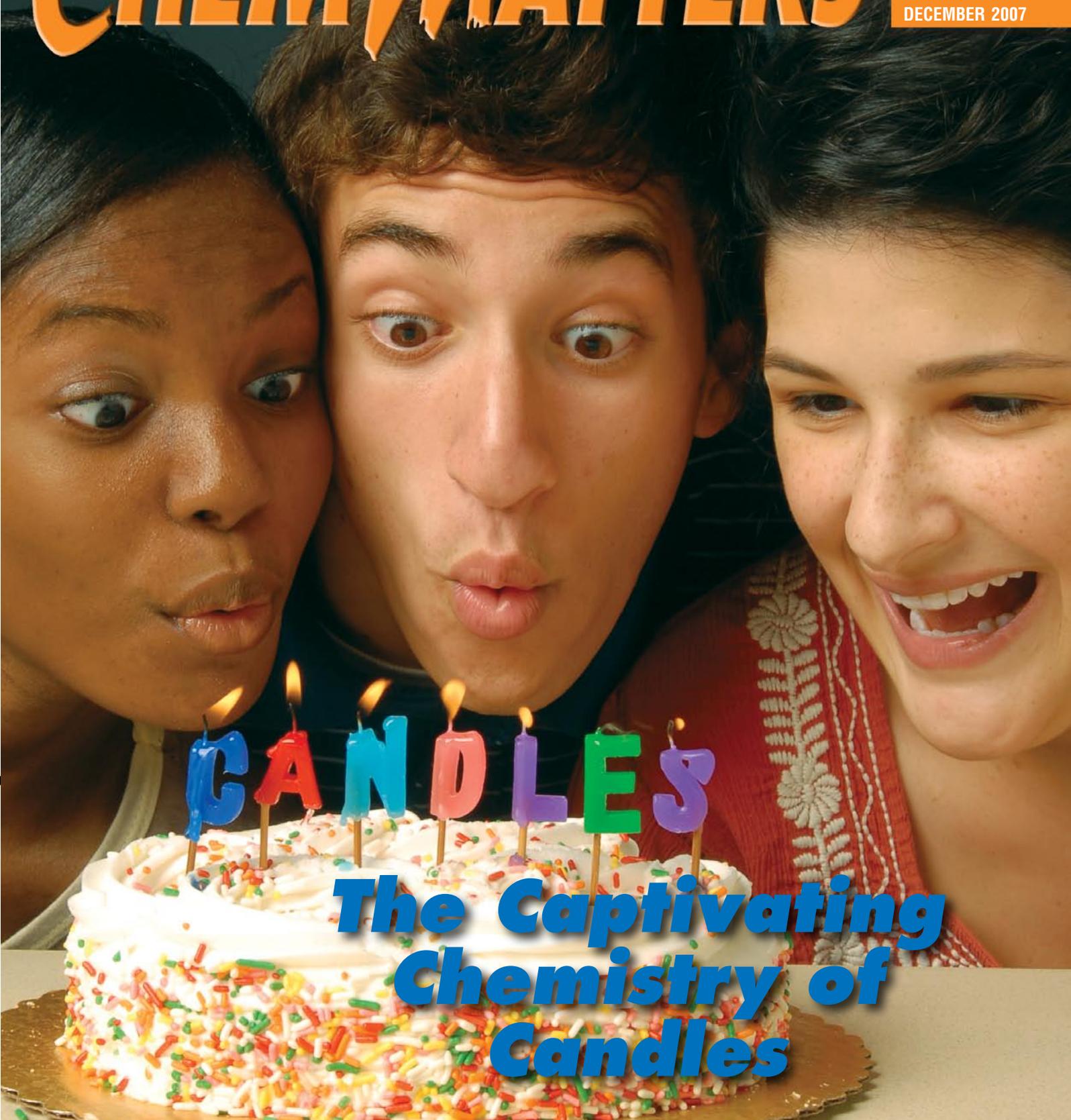


CHEM ¹MATTERS[®]



DEMISTIFYING
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CHEMISTRY

DECEMBER 2007



The Captivating Chemistry of Candles

From Candles to Cookies to Hydrogen ... Energy at Work

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QUESTION FROM THE CLASSROOM

By Bob Becker



ALL PHOTOS BY MIKE CIESIELSKI

Q. Why does shaking a can of soda make the pressure increase?

A. The answer might shake you up: Shaking a can of soda has virtually no effect on the pressure at all. Here's a better question: Why do people think shaking a can of soda makes the pressure increase? The answer to that one sheds some important light on the problems and pitfalls of scientific experimentation.

Here's something to try with a friend who has not read this article.

Line up three or four pairs of identical sodas (or "pop," depending on where you live!)—two Cokes, two Pepsis, two Mountain Dews, or two of any canned carbonated drinks. All cans should have been at room temperature for at least a day. Give your friend an identical pair of cans, with instructions to hold one tightly in each hand and to shake just one of the cans vigorously for 5 s. Now ask which can feels like it has more pressure inside, based on how hard it is to squeeze the can. Record the choice. Repeat this procedure with each of the other pairs. Looks like a solid plan for a controlled experiment, right?

If your friends are like most people, they will "get it right" every time by saying the shaken can is at a greater pressure. But are they really getting it "right" by feeling a greater pressure? Or is their judgment being influenced by what they think the outcome of the experiment should be? Quite likely, they have heard somewhere that shaking a can increases the pressure. After all, shaken cans erupt when opened! Not surprisingly, a little bit of anticipation has influenced their answers. Scientists call this effect "experimenter bias," and good researchers work hard to eliminate it from their work.

So let's work out a better plan. This time, get out 8 identical cans of room-temperature soda. Mark an X on the bottoms of four of the cans. Show these marked cans to your friend and then line them up: four marked cans (X's hidden on bottom) along the right side of the table, four unmarked

cans along the left. Next, have the friend pick up one from each side of the table, but shake only the right-hand marked can vigorously for 5 s. Do the same for the three remaining pairs. As soon as all pairs have been completed, tell the friend to look away while you quickly shuffle all eight cans together. Then ask your friend to pick out the four shaken cans by using the squeeze test. Which ones are under the greatest pressure? Is there a problem? When four have been selected, turn them over to see whether they are actually the marked, shaken cans.

Chances are that your friends found this more frustrating. With no "right answer" for guidance, it's not likely that they picked out all four shaken cans. In fact, the mathematical chances of a person randomly picking the right four cans are pretty slim—just 1 in 70. This time, you've done your best to eliminate experimenter bias.

So what is going on in that can of soda anyway? Here comes the chemistry.

Henry's law states that a gas's solubility in a liquid is directly proportional to that of the gas's pressure on the surface of the liquid. In soda, this means the more CO₂ gas you put in the bottle, the more of it will dissolve, and the fizzier it gets. This makes sense: the CO₂ molecules are in constant motion, dissolving into the soda and popping out again as gas molecules. This way, the system achieves equilibrium. How much CO₂ enters solution depends on the concentration of gaseous-phase CO₂ molecules hitting the liquid's surface. How



much effervesces out of solution depends on the concentration of dissolved CO_2 available to escape. If you pump more CO_2 molecules into the container, the pressure increases and the equilibrium shifts to create a higher concentration of CO_2 in solution.

Thus, an unopened can of soda represents a system at equilibrium. What can be done to change this equilibrium? Ideas? How about just opening the can to let out some of the gaseous CO_2 . You'll see CO_2 bubbles racing out of solution the instant the top is popped open. Here's another idea: Put the unopened can in the refrigerator. At cold temperatures, more CO_2 dissolves leaving less CO_2 in the gaseous phase to maintain the

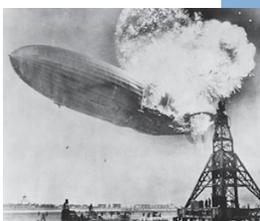
pressure. If the cold sides of the cans didn't give them away, you actually could use the squeeze test to pick them out of a crowd.

But shaking an unopened soda can? Sorry. No impact on equilibrium and no impact on gas pressure for this one. It's true that shaking a can is likely to increase the surface area where the reactions—both dissolving and effervescing—are taking place. Molecules in, fizz out—both will happen more rapidly, but the effects balance one another.

So, why does a shaken can of soda explode and spray all over the place when you pop it open? We're going to give you some time to think about that one yourself before checking the December 2007 issue of *ChemMatters* for more FIZZ-ical chemistry. Meanwhile, remember not to worry if your observations don't always stack up with your notion of a "right" answer. Seeing, and sometimes squeezing, is believing! ▲

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1. <http://www2.corepower.com:8080/~relfaq/fizziks.html> (Accessed July 2007)



QUESTION FROM THE CLASSROOM

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Shaking a can of soda makes its pressure increase...fact or fiction? Explore the answer to this question of FIZZ-ical chemistry. The truth may surprise you!

The Captivating Chemistry of Candles

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ON THE WEB

Candles have been used for thousands of years to provide light in darkness and, more recently, to illuminate birthday cakes and to bring fragrance to our homes. You'll be "enlightened" as you explore the components and operation of the candle.

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ON THE WEB

The Hindenburg airship crashed on its way to Lakehurst, NJ, in May 1937. Seventy years later, debate over the cause of the disaster continues. Has chemistry provided any answers or has it led to more questions?

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It's no accident that some cookies are crisp and others are soft, that some cookies are flat and others are cake-like. Find out how basic chemical principles are used to make the perfect sweet treat.

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In the last several months, you may have noticed labels declaring "No Trans Fats!" or "Trans Fat Free!" on the packaging of your favorite snack foods. But what are trans fats and why should they be avoided?

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As gas prices and global temperatures continue to rise, discussions about the feasibility of fuel cell-powered vehicles intensify. Learn more about fuel cells and the various fuels that could be used in their operation.

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COVER PHOTO CREDITS: MIKE CIESIELSKI



THE CAPTIVATING CHEMISTRY OF CANDLES

Birthdays, holidays, special evenings—all seem better by candlelight. But before electric lights, candles were the dependable source of light for homes.

By Brian Rohrig





Whether you are talking about the most expensive fragrance-enhanced candles or the most basic candles found in emergency supply kits, the components are the same—a source of fuel and a wick. As such, candles have been around for about 5,000 years. Through the ages, candles have been constructed from a variety of materials—beeswax, yak butter, dried fish, and many others. High-quality candles in the 18th and 19th centuries were made from *spermaceti*, an oil extracted from giant cavities in the heads of sperm whales, with yields of up to three tons of fuel from a single 15-meter-long individual! More commonly, candles were made from tallow, or animal fat. While readily available, tallow candles released heavy, odorous smoke—not exactly the stuff of romance.

The fuel

The discovery of paraffin in the mid-1800s revolutionized the making of candles. Paraffin is a by-product of the distillation of petroleum, or crude oil. Today, nearly all candles are made from paraffin. Paraffin refers to a class of hydrocarbons known as *alkanes*, compounds with only carbon-carbon and carbon-hydrogen single bonds. Methane (CH_4), propane (C_3H_8), and octane (C_8H_{18}) are other examples of alkanes. These straight-chain alkanes, like all alkanes, have the general formula $\text{C}_n\text{H}_{2n+2}$, since they consist of a chain of CH_2 groups bonded to each other, and “capped” at each end by a hydrogen atom. Paraffin compounds have more than 20 carbon atoms per molecule.

Paraffin is actually a mixture of several different heavier hydrocarbons. A good average can be represented by the formula $\text{C}_{25}\text{H}_{52}$.

Their large molecular masses make the molecules sluggish, ensuring they exist as solids.

Wax is an even less of an exact term, applied to any substance with a “waxy” feel. Without referring to any specific class of compounds, we ascribe several properties to waxes: they repel water, they are usually less dense than water, they burn, and they may be used as fuel. Wax can be of animal, vegetable, or mineral origin.

The term “paraffin wax” was coined to prevent confusion from other uses of the word paraffin. In Britain, for example, kerosene is referred to as paraffin. Liquid paraffin is commonly used for the fuel used in oil lamps. So “paraffin wax” is the preferred term for the solid hydrocarbon used in candles.

The wick

The wick is generally composed of tightly wound cotton or nylon fibers that make up a sturdy type of twine. All wicks are treated with various flame-retardant solutions in a process known as mordanting. Without mordanting, the wick would be destroyed



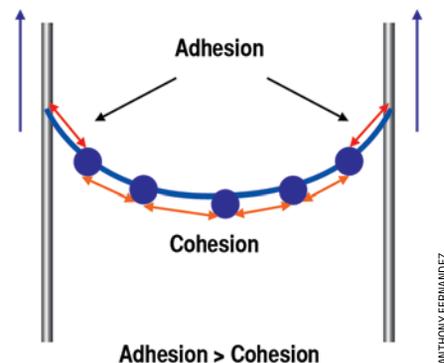
Candle wicks serve as the fuel delivery system for candles.

by the flames. In addition, a variety of substances are employed to make the wick stiff and rigid while supporting a flame. Formerly, candle wicks might contain a lead core to keep them upright. Given concerns about the release of toxic lead vapors, lead cores have been eliminated or substituted with zinc cores if a sturdy wick is required.

The wick is crucial to the proper functioning of the candle, serving as the fuel delivery system. You can think of the wick as the pipeline through which the fuel travels to the surface, making it available for combustion.

Just exactly what happens when a candle is lit? Touched by a flame, the wick quickly conducts heat to the surface of the wax where melting begins. The little pool of molten wax is the key to keeping the candle burning.

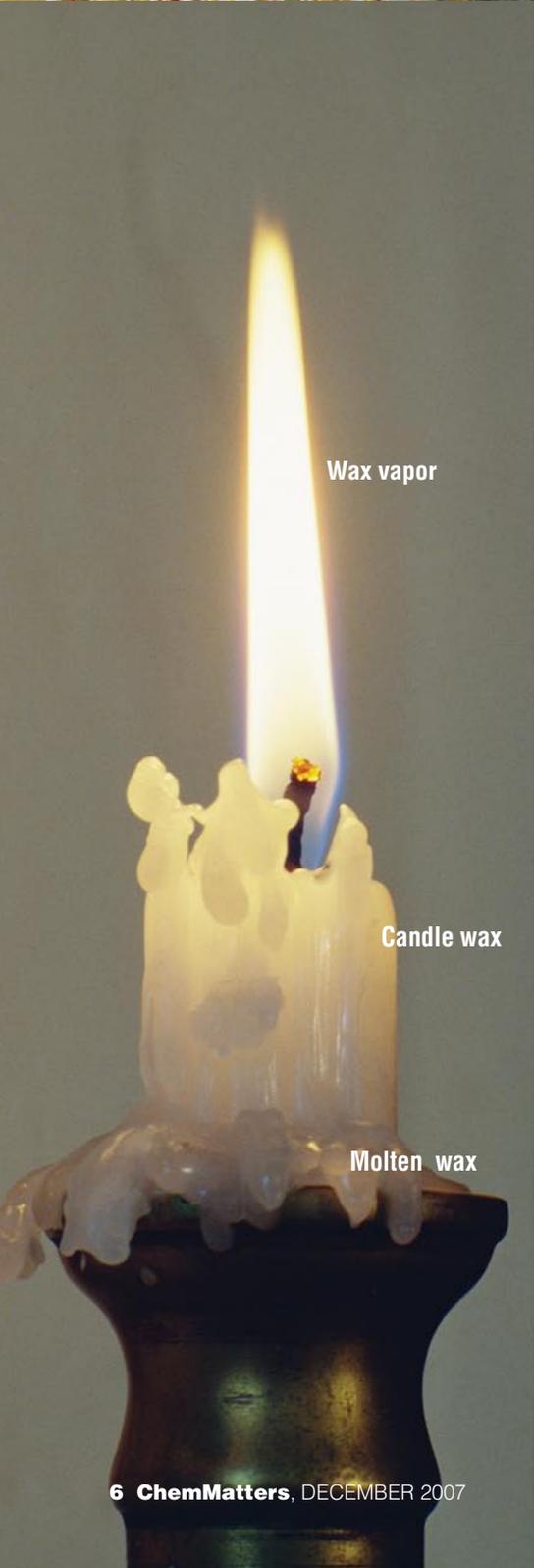
Wax must be in the liquid state to travel upward through the wick and then undergo combustion. Liquid wax travels through the wick by capillary action. Capillary action refers to the ability of a liquid to travel upward through a small tube. This occurs due to the cohesion of the liquid paraffin molecules to



Capillary action occurs due to the cohesion of the wax molecules to each other and their adhesion to the wick fibers.



MIKE CIESIELSKI



Wax vapor

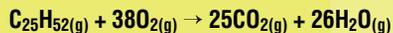
Candle wax

Molten wax

one another and the adhesion of these molecules to the sides of the tube.

Capillary action is the same principle that explains how water travels upward to the tops of trees. In this case water travels through tiny tubes just under the bark called xylem. The absorbency of paper towels is also due to capillary action. Microscopic tubes within the towels facilitate the transport of water through the towel, thereby increasing absorbency.

After the liquid wax travels to the top of the wick through capillary action, it vaporizes upon contact with the burning flame. In fact, wax only burns when it is in the vapor state—never in the solid or liquid phase. Combustion occurs as hot wax vapor combines with oxygen, producing the candle flame. Combustion of hydrocarbons is a rapidly occurring exothermic chemical reaction producing heat and light. The reaction can be summarized by the following equation:



One of the products is easily observed by placing a beaker over a burning candle flame and then quickly removing it. A thin film of water appears on the beaker as water vapor from the combustion reaction condenses onto its cool surface.



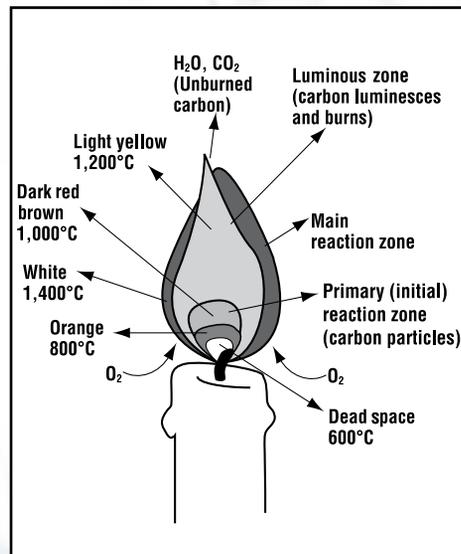
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If you have an oil lamp at home, light it and observe. Liquid oil is carried upward through the wick via capillary action, where it is then burned. A candle works according to the same principle, except the fuel begins as a solid.

JUPITER IMAGES

The flame

Look carefully at a burning candle and you'll see three distinct colors within the flame—light yellow, blue, and a darker yellow. Each color represents a distinct zone in which specific chemical reactions are occurring.



ACS STAFF

Candle flame reaction zones, emissions, and temperature.

Near the bottom of the flame, you'll see the blue zone in which the combustion of paraffin is nearly complete—yielding only water and carbon dioxide. This region of the flame is termed the main reaction zone. In this cleanest and hottest region of the flame, the wax most efficiently reacts with oxygen—reaching temperatures of around 1400 °C. Gas stoves, propane torches, and Bunsen burners used in chemistry labs always produce blue flames if operated properly.

A blue flame typically exists in the plasma phase. Plasma forms when gas molecules get so hot that they collide with enough violence to break apart individual molecules into ions and charged particles. This assemblage of charged particles is called plasma. Plasma also exists in the sun and in lightning bolts.

Next, notice that the inside of the flame is darker in color than the rest of the flame. This center region—called the dark zone—is the coolest part of the flame. It burns at around 800 °C. With limited oxygen available in this region, unburned wax vapor accumulates. If a glass tube is placed in the center of a candle flame, the end of the tube can be lit. Unburned wax vapors coming from the tube can still

undergo combustion. If a glass tube is placed in any other part of the flame, the vapors exiting the tube will not burn, as unburned wax vapors are not present in sufficient quantity in these other regions.

The largest and most conspicuous part of the flame is the bright yellow luminous zone. Its temperature is intermediate between that of the other two zones, typically around 1200°C. In this region, insufficient heat and oxygen cause incomplete combustion. During incomplete combustion, only a fraction of the paraffin molecules are converted into water and carbon dioxide. As a result, free carbon atoms are released as soot. Hold a watch glass in a candle flame for a few seconds and a layer of black soot will form as these unburned carbon particles collect.

The bright yellow color of the candle flame is due to the incandescence of the unburned carbon particles. Incandescence occurs when a solid substance is heated to the point where it gives off light. It differs from combustion in that incandescence does not involve a chemical change. Incandescence

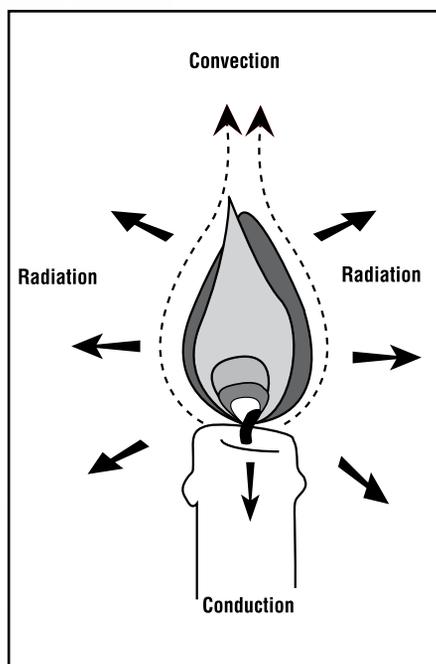


You may be surprised to know that when a candle is blown out, the smoke near the wick can be lit, causing the flame to immediately reignite. This impressive little trick is only possible because the smoke contains unburned wax particles. This invisible wax vapor is what ignites, not the visible smoke particles.

is not burning, but glowing. Similarly, the filament of an incandescent light bulb does not burn, but glows, hence the name.

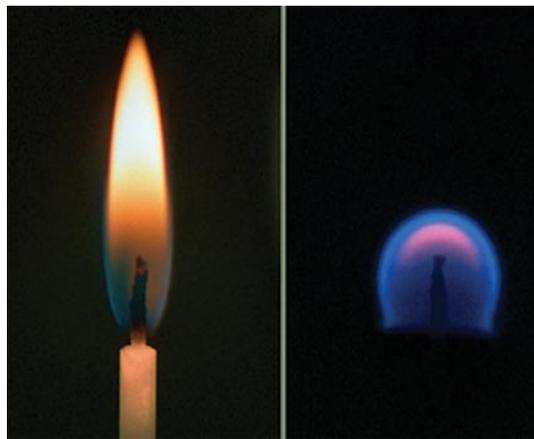
Whenever a breeze causes a candle to flicker, even more smoke is produced. Disrupted by a breeze, the candle burns inefficiently, and more unburned carbon particles—smoke—results. When candles were the primary light sources in homes, the flame was often protected by a glass sleeve, similar to those found on oil lamps today. This glass not only served as a safety measure but it prevented air currents from disrupting the candle flame, producing more soot that discolored walls and ceilings.

The familiar shape of the candle flame, or nearly any flame for that matter, is conical—wider at the bottom and tapering to a



point on top. This characteristic shape is due to convection. Convection occurs as the air around a candle flame is heated. Here, it expands, becoming less dense. Cooler, denser air rushes in from below, pushing up the less dense warmer air to give the flame its shape.

Has this happened to you? You blow out your birthday candles only to have them reignite! These trick birthday candles have some ingenious chemistry behind them. Within the wicks are tiny flecks of magnesium. Magnesium can ignite at temperatures as low as



COURTESY OF NASA

Astronauts aboard the space shuttle have conducted experiments with candles in zero gravity. The flames produced were spherical and generally lasted only a minute. Why? There was plenty of oxygen available, but because of a lack of gravity, there was no convection. As a result, CO₂ accumulated around the flame, and, with no convection to carry it away, it quickly smothered the flame. Convection only occurs in the presence of “heavy” air and “lighter” air. At zero gravity, everything weighs the same.

430 °C, so a glowing ember in the wick can ignite this magnesium, which, in turn, reignites the candle.

Today's candles come in a bewildering array of sizes, shapes, colors, and scents. Candle-making can be done easily at home as a rewarding hobby or a money-making venture. As our petroleum reserves become depleted, new fuel sources may become attractive. Already, soy-based candles are becoming increasingly popular.

What will the candles on your cake look like in—say—50 years? With 5,000 years of development behind them, it's still likely that the flame will come with a wick, a fuel, and some fascinating chemistry. ▲

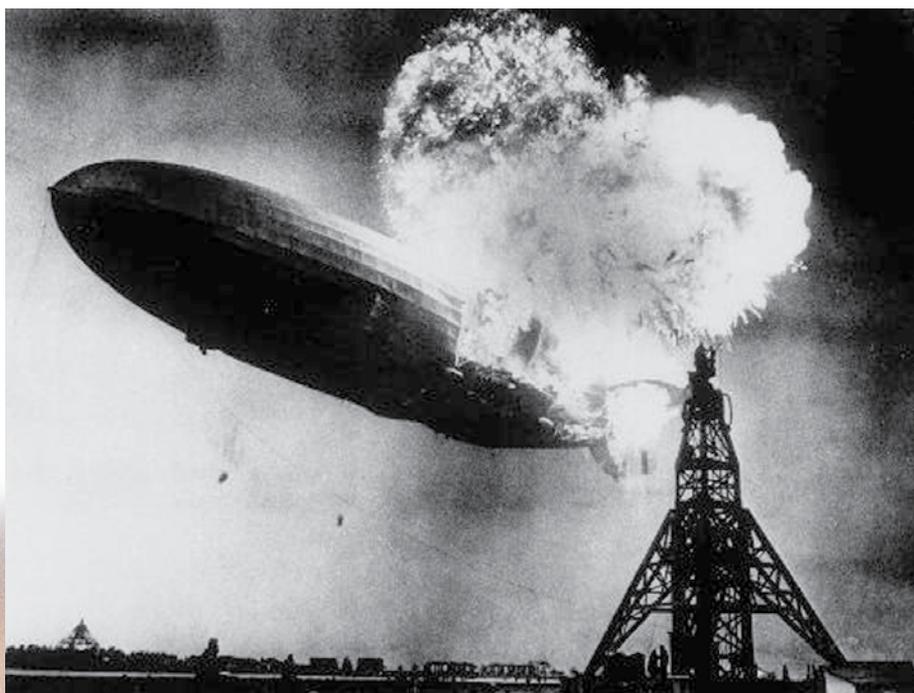
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Brian Rohrig teaches at Jonathan Alder High School in Plain City, OH. His most recent *ChemMatters* article, “Serendipitous Chemistry,” appeared in the October 2007 issue.

HINDENBURG:

Formula for Disaster



COURTESY OF U.S. NAVY

The Hindenburg story

Let's start by setting the record straight. The Hindenburg did not explode. It burned rapidly. There's a difference. The 804-foot-long Hindenburg burned from back to front in less than 35 seconds, but even that rapid burn doesn't qualify as an explosion.

The Hindenburg was a huge ship—larger than four Goodyear blimps combined, longer than three Boeing 747s! Its steel frame was covered by a canvas like material. Within the frame were 16 large bladders that contained the “lighter-than-air” gas called hydrogen. With a density of 0.08988 g/l, about 1/14th that of air, hydrogen-filled objects are very buoyant in the atmosphere. But the use of hydrogen gas in an airship carries one important risk—it is extremely flammable. Once ignited, it burns rapidly in air. In fact, the Hindenburg had been designed to use the inert gas helium, but Germany was unable to acquire the quantities needed to operate a fleet of airships. The United States held most of the world's supply of helium at that time. Suspicious of the political unrest growing in Germany with Hitler's rise to power, the United States was not willing to sell its helium.

As the Hindenburg approached the Lakehurst airfield, it passed through a thunderstorm. The storm had just subsided when the Hindenburg burst into bright yellow flames that shot into the air starting at the rear of the airship. The airship was consumed within 35 seconds! The mystery remains: What ignited the hydrogen? Was it a case of sabotage? Was it ignited by lightning? Could an electrical problem have started the fire? Investigations carried out by the governments of the United States and Germany were inconclusive. The cause of the disaster remained a mystery.

By Tim Graham

“Oh, it's crashing ... oh, four- or five-hundred feet into the sky, and it's a terrific crash, ladies and gentlemen. There's smoke, and there's flames, now, and the frame is crashing to the ground, not quite to the mooring mast ... Oh, the humanity, and all the passengers screaming around here! ... This is the worst thing I've ever witnessed!”

May 6, 1937, from the live radio broadcast of Chicago WLS reporter Herbert Morrison with sound engineer, Charlie Nehlson

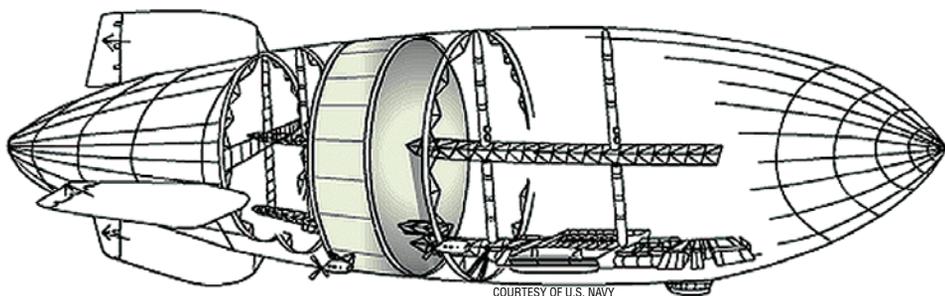
Morrison's dramatic eye witness account of the crash of the German airship Hindenburg, one of the most famous disasters of aviation, still resonates in radio broadcast history. As the Hindenburg prepared to land at an airfield in Lakehurst, NJ, the passengers were treated to views of the Statue of Liberty while enjoying the luxuries of the Hindenburg's spacious cabin—fine food and piano music. Then, without warning there was chaos as the ship burst into flames killing 36 aboard.

Since then, speculation as to the cause of the crash continues. A new theory has only recently rekindled debate over one of the past century's great disasters, and chemistry is at the heart of the discussion.

The Incendiary Paint Theory

In 1997, former NASA scientist, Addison Bain, suggested that the cause of the disaster involved a flammable material used to seal and insulate the airship's fabric covering. It is Bain's Incendiary Paint Theory (IPT) that has stirred up the recent debate. Bain points out that the Hindenburg was coated with a mixture of components commonly found in incendiary bombs! It is his theory that these chemicals ignited to cause the Hindenburg disaster. He argues that flammable hydrogen gas was not the central culprit after all! While his theory has some support, many in the scientific community are unconvinced.

Bain's IPT theory is based on two major points: Hydrogen burns with an almost invisible flame, not like the yellow fireball that was witnessed, and the painted covering of the Hindenburg was responsible for both starting and propagating the fire. Analysis of film from the event supports Bain's first point. The flame that rises for hundreds of feet above the tail section is yellow, suggesting that something other than hydrogen is burning. Also one can



The Hindenburg, classified as a rigid airship had a steel frame with 16 large bladders filled with hydrogen gas.

see that the tail section remains level and buoyant for quite some time, suggesting that the hydrogen bladders are still intact.

Bain's second point is even more compelling. The mixture used to paint the fabric contained iron II oxide (Fe_2O_3), aluminum (Al), and cellulose acetate. Bain points out that aluminum + iron oxide is exactly the mixture used in the thermite reaction (See **ChemMatters February 2002**), the basis for some incendiary bombs. The mixture is extremely difficult to ignite, but once ignited, the reaction is terrifically exothermic.

To support his first point, Bain obtained

remnants of fabric recovered from 1937 and subjected them to burn tests. The results confirmed what he suspected: The fabric burned with a yellow flame similar to the one seen in film footage of the Hindenburg disaster. Bain believes that the storm caused a buildup of electrical charge on the surface of the Hindenburg, generating a spark with sufficient energy to ignite the surface compound on the tail of the ship. Flames moved rapidly across the surface, consuming the Hindenburg in 34 seconds. He argues that hydrogen gas was *not* responsible for initiating or propagating the flame that consumed the Hindenburg.

Ignition!



NASA's Space Shuttles are launched into orbit with lift generated by two solid rocket boosters and one external tank.

The solid rocket booster contains:

- 69.6% ammonium perchlorate (NH_4ClO_4), which serves as the oxidizer;
- 16% aluminum metal (Al), a fuel component;
- 12% rubber binder, for holding the solid components together;
- 2% curing agent, used to ensure a homogenous mixture for proper burn rate; and
- 0.4% iron oxide (Fe_2O_3), the catalyst for the reaction between aluminum and the perchlorate salt.

A typical fireworks "sparkler" recipe might contain:

- 70% potassium chlorate (KClO_3), the oxidizer;
- 15% aluminum metal (Al), a fuel component (reducing agent); and
- 15% dextrin (carbohydrate derived from corn starch) acts as a binder and contributes to the fuel.

Clearly, the components of solid rocket boosters and sparklers are similar to those found in the mixture used to coat the fabric covering of the Hindenburg. Mystery solved? Maybe.

IPT: Fatally flawed

A. J. Dessler, a scientist at the University of Arizona and former director of the Space Science

Laboratory at NASA's Marshall Space Flight Center, suggests that Bain's theory is "fatally flawed." Dessler's arguments are based on chemistry concepts of stoichiometry and reaction rate. Could the Hindenburg fabric burn as quickly as it did without hydrogen being involved? Were the chemical components in the right ratios to support the reaction?

Dessler emphatically says, "No." to both questions. Dessler's experimental data suggest that the coating compound should not be compared to "rocket propellant." Although some of the components are the same, the proportions or *stoichiometry* are very dissimilar. In fact, historical records show that the Hindenburg had been struck several times in previous flights by lightning. The outer covering even had burn holes from such strikes, yet Dessler points out that it had never reacted as it did that day in May of 1937.

Next, Dessler points out that a spark of sufficient energy could not have been produced to ignite the coating mixture. Instead, he argues, an electrical discharge, possibly from a buildup of static electricity from a storm, would have sufficient energy to ignite the hydrogen gas. Most who have viewed the Hindenburg film believe it looks as though the Hindenburg is burning from the inside-out. This strongly suggests that the hydrogen was the source of the fire. As hydrogen rushed out of the bladders, oxygen from the air would be pulled in to sustain the fire. This scenario would also explain why the Hindenburg appeared to remain level in the film footage. The forward momentum of the Hindenburg along with updrafts produced by the burning hydrogen kept the airship buoyant. Finally, the invisible burning hydrogen would continue until the outer fabric caught on fire. Only then would the flame take on the observed yellow color.

Dessler's most convincing argument against Bain's IPT is that of reaction rate. Even if the Hindenburg were coated with the exact composition as the propellant used in a Shut-



COURTESY OF U.S. NAVY

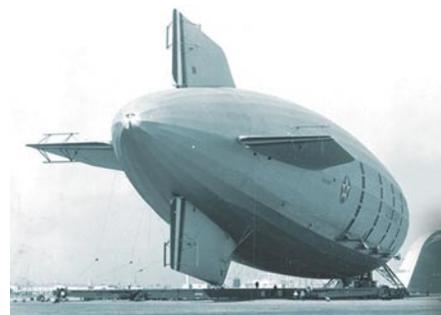
Could the Hindenburg fabric burn as quickly as it did without hydrogen being involved? Were the chemical components in the right ratios to support the reaction?

tle solid rocket booster, the fabric would need approximately 12 hours to burn from tail to nose. Solid rocket fuel is not designed to burn quickly. Even a sparkler takes about 1 minute to burn completely. If a sparkler burned at the

rate of the Hindenburg, it would be consumed in 0.04 seconds! Hardly enough time to enjoy the show!

Thus, Dessler concludes that the fabric coating alone could not be responsible for the Hindenburg's rapid burn rate and that Bain's theory simply lacks experimental support.

That's also the conclusion of the Discovery Channel's popular "Myth Busters." In a program airing in January 2007, the intrepid science team explored the incendiary paint theory and the hydrogen theory. Using two 1:50 scale models, they demonstrated that while a thermite reaction was possible with the Hindenburg's skin and would make the fire accelerate considerably faster, hydrogen was the main fuel. The model burned twice as quickly when it was filled with hydrogen instead of inert gases and produced a fire that matched the newsreel footage quite well. It was only with hydrogen that the fire actually



JUPITER IMAGES

came out of the nose in the same way as the Hindenburg. The program concluded that the IPT myth was "Busted."

Is that the final word? Even the Myth Busters would agree that in science there is never a *final* word. New information, new discoveries, and new lines of thought are always on the horizon. We may agree on a most probable explanation for the Hindenburg disaster. But we need to be prepared for it to be "busted" like countless others. That's what makes science interesting! ▲

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Tim Graham teaches chemistry at Roosevelt High School in Wyandotte, MI. His most recent article in *ChemMatters* was "Unusual Sunken Treasure," which appeared in December 2006.