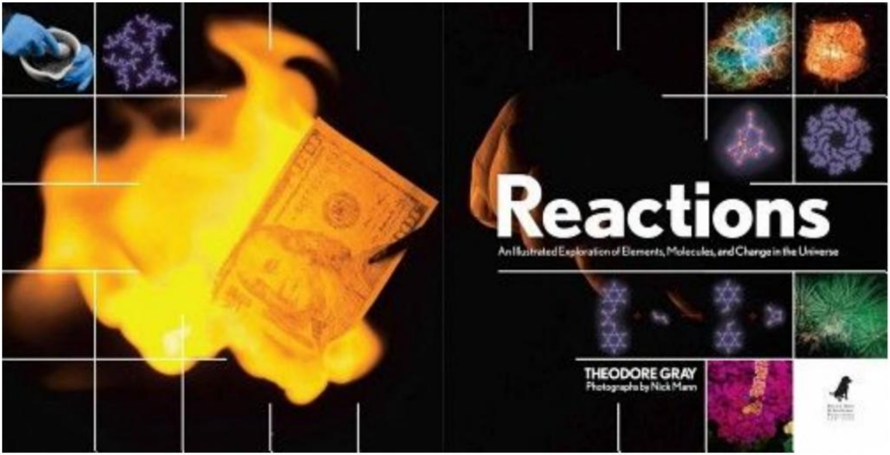

Reactions
An Illustrated Exploration of Elements, Molecules, and Change in the Universe
THEODORE GRAY
Photographs by Nick Mann

ISBN 978-0-316-50874-2

E3-20180703-JV-PC

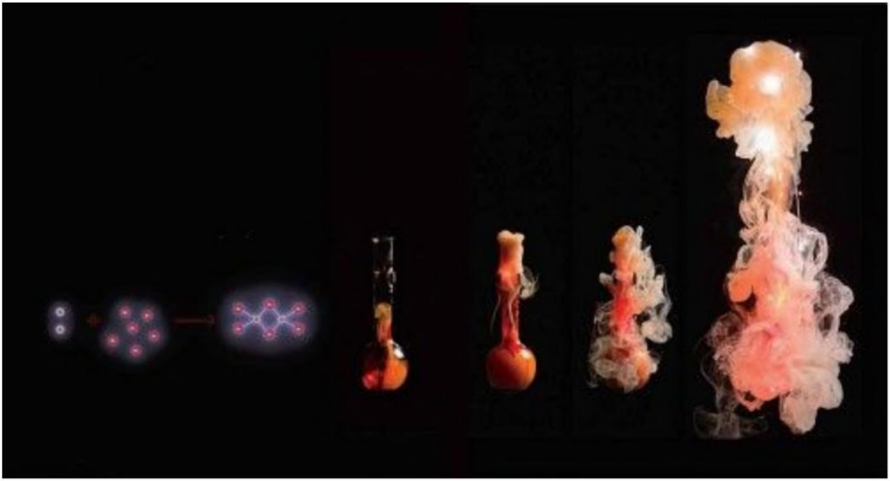
Contents

Introduction

WHEN I FIRST STARTED writing my book *The Elements* in 2008, I had the idea that it should be the first in a three-part series—*Elements*, *Molecules*, and *Reactions.* Together these three books would represent a tour of the world of chemistry. You start with elements, because everything starts with elements. Then you put them together into molecules. Then you send those molecules at each other in a sort of nanoscale fight club.

It's been nearly ten years (*ten years*!), but the trilogy is now finished! In the time it's taken to write these books, and live the life necessary to make them possible, I feel that I have been transformed as much as any of the molecules I talk about. My children have grown and my hair has shrunk. It's been worth it.

I hope you enjoy reading any or all of these books, as much as I've enjoyed writing them.



1

Chemistry Is Magic

IT IS IMPORTANT to stand in awe of nature, and to be no less dazzled by the energies and forces of the world just because we have learned to understand and control them.

Push two strong magnets against each other and feel the invisible force that repels one from the other. Go on—do it now if you can. Come back when you are filled with a sense of miracle and wonder that such things exist and that you have the supreme privilege of holding not one, but *two* of them.

Do not be misled by the fact that magnets are dirt common, or that we know exactly how they work and how to make more of them. A magnet is an object from another world, like a moon rock or meteor that fell from another star. It is a visitor to our human world that carries with it the knowledge and power of its home world.

That home is not another planet, but another scale. It is the vanishingly small world whose native inhabitants are the quantum forces that control the nature of matter and energy.

Quantum magnetic forces exist in all matter, all the time, but normally they work in opposite directions, cancelling each other out. They are hiding in plain sight. But when we create a strong magnet, we align a vast number of individual quantum forces in the same direction, coaxing this astonishing force up into our world where we can feel it push and pull on our hands.

The quantum world of the very small is also the home world of chemistry. When we see a fire burn or a leaf change color, this is the action of atoms in numbers beyond imagination, all working together to create an effect visible on the human scale.

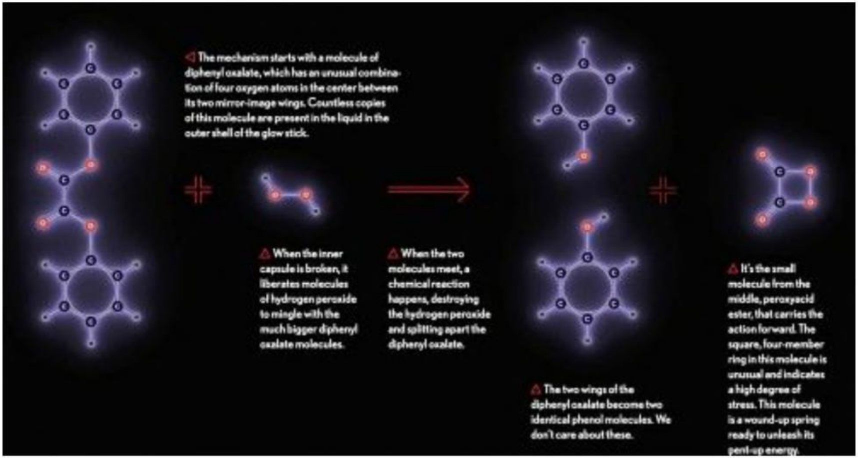
This is the world we will explore in the chapters to come.

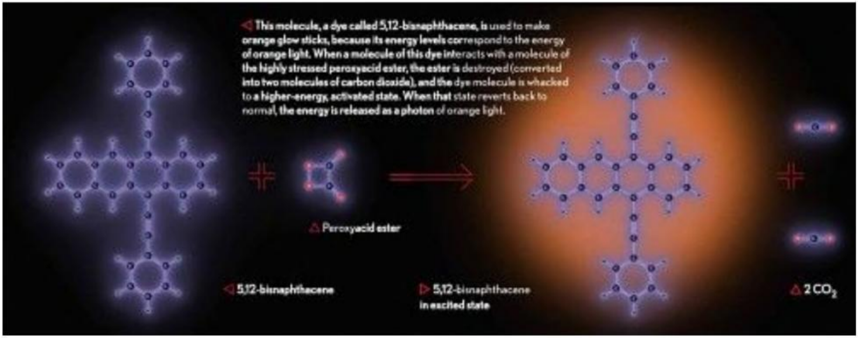
Consider the humble glow stick. You break an inner capsule to mix two solutions together, and suddenly the whole thing starts to glow! How on earth is that even possible? I insist that you be amazed by this object, even though it is available at gas stations for less than the price of a bottle of water.

Where does the light come from?

Light is made of countless individual photons—packets of energy that travel through space at the speed of light. There are many different ways of making photons. The way it's done in a glow stick is one of the most complicated: each photon is lovingly handcrafted by its own single-use chemical machine.

We designed and built these machines from scratch, so we know exactly how they work, and I can explain them to you. (Don't worry if many of the words in this explanation are not familiar: we'll come back to them one at a time later in the book.)

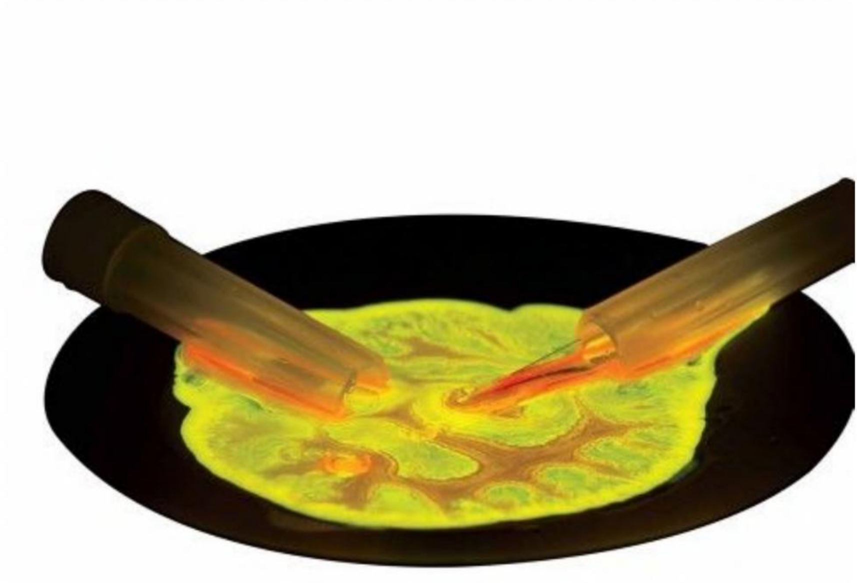

The mechanism starts with a molecule of diphenyl oxalate, which has an unusual combination of four oxygen atoms in the center between its two mirror-image wings. Countless copies of this molecule are present in the liquid in the outer shell of the glow stick.
When the inner capsule is broken, it liberates molecules of hydrogen peroxide to mingle with the much bigger diphenyl oxalate molecules.
When the two molecules meet, a chemical reaction happens, destroying the hydrogen peroxide and splitting apart the diphenyl oxalate.
The two wings of the diphenyl oxalate become two identical phenol molecules. We don't care about these.
It's the small molecule from the middle, peroxyacid ester, that carries the action forward. The square, four-member ring in this molecule is unusual and indicates a high degree of stress. This molecule is a wound-up spring ready to unleash its pent-up energy.


This molecule, a dye called 5,12-bisnaphthacene, is used to make orange glow sticks, because its energy levels correspond to the energy of orange light. When a molecule of this dye interacts with a molecule of the highly stressed peroxyacid ester, the ester is destroyed (converted into two molecules of carbon dioxide), and the dye molecule is whacked to a higher-energy, activated state. When that state reverts back to normal, the energy is released as a photon of orange light.
Peroxyacid ester
5,12-bisnaphthacene
5,12-bisnaphthacene in excited state
2 CO_2

To get light from a chemical mechanism, you need a molecule that is able to absorb and emit photons of light with the right amount of energy to be visible (too little energy and the photons are invisible infrared light, too much energy and they are invisible ultraviolet light).

The dye molecule in this reaction can be reused indefinitely, but the other molecules can only be used once: Their destruction supplies the energy needed to create the photon. All the work of this elaborate machine goes into creating *one single photon* of light. If you want another photon you have to use up another set of molecules.

A typical glow stick activates and destroys about 10,000,000,000,000,000 (ten thousand million million) of these machines *every second* to produce the light we see coming from it.



Is That Really Magic?

THE TITLE OF this chapter is "Chemistry Is Magic," yet I just told you exactly how one particular bit of chemical "magic" works. Doesn't that mean it's not magic?

I like to use the word *magic* the way it's used by stage magicians. A magic trick is "magic" because it *seems* to be supernatural, until you understand how the trick is done. Some people enjoy the mystery of not knowing, but I always find it far more satisfying to learn the trick. The cleverness and skill involved are much more interesting than the end result.

Professional magicians, and ancient conjurers, carefully guarded their secrets as a matter of commercial necessity: if everyone knew how they did their tricks, they'd be out of a job. Scientists are the opposite. When they discover a particularly clever trick, something that makes the seemingly impossible suddenly possible, they want to tell the whole world about it.

I am definitely in the science camp: I am eager to tell you about all the clever but invisible chemical magic going on all around you. This doesn't make it any less magical. It just means you will have the opportunity to tell someone else how the trick is done—next time you see someone with a glow stick, you can tell them about the tiny machines inside making the light one photon at a time.

> Any sufficiently advanced technology is indistinguishable from magic.
>
> –Arthur C. Clarke

Machines from a hundred years ago are wonderfully understandable: All the moving parts actually move, and they really are separate parts that you can see and dismantle. These machines are marvelous, but you can plainly see that they are not magical.

But imagine if you showed someone from the Steam Age a modern phone. It would seem like magic, right?

The thing that makes phones seem magical, even today, is that you can't see how they work *at all*. There's no part of their mechanism that is visible. If you take one apart, all you see is some little plastic blocks with tiny metal pins coming out. If you take those chips apart, there doesn't seem to be anything interesting inside. All the action is happening in circuits that are literally smaller than the wavelength of visible light—they are not just microscopic, they are smaller than light itself.

"Magic" machines whose parts are too small to see are a modern invention, but chemistry has always been this way, with its mechanisms of action completely invisible. Today, chemistry only seems magical: we know it actually isn't. But in ancient times no one had the slightest idea how it worked, which left a lot of room for both mystical nonsense and serious study.

A phone. You can't tell one single thing about how it works from the outside, and not much more even if you take it apart.

Every single part of this beautiful old machine is immediately visible. You can practically see it working just by looking at it.

Ancient Magic Was Mostly Chemistry

SOME PEOPLE MAKE a big deal about ancient "secret knowledge," the supposed keys to unlocking great powers, lost in the crass modern world of fast food and stupid television. The fact is that most of this secret knowledge was either pretty simple by modern standards, or plain wrong. There's more interesting new knowledge discovered in an average week today than in all the secret books of the ancients.

What I find interesting is that much of what passed for magic and secret knowledge in the ancient world was actually chemistry, or at least attempted chemistry. And *all* of the ancient magic that actually works is chemistry. Exactly none of the spells and incantations work, but a few of the *potions* do.

The potions that worked became modern chemistry. The potions that didn't work live on in the quack medical products, homeopathic remedies, and bogus "age defying" creams that remain as popular as ever.

Eye of newt, and toe of frog,
Wool of bat, and tongue of dog,
Adder's fork, and blind-worm's sting,
Lizard's leg, and howlet's wing, _
For a charm of powerful trouble,
Like a hell-broth boil and bubble.

–William Shakespeare

It's easy to mix together a bunch of ingredients that sound exotic, boil them for a while, say some silly words from a book of spells, and hope that the result is a powerful potion. But potions made with eye of newt do not work, no matter how bad they smell, and no matter how passionately you ask the forces of darkness to make them work for you.

Fortunately not everyone in the ancient world based their potion-making on wishful thinking. Some of them knew that nature is very picky and really doesn't care about your pleadings. These people knew that in order to make a functional potion, they were going to have to work hard, study the world, follow up on lucky breaks, and try a lot of variations before homing in on a combination that gave them something interesting. In other words, they were scientists long before that word had been invented.

The Three Witches from Shakespeare's Macbeth by Daniel Gardner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URANIUM NITRICUM
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by 31/3/2013 BN

The best modern example of commercially available witch's brews are homeopathic "medicines." They list a bunch of exotic ingredients, but don't actually contain any of them (yes, this is legal due to a stupid law authorizing lying for these specific products). To make them "properly" the manufacturer has to dilute the solution a certain number of times, and with each dilution shake and tap the solution in a certain direction a certain number of times. It's all complete nonsense, and would be funny if not so widely sold for so much money to so many people who are being completely ripped off.

The ingredients for gunpowder: charcoal (black), saltpeter (white), and sulfur (yellow).

If you pick three powders at random and mix them together, it's very unlikely that the result will have any special properties.

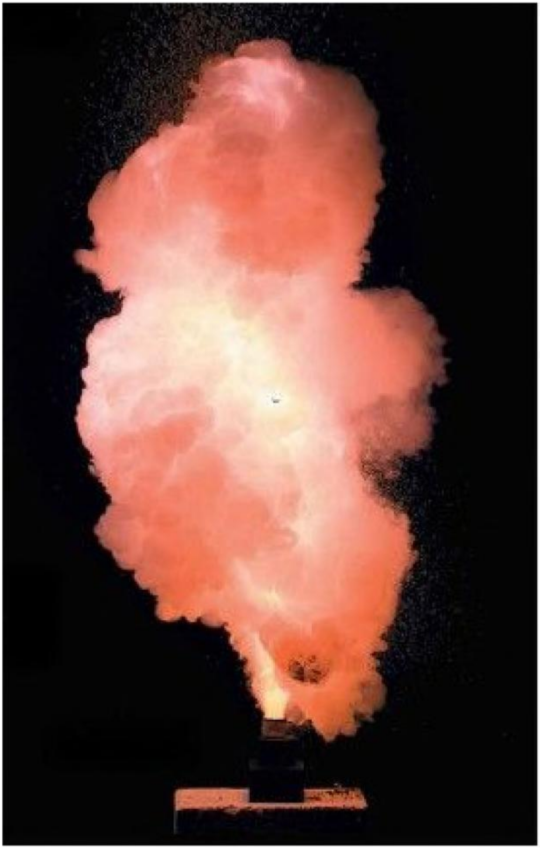
But if you pick *these three specific powders*—this particular white one, this particular black one, and this particular yellow one—and if you mix them in just the right proportions, you get a powder that vanquishes your enemies, consumes them in the fire of damnation, or blows them to bits on your command.

In other words, these are the ingredients for gunpowder.

Gunpowder is like a magic potion—a really strong one—in that it does amazing things and unleashes great power in the world. But it's not like a magic potion in that you don't have to say any silly words while mixing it, and if you get the mixture right, it works every time.

This is the key: we don't usually call gunpowder "magic" only because it actually works. And because it works, you can *use* it. It leads to new inventions, like fireworks and guns. It is an invention that carries true power, unlike the non-functional dead ends you find in witches' brews (both ancient and modern). We're going to learn how gunpowder can be arranged in beautiful ways (see here), about a better substitute (see here), and finally, here, we will learn the details of the chemical reaction that makes it work.

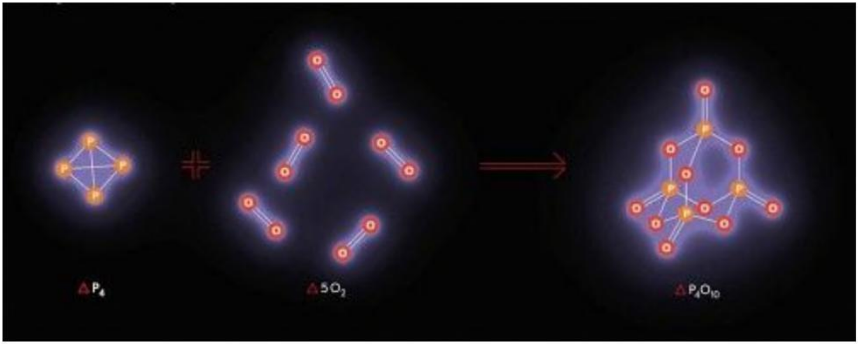
Finished gunpowder



Ancient alchemists are sometimes made fun of because of their obsession with trying to do things that we now know are impossible, like turn lead into gold or find a potion for eternal life. But this criticism is unfair, and confuses alchemists with the mystics and charlatans of their age.

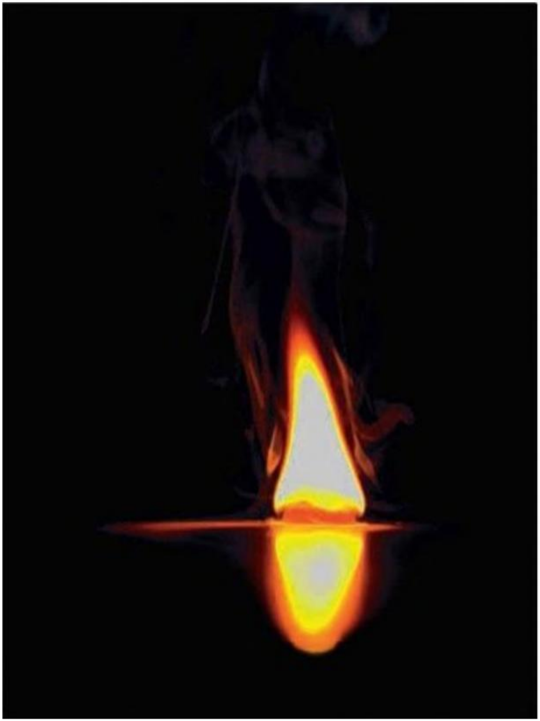
The alchemists worked diligently to identify and understand powerful substances—chemicals—that they could experiment with and combine with each other in an attempt to advance toward their goals. They got a long way toward unraveling the nature of chemical change, including the notion of immutable elements (which they were interested in studying precisely because they wanted to find an exception that allowed them to make gold from base metals).

They were wrong about a lot of things, but they were also right about a lot of other things. More importantly, they based their work on reality. They believed in testing their ideas through experiment—a thoroughly modern, scientific way of doing things. They believed in evidence, study, and confirmation. When the modern field of chemistry emerged as a solid science in the 1700s, it was built on a platform of alchemy.



The reaction between white phosphorus and oxygen (from the air) creates lovely 3-dimensional molecules, each containing four phosphorus and ten oxygen atoms.

The Alchemist by Newell Convers Wyeth, 1937



Phosphorus burning in the air

Glowing chemicals endlessly fascinated the alchemists. When

Hennig Brand discovered phosphorus in 1669, he was absolutely convinced that it must be the key to making gold, because he derived it from pee (which is yellow like gold) and because it glows in the dark (which he thought proves that it must have inherited some kind of life force from its origins). He was correct that white phosphorus is powerful stuff, just not in quite the way he hoped it would be.

The “phosphorus sun” demonstration is a favorite of those comfortable handling highly toxic, spontaneously flammable chemicals in front of crowds. Here we see my intrepid colleague Prof. Hal Sosabowski performing the demonstration, in which a small chip of white phosphorus is suspended in a ball of pure oxygen.

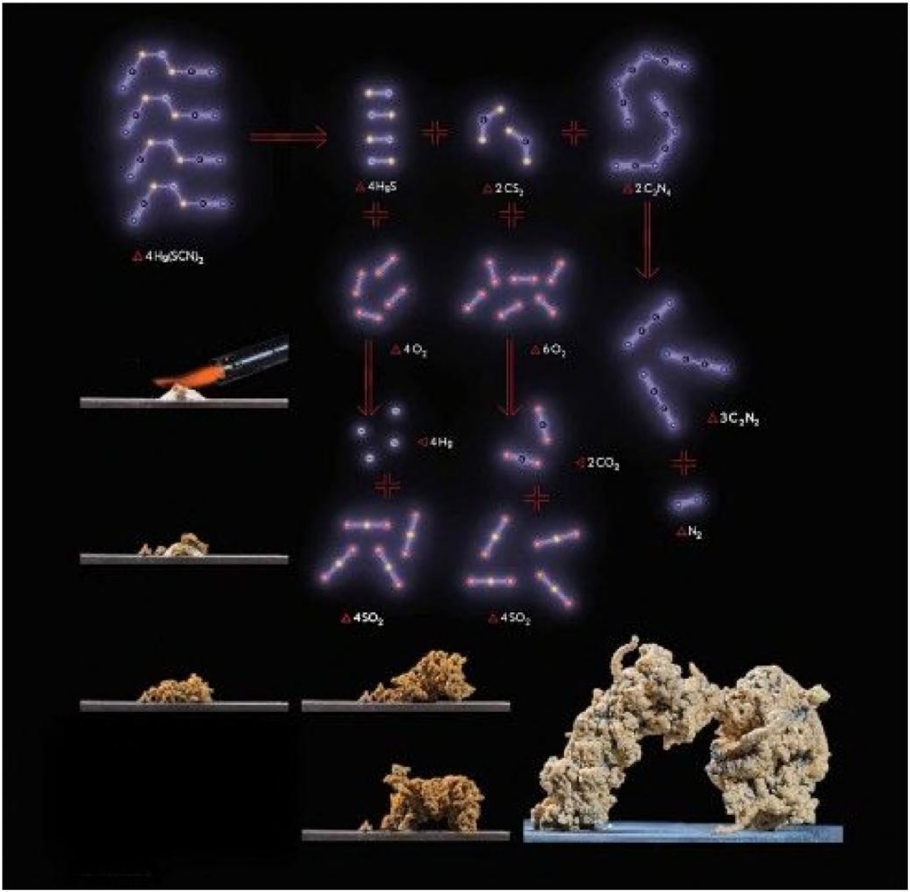
Hennig Brand discovered phosphorus while working in Hamburg, Germany. This is what Hamburg looked like 270 years later, after Allied forces in World War II dropped thousands of bombs, many of them white phosphorus incendiaries, on the city. Power is not about good or evil. Phosphorus is powerful, and whether you use that power to grow plants or level a city is up to you.

White phosphorus is extremely toxic, and it catches fire spontaneously in air at just a few degrees above normal room temperature. It also glows with an eerie light when dissolved and spread on skin (or, in modern times, very carefully on double-gloved hands).

Lycopodium powder was a favorite of alchemists wishing to put on a good show, or convince a king of their power to control nature. Throw a handful into a candle and you get a powerful burst of flame that vanishes as quickly as it arrived, leaving no trace of smoke.

Lycopodium seems almost like gunpowder (when thrown in the air), but it's actually the spores of club moss: It's a plant, not a mixture of simple chemicals. But its incredibly high surface area makes it burn so rapidly that it seems very "chemical" in nature.

When you see this stuff in action you can really understand why people of earlier times thought it was true magic!


$4\,Hg(SCN)_2$
$4H_2S$
$2\,CS_2$
$2\,C_3N_4$
$4\,O_2$
$6\,O_2$
$3C_2N_2$
$4\,Hg$
$2\,CO_2$
N_2
$4SO_2$
$4\,SO_2$

[redacted]

This “Pharaoh’s Serpent” looks like, and is named like, an ancient alchemical magic trick, but it’s actually a relatively modern (1821) discovery. The chemical is mercury thiocyanate, which is really quite seriously toxic (because of its mercury content). As fun as the versions sold to children in an earlier time must have been, it’s better to use a safer modern variation.

These very cheap kids' Black Snake fireworks nicely replicate the Pharaoh's Serpent without the heavy metal poison. The ingredients in commercial versions are trade secrets, but include something that decomposes into carbon (often linseed oil), something that burns (perhaps naphthalene), and just enough oxidizer (typically potassium nitrate) to make it burn at a good rate, not too fast and not too slow. (Normally you light one pellet at a time, but here we have ground up several hundred of them, because it looks really cool when you do that.)

The Reactions I Remember from When I Was but a Wee Lad

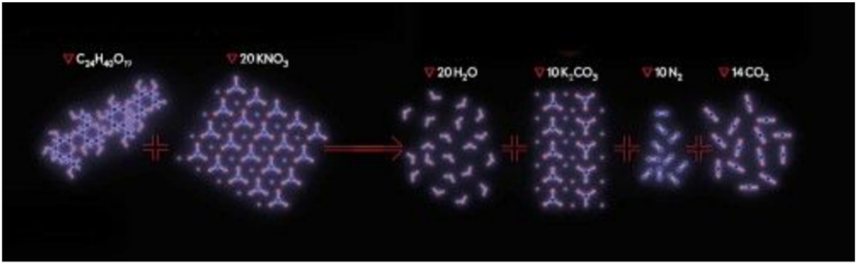
I'VE LIKED CHEMICALS since I was little, for pretty much the same reason people a thousand years ago were fascinated by them. Unlike a lump of clay or the eye of a newt, the right chemicals actually *do something* when you mix them up. It took the first alchemists hundreds of years of messing around to find just a few really cool chemicals, but as a wee lad I had the advantage of all their experience and more—captured in a pre-internet encyclopedia and later at a university—to guide me.

The day I found a list of the ingredients for gunpowder (with percentages!) was a major thrill for me. I can remember it like yesterday, taking the “G” volume off the high shelf, flipping through the pages, getting closer and closer... and there it was, just as plain as day: 75% potassium nitrate, 15% charcoal, and 10% sulfur.

These proportions are pretty flexible: Historical versions of gunpowder vary them by plus or minus 10% or more. Different ratios give you different burning rates, useful for different applications. (For example, the gunpowder in a rocket engine needs to burn over at least a few seconds, while the gunpowder in a gun has to expend itself in a tiny fraction of a second. Much more on the speed of gunpowder here.)

The flexibility of the gunpowder formula is no doubt why it was possible for the Chinese to have discovered it long before there was any understanding of why it works. You don't have to get the mixture right at all to start seeing something interesting. In fact, all you really need is the potassium nitrate: add it to just about anything that burns, even ordinary paper, and the result is something that burns *more*. If you're paying attention to the world, this is a clear sign that potassium nitrate is something worthy of further study. It's not a huge leap to try adding it to other things that burn, including charcoal, sulfur, or—bingo—both of them at the same time. From there it's just a question of systematic tests to find the best proportions.

(Full disclosure: This is actually a photo of paper soaked in the closely related chemical strontium nitrate, not potassium nitrate–frankly for no other reason than that this picture came out way more attractive than the one using potassium nitrate, and they both demonstrate basically the same phenomenon.)



With badly handmade gunpowder like mine was, you get what might be described as “vigorous burning,” not a real explosion. It’s great for making sparkle cones, terrible for making a cannon. I’m sure that when people first stumbled on this mixture of ingredients, this is the kind of reaction they got. It’s not an explosion, it’s not obviously useful for anything, but it sure is *interesting*. It would have grabbed their attention and encouraged further experimentation. Slowly, as they worked out what made the powder work better, they developed it into something that could be used for rockets and cannons.

We’ll see an example of how gunpowder is used in commercial fireworks in Chapter 4, and learn about how fast it burns in Chapter 6.

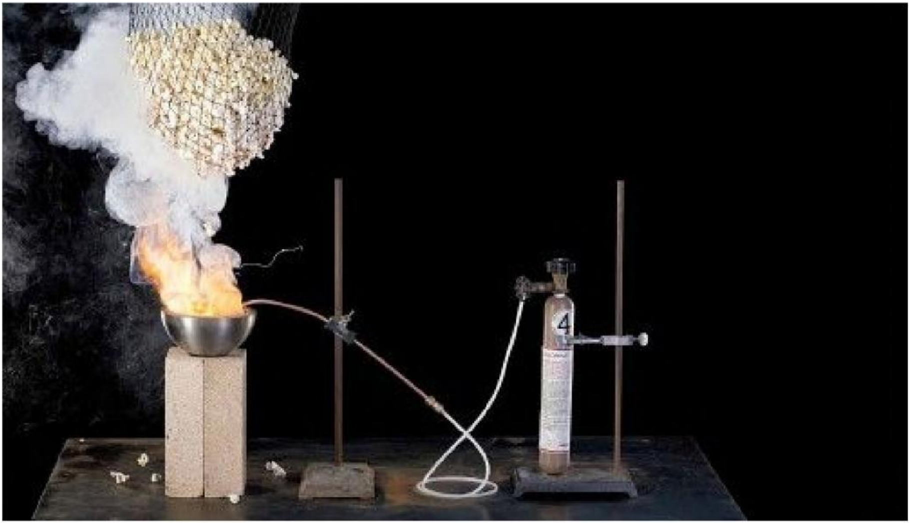
This missing photograph represents the flash powder rockets I made as a kid. There is no picture because I am not willing to make another one. It's just too dangerous. What I did, and would never do again, was to tightly pack special effects flash powder (a mixture of aluminum powder and potassium perchlorate) into thick-walled cardboard craft straws. I'm not sure where I got the idea to do this, but it actually worked: packed tightly in a thin tube, the flash powder did not "flash," but rather burned quickly, generating enough thrust to lift the rocket 20 or 30 feet into the air. Sometimes, for added stupidity, I added a firecracker on the end. Yes, it was a really dumb thing to do, and I even knew that at the time, but what can I say, kids are dumb. None of the rockets ever exploded in my face while I was packing the powder, which could very easily have happened. One reason I'm careful around chemicals to this day is the feeling I get in the pit of my stomach when I think back to when I was sitting at the dining room table, looking out the back windows with an open bottle of flash powder, a straw, and a nail, thinking to myself, "Why am I jamming this nail repeatedly down into a straw with enough friction to set off the flash powder, when I know that's very dangerous?" Seriously, kids are very dumb sometimes. If you're currently a kid like I was, remember that. You'll get smart, but in the meantime, please don't blow yourself up.


Clear Polyester
Casting Resin
Resina de poliéster
transparente para
coladas
Liquid Plastic
Plastico Liquido
DANGER:
PELIGRO:
Castin' Craft
Net 16 fl oz / Neto 16 oz fl / 473 mL

I love this stuff! It’s a clear liquid, but if you put a few special drops in it, an hour later it looks exactly the same except now it’s a clear solid. Magic. Tremendous fun to embed things in. This is polyester casting resin, commonly available in hobby shops for craft projects. The special drops are usually called the catalyst, but this is an incorrect use of the term. They are actually a free-radical initiator which kick-starts a chain reaction that eventually consumes the entire mass. Vast numbers of small molecules end up linked together into a small number of very large ones. A dense web of cross-links connecting all parts of these giant molecules makes the resulting material hard and strong.

Light-cured glues have existed for decades, but it's only in recent years that it has become widely available in retail packaging. It was worth the wait (and the fairly high cost).

One of the ground rules we expect objects in our daily experience to obey is that just looking at them isn't supposed to cause them to change form. But this stuff, a type of light-cured epoxy glue (see here for more on the chemistry of epoxies), turns rock solid in a few seconds when you do nothing more than shine some blue or UV light on it! Keep it in the dark and it stays liquid. Try to look at it under too strong a light source, and suddenly it's a solid. (Fortunately there is a wide middle ground where you can work with it under normal indoor lighting without setting it off. Convenient kits include a tube of glue and a blue/UV LED flashlight to solidify it on command.)

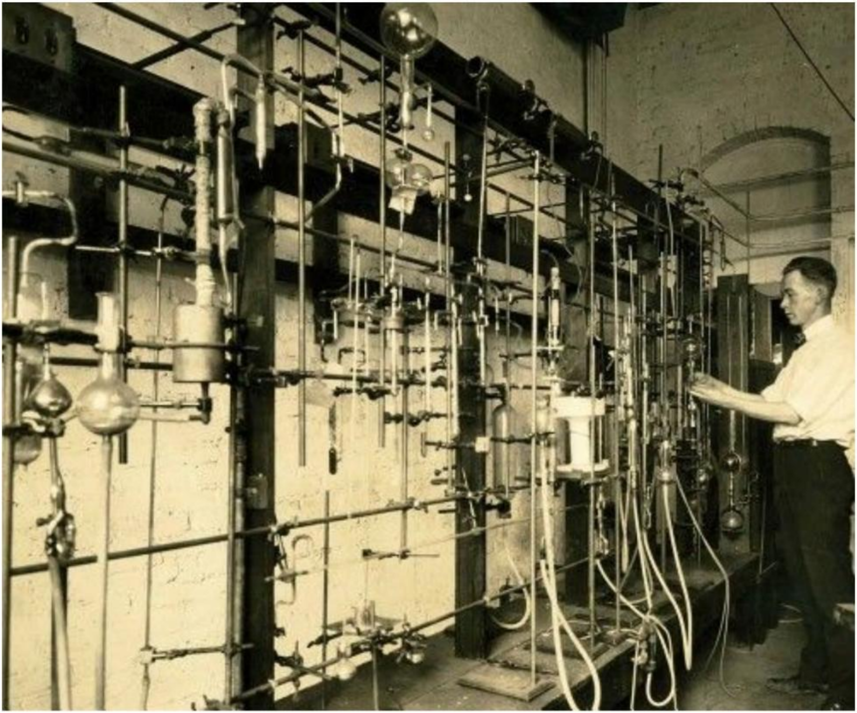


Making salt from scratch is something I'd wanted to do for many, many years before I finally got a chance. It still scares the pants off me on the rare occasions I film it again for one reason or another.

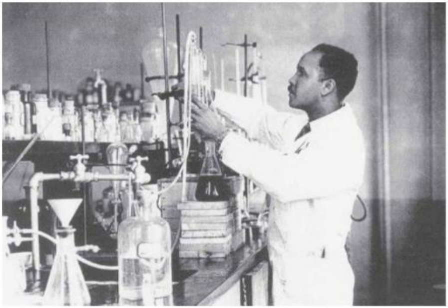
I like it because it's such a primal demonstration of elemental chemistry in action. You blow chlorine gas (a pure element that kills quickly and painfully) at sodium metal (a pure element that explodes on contact with water) and the result is a fire whose smoke is common table salt (sodium chloride, NaCl).

astonished at the skill of the glass blower, but not fundamentally mystified by the purpose of the various parts. They would recognize boiling flasks, condensation columns, and receiving pots. Mostly I imagine them admiring the clever advances in design, and the incredible precision in manufacture. And I imagine that they would take pride in knowing that it was their original invention of the alembic and the retort that led to this magnificent creation. (There are even modern glass versions of the retort design, thought they are rarely used these days.)

This kind of apparatus is how chemistry students first encounter the world of classical chemistry. If chemistry had a "golden age," it surely was the late 1800s to mid 1900s, when a tremendous number of discoveries and advances in techniques were made in synthetic organic chemistry. Today it's possible to create, from scratch, molecules with nearly any chemically possible configuration of atoms you like. That's due to generations of work by chemists who figured out thousands of individual reactions that can be used to transform one molecule into a slightly, or completely, different one.



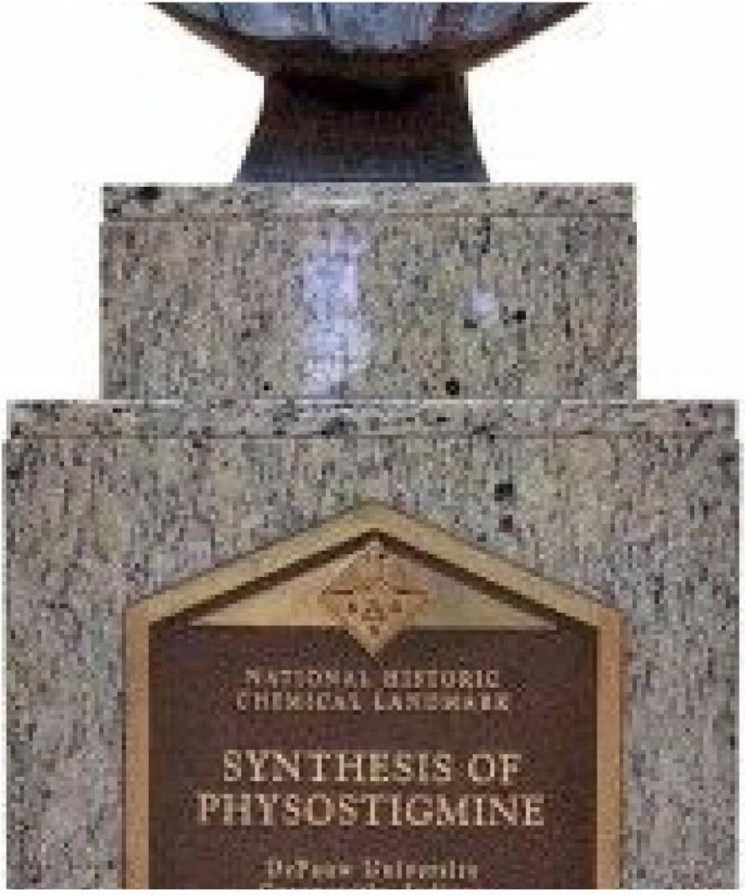

Glass retorts
3-necked reaction vessels
Broken heart
Soxhlet extractor
Coil condenser
Straight condenser
Ground glass "T" connectors
Fritted glass filter funnel



This is Percy Julian, and on the next full-page spread you can see his molecule, physostigmine (along with the steps needed to make it from scratch, which he figured out in 1935). So significant, and so difficult, was this “total synthesis” of physostigmine that it made Julian famous and led to a long and lucrative career as an industrial chemist. (You know you’ve had a financially successful career when there’s a university building named after you. Generally speaking, they name these things after whoever donated the money to build them.)

The leap from alchemists stumbling into the discovery of phosphorus, to Julian’s systematic engineering of a synthesis of this complex molecule, is as great as the leap from Orville and

Wilbur Wright's bicycle shop to the first moon landing.


NATIONAL HISTORIC
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