## The Physics and Chemistry Underlying the Infinite Charm of a Candle Flame

by Jearl Walker April, 1978

■I GREW UP with candles. They provided the illumination that held back the night in the midst of a big Texas storm. I mostly remember lying in bed before going to sleep, hypnotized by the flame and wondering how the candle burned. I had seen other things burn, but they usually did so much faster. The candle burned so slowly that the wick lasted all night or even for two nights.

Other features of the candle intrigued me almost as much. Why was a candle made of wax rather than some other material? Why was most of the flame yellow and a small region at the base of it blue? Why was there a dark inner cone between the wick and the yellow part of the flame? Why did some candles smoke, others burn nicely and others flicker weakly? Finally, why was the soot from a smoky candle black whereas a white vapor came from a candle that had just been blown out?

These are all old questions, and surely some of them have old answers. The fact remains that several of them have yet to be answered with any certainty. In this piece I shall describe how you can make your own candles and how you might explore the physics and chemistry of a burning candle. Answers to some of the basic questions will emerge. In part I shall be retracing the path of investigation followed by Michael Faraday, who was fascinated by both the simplicity and the complexity of candle flames.

In addition to the paraffin from which my grandmother made her candles many other materials have been employed: tallow, stearin, spermaceti (from the sperm whale) and beeswax. Today you can buy paraffin in a grocery store or a hobby shop. Often it is already mixed with stearin (stearic acid) to raise the melting point of the paraffin and therefore provide a stronger and slower-burning candle.



Diagram of colors and typical temperatures of a flame

Wicks are also readily available. They are commonly made of plaited cotton yarn that has been mordanted (pickled in a substance that inhibits smoking). The treatment is necessary because normal cotton would burn too fast and smoke. The idea is to make the wick burn in such a way that it tends to lean out of the flame. Then the inorganic salts of the cellulose in the wick combine with the phosphates and borates of the mordanting salts for an ashless decomposition.

Making a candle is not hard. I was shown how by Liz Knepp of Cleveland, but you will find similar procedures and more details in the many books on making candles. Set up a double boiler so that water is boiling in the bottom part and paraffin is heating in the top part. Monitor the temperature of the paraffin with a wax or candy thermometer. If the paraffin has not already been mixed with stearin for strengthening, it will melt in the temperature range from 48 to 74 degrees Celsius (118 to 165 degrees Fahrenheit). If the stearin has not been included, add an amount equal to about 5 percent of the volume of the paraffin. The stearin raises the melting point and will prevent the candles from burning too fast. Church candles are often pure stearin. Do not overheat your paraffin in the boiler and do not expose it directly to an open flame. If the paraffin should catch fire, douse it not with water but with baking soda.

While the wax is melting you should prepare the candle mold. Depending on the shape you want, you can use many types of metal containers, avoiding any from which the removal of the candle would be difficult. Punch a hole in the bottom of the mold. Draw an appropriate length of wick through the hole and tie it off with a knot. Lay a pencil across the open end of the mold and tie the



other end of the wick to it so that the wick is taut and straight in the mold. Anoint the inside of the mold with a silicone spray to facilitate the removal of the candle.

The successful burning of your candle will depend in part on the proper selection of the wick. Too wide a wick will result in a smoky flame. Too narrow a wick will yield a weak flame that may die out. A rough rule of thumb is that the wick should be chosen according to the diameter of the candle. If the diameter is from one to three inches, use 15ply wicks; for four-inch or small tapered candles use 24-ply wicks and for larger candles use 30-ply wicks.

When your wax has melted, carefully pour it into the mold. Let it cool for a while and then push a long, thin screwdriver (or some other tool with a similar shape) down the long axis of the candle near the wick to eliminate air bubbles and promote a uniform contraction of the cooling wax. Fill the hole left by the screwdriver with more melted wax. You might have to repeat this procedure several times to allow sufficient contraction. Wait until the next day and then invert the mold, cut the knots on the wick and tap the candle from the mold. You then have a candle with which you can begin to experiment.

## A candle flame

Faraday, whose name is usually associated with his far-reaching work on electricity and magnetism, also did the classical work on the physics and chemistry of candles. In 1860 and 1861, as part of his celebrated Christmas performances for a "juvenile auditory" at the Royal Institution, he gave six lectures designed to show the vast amount of science in the deceivingly simple candle. In trying to understand why a candle burns I have repeated some of Faraday's experiments, added a few and investigated current theories of flames. Except for modern theories of molecular and atomic emissions the elucidation of the candle flame has progressed surprisingly little since Faraday's time.

Once you light your candle you will quickly notice that the heat radiated from the flame melts the wax near the wick. The liquid wax is pulled up the wick by capillary attraction, which is to say that the attractive molecular forces between the wax molecules and the wick molecules pull the wax

upward. Once the wax climbs to near the top of the wick it is vaporized. The released hydrocarbon molecules play a variety of roles in the flame.

The flame has the interesting features I noticed as a child. Just above the wick you see a dark cone that is topped by the yellow region responsible for most of the light. On the sides of the flame and near the wick are the blue regions. Depending on the diameter of the wick and the height of the flame, the blue regions may be only a fraction of the height of the flame or may reach nearly to the top of the yellow region. It is surprising that the vaporized fuel molecules give rise to these three distinct regions instead of a single region of uniform color.

In the modern classification of flames the type of flame produced by a candle is called a diffusion flame. Another familiar type is called a premixed flame; its commonest examples are seen in the Bunsen burner and the gas stove. In a diffusion flame the rate of combustion is determined by the rate at which the gases diffuse through each other, whereas in a premixed flame the gases are mixed prior to the burning and the rate of combustion depends on the flow rate. For example, stove gas is mixed with air before it reaches the burner outlets. Further classifications of flames include the possibility of turbulence, but here I consider only a nonturbulent diffusion flame.

Perhaps surprisingly the highest temperatures in a flame are not found near the wick. The top of the wick is actually a comparatively cool place, its temperature being only about 600 degrees C. As you consider points progressively higher the temperature rises until it is about 1,200 degrees C. in the



perature rises until it is about 1,200 degrees C. in the central portion of the yellow region. Somewhat higher temperatures, about 1,400 degrees C., lie off center and on the edge of the yellow flame. This nonuniform temperature distribution through the flame is one reason why the details of the light emission from the flame are so difficult to ascertain.

The relatively cool region just above the wick is the dark cone. There the released molecules of fuel are insufficiently heated and have so little oxygen that little or no light is emitted. What form the released molecules take in this region-how they break down into single atoms or diatomic molecules and where they combine to form solid carbon particles-is not understood. One of the most curious features of the flame is that although vaporized fuel is found just above the wick, at no point in the flame does vaporized fuel ever come in contact with any significant amount of oxygen. Contrary to my own intuitive picture of the flame, neither the heat nor the light of the flame results from a simple oxidation of the fuel vaporized from the wick.

Effects with glass tubing

The blue regions of the candle flame are part of what is called the reaction zone. In that zone the large hydrocarbon molecules vaporized from the wick are broken down into smaller molecules, which then react chemically with one another and with the oxygen diffusing in from the air outside the flame. The bluish light is primarily due to the emission of two excited molecules, molecular carbon (C<sup>\*</sup>) and a hydrocarbon (CH), that are produced in the chemical reactions. These molecules, instead of being excited thermally by the hot environment, may actually be produced in their

excited states by the chemical reactions creating them. Thus the blue light may not be an emission resulting directly from the heat.

Whereas single atoms emit light at particular wavelengths, molecules emit light in what are called band emissions, which are rather closely spaced groups of wavelengths. Unless you were to examine the emitted light by greatly spreading the spectrum, a molecular-band emission would appear to extend uniformly over a large range of wavelengths compared with what you would find from single atoms. The strongest emission of the CH molecule lies in a band around a blue wavelength (432 nanometers), with other emissions occurring in bands at shorter wavelengths in the deeper blue. The C<sub>2</sub> molecule strongly emits in what are called the Swan bands, a compact system of bands in the green, with less intense contributions lying toward the blue and deep blue. In a candle flame the net effect of these molecular emissions is a bluish emission from at least the lower portion of the reaction zone.

To me the most interesting portion of the candle flame is the yellow region which is called the carbon zone or the luminous zone. There solid carbon particles are heated to incandescence by the hot gases and by heat radiated from the reaction zone. It is this incandescence that produces the yellowish light. In actuality the full visible spectrum is emitted, but the emission in the yellow is more intense and dominates one's perception of the light. The emission is not like molecular or atomic emissions, because the full spectrum is produced rather than individual colors. You might have seen something similar if you have ever heated a poker white hot. The poker was then so hot that the thermal radiation from it spanned the entire visible spectrum, emitting all the colors and therefore giving you a net perception of white light.

The solid carbon particles in the luminous zone are from 10 to 200 nanometers in size, most of them no larger than 50 nanometers. If your candle smokes, solid carbon particles are being released by the flame; most of them are larger than 50 nanometers. The first person to explain the yellow light in terms of incandescent particles of solid carbon was Humphry Davy, Faraday's mentor. Although Davy presented his explanation over a century ago, the mechanism that gives rise to the particles is still not understood.



Processes in the flame

One popular hypothesis pictures the fuel o£ large hydrocarbon molecules as being first broken down into carbon atoms or diatomic carbon molecules and then somehow nucleating on some agent to form the solid particle. Another hypothesis is that the hydrocarbons first aggregate to form the solid particle and then lose their hydrogen. In either case a key requirement for the formation appears to be the deficiency of oxygen in the dark zone above the wick. Whatever the true mechanism, the particles of solid carbon are formed by the time they reach the luminous zone, become incandescent and produce the candle's delicate yellow flame.

As the particles rise through the luminous zone they are consumed by reacting with water and carbon dioxide (the principal products of the flame) to yield carbon monoxide. In a smokeless flame the particles are totally consumed by the time they reach the top of the flame. Otherwise they are released as soot. Sooting usually occurs if the wick is too large in diameter, so that it transports upward too much fuel to be consumed in the flame.

Now for the experiments. One of the simplest of Faraday's demonstrations was to place the candle in strong sunlight and examine the shadow cast by the flame. The darkest portion of the shadow came from the luminous region, which is the brightest area of the flame itself. The darkness of the shadow results from the fact that the collection of solid particles is densest there. To update Faraday somewhat I played a beam from a low-power (20-milliwatt) helium-neon laser over the flame, expecting to see laser light scattered by the solid carbon particles. The scattering was not sufficiently intense, however, to be noticeable to the unaided eye.

Over a Bunsen burner or a gas stove bend a short length of narrow glass tubing as is shown in the lower left illustration on page 157. Taper one end and put the other in the lower portion of the dark zone of a candle flame. Vaporized hydrocarbons enter the tube and leave the tapered end as a stream that is transparent or, if the vapor condenses somewhat to form wax droplets, white. The vapor would have produced carbon particles if it had been allowed to rise into the luminous zone, but it can still burn if you light the free end of the tube.

Instead of burning the vapor in this fashion you can collect it in a cool glass or flask. The vapor will condense to form a thin coating of wax on the inner walls. Such a recapture of solid wax implies that the vapor entering the tube had not had a chance to complete the mechanism giving rise to the solid carbon particles in the luminous zone.

Next lift the flame end of the glass tubing to the luminous zone. Now soot rather than vapor will come from the free end. The glass tubing is no longer collecting vaporized hydrocarbons but is diverting some of the solid carbon particles from the luminous zone. Since the carbon particles have not had a chance to be consumed by reacting with water and carbon dioxide, they leave the tubing as they are just soot.

Any kind of obstacle, particularly a cool one' placed in the luminous zone can cause sooting because the obstacle interrupts the consumption of the solid carbon particles. Try a straightened paper clip. It is immediately covered with soot. A piece of wire gauze placed across the yellow region can fully interrupt the burning of the carbon particles and eliminate the flame higher than the gauze.

Another demonstration by Faraday showed how combustible the vaporized hydrocarbons are. Carefully blow out the flame of a candle with a quick exhalation, but do not otherwise disturb the rising stream of white vapor that remains. Hold a lighted match above the wick and in the rising stream. If you do it soon enough, the flame will leap downward from the match to the wick and relight the candle. When you blow out the candle, some of the wax continues to be vaporized by the remaining hot gases and the wick. It is this rising stream of vapor that is combustible.

I tried pouring melted wax into a small Pyrex beaker, heating the beaker on an electric stove until the released vapor was noticeable and then lighting the vapor. The flame would catch inside the beaker but would quickly disappear because of the lack of oxygen in the small confines of the vessel. The vapor rising from the wick in the flame of a candle is combustible but does not burn and emit light because of the lack of oxygen there. Hence just above the wick the flame is dark. Only when the solid carbon particles are formed and become incandescent does the flame yield light.



The inverted-jar experiment

You can demonstrate the rapid consumption of small particles, such as the carbon particles in the luminous zone, by blowing a fine combustible powder into the candle flame. Faraday used lycopodium powder, which is still available from scientific supply houses such as the Fisher Scientific Company (1231 North Monroe Street. Chicago, III. 60622) at about \$1.90 per ounce. Alternatively you can use sifted flour. When you blow the powder lightly across the flame, the powder burns rapidly and with a noticeable sizzle. If you were to toss the clumped particles of unsifted flour through the flame, they would not burn as readily and perhaps would not burn at all. The smaller grains burn more readily because more surface area is exposed. This effect leads to a serious danger in mines and industrial plants having a large amount of fine airborne dust in them. In such an atmosphere an accidental spark can cause an extremely rapid combustion that sets off a violent explosion.

The temperature distribution of a candle flame can be roughly demonstrated by laying a sheet of paper across the flame. Just before the paper itself begins to flame, notice the blackened regions on it. They lie roughly in a circle around the center of the candle flame, indicating that the center of the flame is cooler than the outside edge.

I tried interfering with the mechanism of my candle by shielding the top of the paraffin with aluminum foil to block the heat radiated from the flame. Predictably the wax flow to and up the wick decreased and the flame waned. I could have accomplished the same thing if I had covered the paraffin with an infrared filter, that is, a filter blocking infrared radiation but passing visible radiation, because nearly all of the candle's radiation lies in the infrared. Less than .4 percent of the heat is radiated as visible or ultraviolet radiation.

The effect of electric fields on candle flames has long been noted. I placed my candle between the oppositely charged poles of a Wimshurst machine, the ancient hand-crank generator of high-voltage static electricity. The flame was attracted toward the negatively charged pole and repelled from the positively charged one.

Apparently when the flame is in the electric field that lies between the poles, the free electrons in the flame are deviated to the positive pole. Since you cannot see such an electron stream, the effect is unnoticed. The flame is then left. however, with an abundance of positive ions, which are relatively heavy and not as mobile as the electrons. The positively charged flame is therefore repelled from the positive pole and attracted toward the negative one.



Spectra from a sodium lamp and a candle flame

One of the products of the burning of the hydrogen released by the vaporized fuel is water. You can collect it by passing a cold spoon over the top of your candle's flame taking care to avoid accumulating soot. To measure the amount of water put a funnel over the flame and collect the water in a cool flask by means of a rubber tube. You might want to measure how much water is produced by a given amount of depletion of the candle's wax.

A common demonstration involving the burning of a candle has occasionally been interpreted wrongly. Fix a candle in the bottom of a pan with a bit of hot wax. Pour water into the pan to a depth of about a quarter of the candle's height. Light the candle and put a large clear jar over it upside down. The mouth of the jar should be submerged but held above the bottom of the pan (perhaps by small pieces of wood) to allow water to flow into the jar. As the candle flame consumes the oxygen in the inverted jar and eventually is extinguished, watch the water level inside the jar. It will rise dramatically, perhaps even flooding the candle.

This effect has sometimes been erroneously attributed to the loss of the oxygen from the trapped air as the candle burns. That cannot be the reason, because the burning itself releases gases and vapors, notably carbon dioxide and water. The rise in the water level is actually due to the cooling of the air inside the inverted jar as the candle flame dims and dies out. When you first place the jar over the candle, the trapped air is heated; it expands, and some of it may even bubble out through the submerged mouth of the jar. As the flame dims, the air cools and contracts, and then the atmospheric pressure outside the jar forces the water up into the jar. By making a series of candles that differ only in the diameter of their wick you can demonstrate the possible types of candle flames, from the kind that barely keeps burning because of poor fuel flow to the kind that smokes abundantly because there is too much fuel flow. To save time I used a commercially available candle called "The Uncandle," which consists of a wick placed in a plastic holder that floats on a pool of fuel such as vegetable oil. The floating holder has two compartments. The center section has holes to allow the oil to flow to the wick. A separate outer section has no holes, so that the platform remains afloat. When the wick is lit, the oil rises through it and is vaporized and burned in the flame.

When I pushed the platform down slightly, the flame dimmed. When I pulled the platform up slightly, the flame lengthened, eventually so much so that soot was produced. You could probably make such a floating platform from an appropriate plastic lid. Whether you make one, buy one or just make a series of candles with different wicks, examine the characteristics of the flames. The dimmest possible flame is entirely a reaction zone and thus has only blue light. In a larger flame the luminous carbon region begins at the top of the reaction zone or just inside it and grows upward to split the reaction zone apart. In a higher flame the blue reaction zone is around the base, and the top of the luminous carbon zone is exposed directly to the outside air. Eventually the flame rises so high that the inner core of the luminous carbon zone cools; the carbon particles are no longer consumed by the time they reach the top of the flame, and so they are released as soot.

I checked the spectrum of my candle's emission with an inexpensive diffraction grating (50 cents) and with a glass prism (a few dollars). Both devices can be obtained from the Edmund Scientific Company (7778 Edscorp Building, Barrington, N.J. 08007). The luminous carbon zone dominated the light emission, and I saw a complete spectrum from red to deep blue, with no hint of any molecular emissions. To see the C<sup>1</sup> and CH emissions I had to use a spectrometer of the type often employed in introductory physics classes. Light from the candle entered a narrow slit and was directed by a lens onto either a diffraction grating or a prism, which deflected and dispersed the light to show individual colors. The spectrometer had a movable telescope with which to examine the dispersed light.

When I allowed light from the luminous carbon zone to enter the slit, I saw a complete visible spectrum again. When I allowed only the light from the blue reaction zone on one side of the flame to enter the slit, however, the full spectrum from the incandescent particles was not as bright, and I could distinguish several molecular emissions. Once I noted the angular positions of these emissions I calibrated the spectrum of colors in terms of wavelengths by removing the candle, replacing it with a sodium lamp and noting the angular positions of the sodium emissions. The wavelengths of sodium emissions are listed in reference books. I was then able to identify the molecular emissions as being from the C $_4$  and CH molecules by calculating the wavelengths associated with the angular positions I had recorded and then referring to previous work listing the wavelengths of the emissions from those molecules.

The construction of spectrometers has been described previously in "The Amateur Scientist." An excellent diffraction-grating spectrometer was described in <u>September, 1966</u>. With the spectrometer you would be able to photograph the flame's molecular emissions in great detail, including emissions in the near ultraviolet.