yellow color.

Second, you must provide for an oxidation-reduction reaction to supply the energy necessary to produce the photons. This amount of energy is considerable for most color agents. Supplying the excitation energy to the electrons is only one step in a power-hungry process. The detailed mechanism is beyond the scope of this paper, but it involves such operations as vaporizing solids, bringing the flame to a high temperature, and creating specialized (color producing) molecules within the flame. Generally, only the chlorate and perchlorate oxidizers in Table 2 and/or the metal fuels in Table 3 are potent enough to deliver this requisite flood of energy. But once you get the flame conditions right, you can banish the darkness with rainbows of light.

The Workhorse of Pyrotechnics

For all the centuries that mankind has thrilled to the splendor of pyrotechnics, they have been experiencing the effect of electrons. Whether the electrons are moving from one atom to another or whether they are jumping energy levels within an atom, their mysterious quantum mechanical compulsions have made all fireworks possible.

Acknowledgments

The figures and tables used in this article are taken from the *Chemistry of Fireworks Lecture Notes*, published by the Journal of Pyrotechnics, Inc.

References

1) W.D. Smith, "Introductory Chemistry for Pyrotechnists, Part 1: Atoms, Molecules, and Their Interactions", *Journal of Pyrotechnics*, Issue 1, 1995.