Chemical History of a Candle:

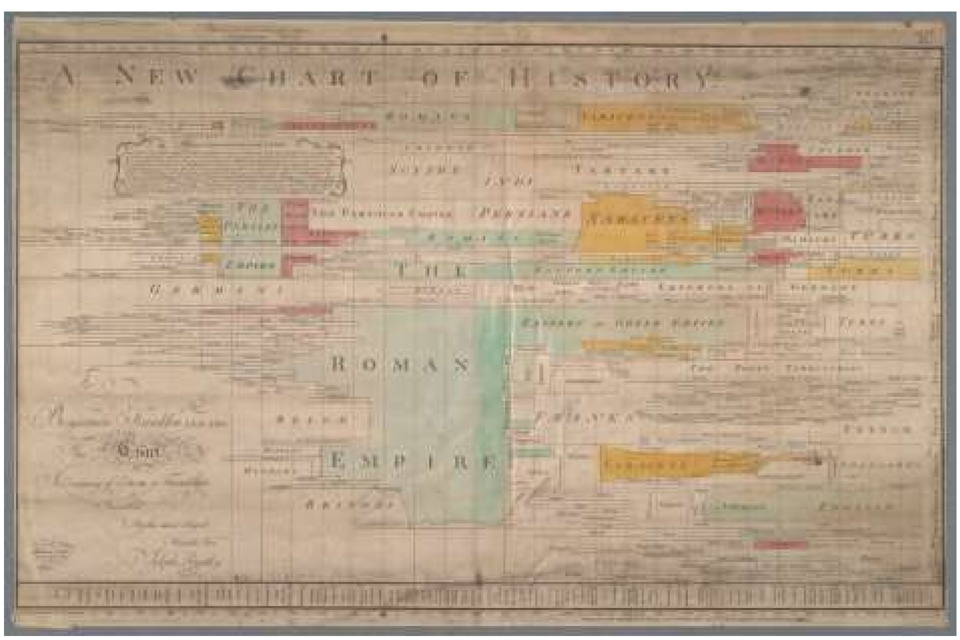
Converting Hydrocarbons into Light and Carbohydrates into ATP

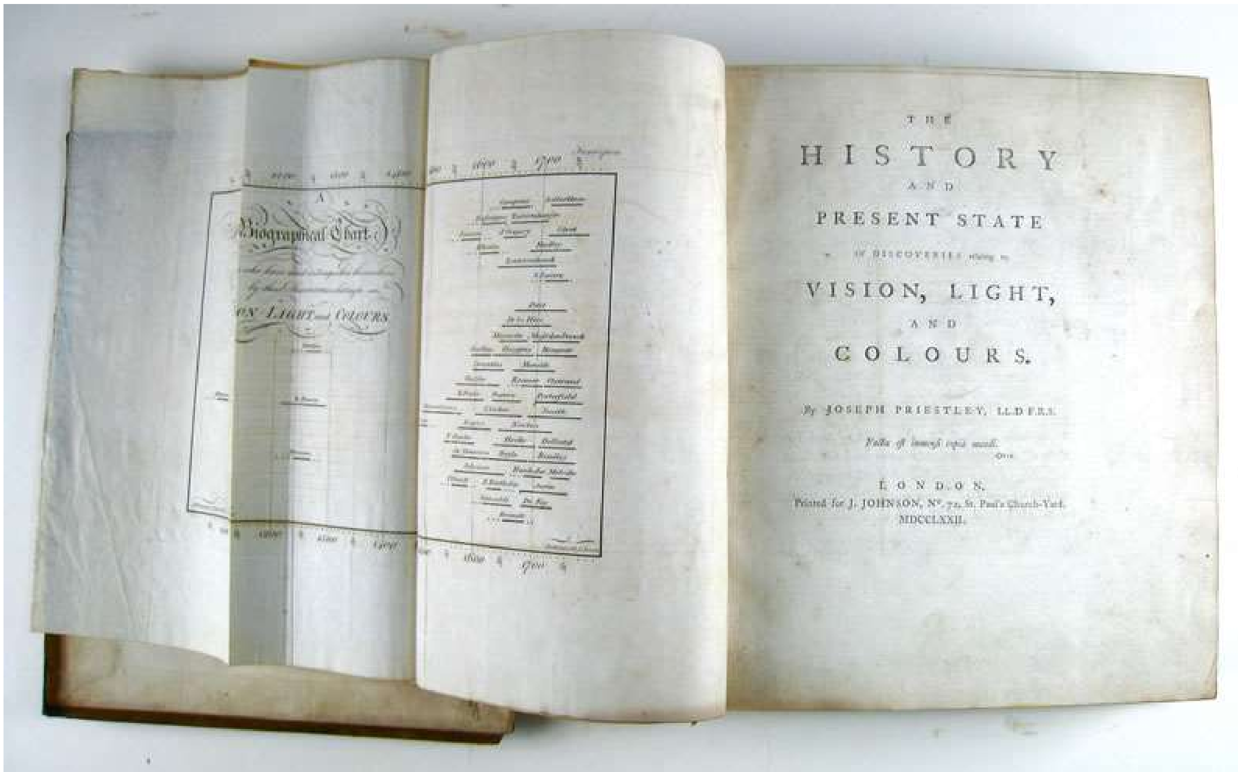
Benjamin Franklin (January 17, 1706-April 17, 1790), like most other children in colonial Boston, only went to school for two years before he started work at the age of ten as an apprentice in his father's soap and **tallow candle** making shop. The tallow chandler had to boil the **suet** or **animal fat** in a vat of water to produce tallow and then pour the tallow that had been skimmed off the water into molds. We now know that tallow is primarily a mixture of the following fatty acids: palmitic acid (16:0), stearic acid (18:0) and oleic acid (18:1). Ben cut wicks, filled molds, attended the shop and went on errands, but he disliked the hot, smelly, and dirty work of a tallow chandler. His father, Josiah Franklin, not wanting Ben to run off to sea like Ben's oldest brother, Josiah Jr. had, took Ben to the shops of various craftsmen so that Ben could pick a trade more to his liking. The fact that Ben liked to read and could write and spell well, made printing seems like the ideal craft. At the age of twelve, Ben apprenticed as a printer with his brother James. While he was never to be a chandler, as a **writer and a printer**, he held the **light of liberty** high.

In *From Boyhood to Manhood. The Life of Benjamin Franklin,* William M. Thayer (1889) wrote, "*He believes that 'one to-day is worth two to-morrows'; and he acted accordingly, with the* ***candle-shop and printing office for his school-room****, and* ***Observation for his teacher****. His career furnishes one of the noblest* *examples of success for the young of both sexes to study. We offer his life as one of the* ***brightest*** *and best in American history to inspire young hearts with lofty aims*."

In fact, Ben Franklin, who had dinner with **William Wilberforce** at the Marquis de Lafayette's home on October 20, 1783, was the first of the founders to break the silence about slavery, Franklin petitioned Congress in 1790 to abolish slavery.
http://www.archives.gov/legislative/features/franklin/

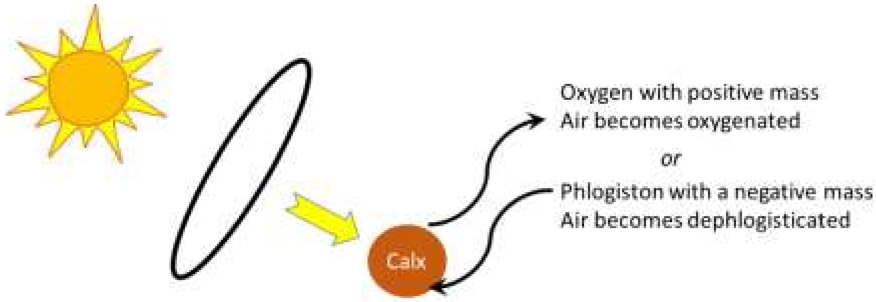
Joseph Priestley met Benjamin Franklin in London in the 1760s and they became friends. Ben Franklin encouraged Priestley, who up until this time dedicated his life to the ministry and to teaching, to also pursue his scientific interests. Joseph Priestley was inspired and in addition to his theological and pedagogical writings, he wrote books on Electricity, Perspective, Vision, Light and Colours, and different kinds of Airs. As a teaching aid, Priestley had produced beautiful charts as a useful way of seeing the **unity in diversity**.





Priestley wrote in the preface to *The History and Present State of Electricity with Original Experiments*, "*Human happiness depends chiefly upon having some object to pursue, and upon the vigour with which our faculties are exerted in the pursuit.* ***And, certainly, we must be much more interested in pursuits wholly our own, than when we are merely following the track of others****.*"

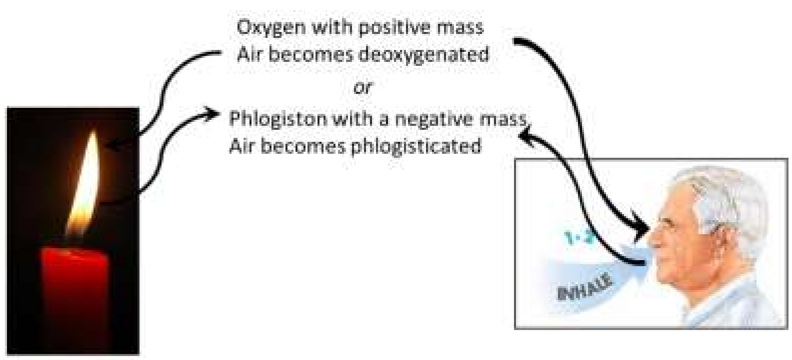
One way in which Priestley studied air on August 1, 1774 was to **focus sunlight** with a twelve-inch in diameter **converging or burning lens** onto orange mercuric calx. The mercury calx turned into liquid metallic mercury as if it captured **phlogiston** from the air so that the air became **dephlogisticated**. We now know that **mercuric calx** is **mercuric oxide** and the mercuric oxide releases oxygen in response to sunlight as opposed to gaining phlogiston from the air. That is, sunlight breaks the chemical bond between mercury and oxygen. I will call what **Priestley studied oxygen**, although he went to his grave believing it was dephlogisticated air.



The **Gaussian lens equation** tells us that the image of the sun appeared at the focus of the lens, since the object distance, s_o is 1.5×10^{11} m, which made $\frac{1}{s_o}$ practically zero and thus made s_i practically equal to f.

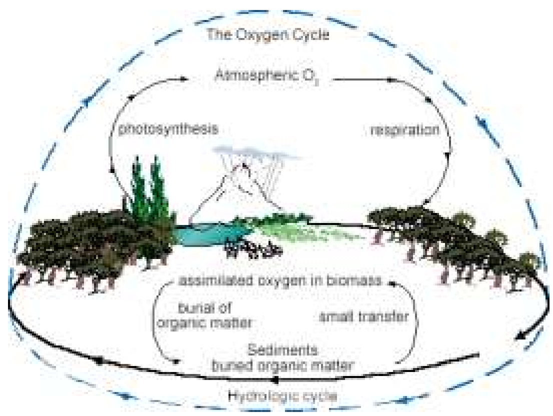
$$\frac{1}{s_o} + \frac{1}{s_i} = \frac{1}{f}$$

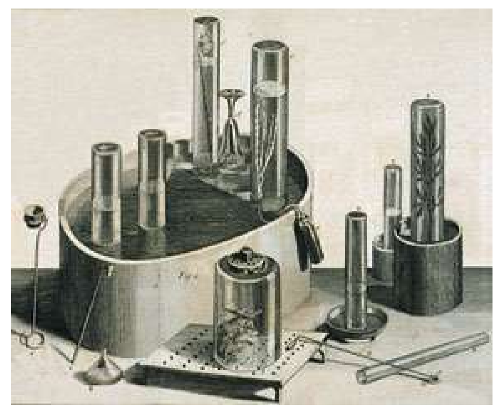
In order to test the nature of the **dephlogisticated air** or really the oxygen gas given off by the mercuric calx, Priestley collected it in a bottle. He then placed a candle in the bottle and saw that it burned with a "*remarkably vigorous flame*." Priestley also saw that a **mouse** would live longer in this **dephlogisticated air** than it would in **common air**, and he called dephlogisticated air, **vital air**.



Priestley wrote, "*…to complete the proof of the superior quality of this air, I introduced a mouse into it; and in a quantity in which, had it been common air, it would have died in about a quarter of an hour; it lived at two different times, a whole hour, and was taken out quite vigorous."* This was a special air. If this air was good for a candle and a mouse, could it be good for humans too? Priestley tried breathing the oxygen he produced and wrote, "*My reader will not wonder, that, after having ascertained the superior goodness of dephlogisticated air by mice living in it…,* ***I should have the curiosity****, by breathing it….The feeling of it to my lungs was not sensibly different from that of common air; but I fancied that my breast felt particularly light and easy for some time afterwards. Who can tell but that, in time, this pure air may become a fashionable article in luxury….From the greater strength and vivacity of the flame of a candle, in this pure air, it may be conjectured, that it might be particularly salutary to the lungs in certain morbid cases, when the common air would not be sufficient to carry off the putrid effluvium fast enough."* He also remarked, "*But, perhaps, we may also infer from these experiments, that though pure dephlogisticated air* [oxygen] *might be very useful as a medicine, it might not be so proper for us in the usual healthy state of the body; for, as a candle burns out much faster in dephlogisticated than in common air, so we might, as may be said, live out too fast and the animal powers be too soon exhausted in this pure kind of air. A moralist, at least, may say, that the air which nature has provided for us is as good as we deserve.*" Otherwise the candle burns out long before the legend does.

The figure below shows the global oxygen cycle that provides the "*air which nature has provided for us* [that] *is as good as we deserve*."

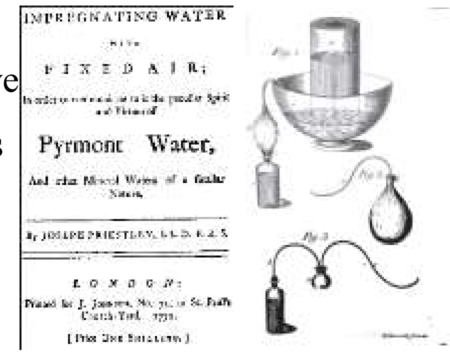




On August 17, 1771, Priestley found that if he put a **sprig of mint** in the jar, it **refreshed the air** so that a candle could burn and a mouse could live. A sprig of groundsel, the worst smelling weed he could find, also refreshed the air. In fact it was a **general property of plants** that they could refresh the air. We now know that plants evolve oxygen. Priestley's experiments were irreproducible because he never got the chance to discover that light was required for oxygen evolution.

This is because his home, his lab, and the Unitarian Meeting House where he preached were burned down on July 14, 1791, the second anniversary of the storming of the Bastille, by a mob who did not agree with his **anti-authoritarian views** regarding church and king, specifically his Unitarian philosophy and his support of the American and French Revolutions. Veto power, whether exercised by mobs and monarchs, is still veto power. *Veto* is Latin for "*I forbid*."

Joseph Priestley was an original thinker and a remarkable chemist who discovered other gases in addition to oxygen, including nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), hydrogen chloride (HCl), carbon monoxide (CO), ammonia (NH_3) and sulfur dioxide (SO_2). Living near a brewery, he also did many experiments on the **carbon dioxide** gas that was given off by the brewery. Again we see the relationship between beer and science. One of the things Priestley (1772) did was to impregnate water with the carbon dioxide to invent **seltzer water**. Priestley generated CO_2 gas by adding sulfuric acid to chalk ($CaCO_3$) and bubbling the gas through water.



$$CaCO_3 + H_2SO_4 \rightarrow H_2O + CaSO_4 + CO_2 \uparrow$$

In 1883, carbonated water was marketed by Joseph **Schweppe,** who kept the bottles horizontal to retain the carbonation because the cork stayed wet and expanded. Schweppes was the official drink of the **Great Exposition of 1851** in the Crystal Palace, designed by Joseph Paxton, based on the architecture of the leaf of *Victoria regia*.

In 1794, Joseph Priestley emigrated to **Northumberland, Pennsylvania**, where his family would be safe and he would be near his friends, Ben Franklin and Thomas Jefferson. There he helped found the Unitarian Church of America and continued to do experiments.

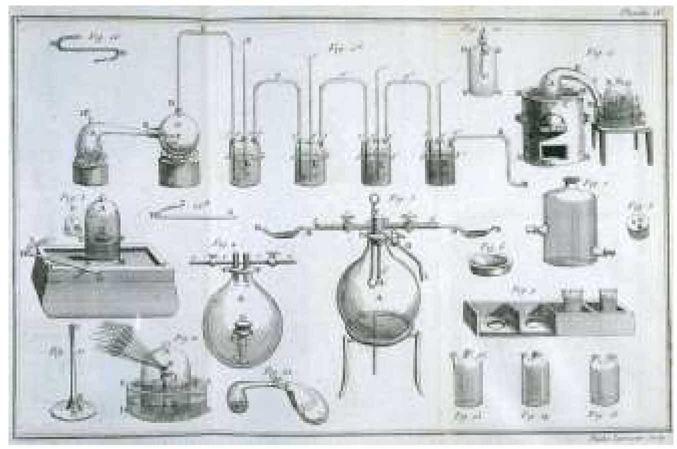
Joseph Priestley had shared his results on dephlogisticated air with **Antoine Lavoisier** over dinner in October 1774. **Antoine Lavoisier** questioned Priestley's interpretation and later **reinterpreted** Priestley's **dephlogisticated air** in terms of **oxygenated air**. Lavoisier coined the word oxygen in 1778 from the Greek *ὀξύς*, which means the sour taste of acids and *γενής*, which means "to produce." At the time, Lavoisier's proposal of the properties and existence of oxygen did not seem all that strong since hydrochloric acid (HCl), which was certainly an acid, had no oxygen at all. Humphry Davy (1812) later showed that acids were more correctly defined by the presence of hydrogen rather than oxygen.

After weighing the reactants and products of various chemical reactions, Lavoisier proposed a chemical theory of the elements that stated all elements have a **positive mass** and thus calx was a combination of a metal and oxygen. When the calx was burned with a magnifying glass, it lost mass because it lost oxygen, not because it gained negative mass phlogiston. When a metal was heated, it gained mass as a result of combining with oxygen. Radiant energy provides the force to overcome the electrostatic attractive force between a metal and oxygen while thermal energy provides the force that allows a metal to **rust**, **burn** or **combust** by combining with oxygen.

Lavoisier believed that **respiration** and **combustion** were **analogous** reactions in terms of chemistry. That is the **burning of food** is like the **burning of wood**. Lavoisier determined that in both cases, **combustion** results from the combination of **oxygen** with **carbon** and **hydrogen**.

Antoine Lavoisier relied on the relationship between light and life when he stated, *"In respiration, as in combustion, it is the atmospheric air which furnished* *oxygen…; but since in respiration it is…the blood, which furnishes the combustion matter, if animals did not regularly replace by means of food…that which they lose by respiration,* ***the lamp would soon lack oil****, and the animal would perish as a* ***lamp is extinguished*** *when it lacks nourishment."*

According to Antoine Lavoisier, "*The proofs of this* ***identity of effects*** *in respiration and combustion are immediately deducible from experiment. Indeed, upon leaving the lung, the air that has been used for respiration no longer contains the same amount of* ***oxygen****; it contains not only* ***carbonic acid gas*** *but also much more* ***water*** *than it contained before it had been inspired."*



That is, the formula for respiration of carbohydrate is:

$$C(H_2O) + O_2 \rightarrow CO_2 + H_2O + \text{heat}$$

Or in terms of glucose:

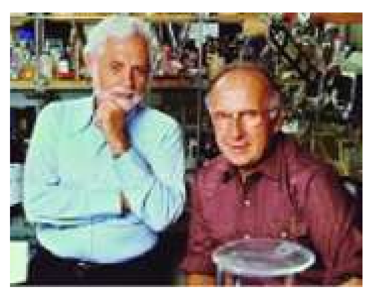
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{heat}$$

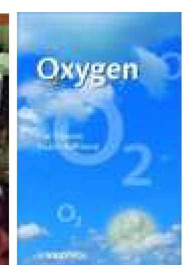
During combustion, the chemical energy in the reduced CH bonds is transformed into thermal energy, heat or the product of temperature and entropy. Originally, it was thought that food powered the body by producing heat. After all human life is associated with warm bodies and death is associated with cold bodies.

We will see that, according to the **First Law of Thermodynamics**, we can transform the chemical energy of the CH bonds into the chemical energy of ATP when we consider combustion during respiration, and we can transform the chemical energy of the CH bonds into radiant energy when we consider combustion in candles. According to the **Second Law of Thermodynamics**, both processes increase entropy. The so-called reverse reaction of photosynthesis that decreases the entropy of the chemicals involved, still increases entropy overall when you take into consideration the transformation of light energy in the visible range into thermal energy in the infrared range.

Antoine Lavoisier not only showed that **respiration** could be defined as a **combustion** process measured by the **uptake of O_2** and the **expulsion of CO_2 and H_2O**, but he and **Pierre Simon de Laplace** found using an **ice calorimeter**, that for equal outputs of CO_2, the same amount of heat was generated to melt the same amount of ice, by a respiring guinea pig and burning wood.

Like Joseph Priestley, Antoine Lavoisier never finished his experiments on respiration because he was "politically incorrect." Lavoisier, who owned shares in a tax collection business, lost his head in a **guillotine** on May 8, 1794, during the French Revolution. After Antoine's death, Madame Lavoisier married Count Rumford. We will see Antoine and Madame Lavoisier's own books and the copper plates **Madame Lavoisier** made to illustrate *Traité Élémentaire de Chimie* when we go the Rare and Manuscript Collections.





Roald Hoffmann (Cornell) and Carl Djerassi wrote a play about the nature of discovery in terms of the role of Joseph Priestley, Carl Scheele, Antoine Lavoisier, and their wives. Discovery in science is often a result of the work of many people over time. Scheele produced "fire air" before Priestley produced "dephogisticated air," but Priestley published first. Lavoisier had a better understanding of its chemistry and named it oxygen.

Davy found that the chemistry of acids, was not given by the possession of oxygen, from which oxygen got is name, but was given by the possession of hydrogen. Just who did discover oxygen?

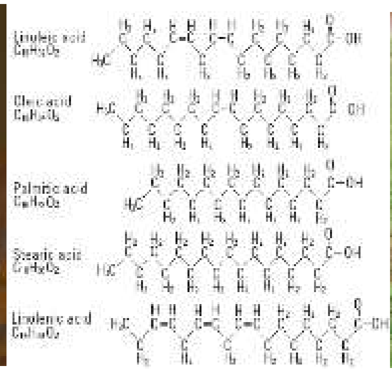
Michael Faraday, Humphry Davy's assistant, gave a series of lectures on chemistry to children at the Royal Institution at Christmas time. His most famous lecture series is on ***The Chemical History of a Candle***, which he began by saying, *"I propose to bring before you, the Chemical History of a Candle....There is not* ***a law under which any part of this universe is governed which does not come into play****....There is no better, there is no more open door by which you can enter into the study of natural philosophy, than by considering the physical phenomena of a candle. I trust, therefore, I shall not disappoint you in choosing this for my subject rather than any newer topic, which could not be better, were it even so good."* Today we will replicate to some degree his lecture series on ***The Chemical History of a Candle***.

Look at all the candles in the room. They are made of malleable solids composed of water-**insoluble hydrocarbons**, **rich in CH bonds**, that are in the form of **hard fats** (ester of fatty acids and glycerol) or **waxes** (esters of fatty acids and fatty alcohols). One is made from **tallow**, one is made from **spermaceti**, one is made from **beeswax**, one is made from **bayberry wax** and one is made from **paraffin**. Each of them transforms the chemical energy of the hydrocarbon into radiant energy of light and heat after being ignited by a match. This **transformation**, which **disperses heat and gases** and thus **increases entropy**, is known as **combustion**. Consequently, the transformation is **irreversible** and must follow the **First and Second Laws of Thermodynamics.**

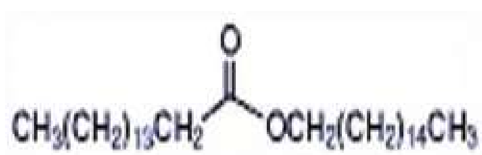
Fat is good in that it is a **very efficient form of energy storage** in warm- blooded animals since 1 gram of fat can store **9 Calories**, whereas 1 gram of carbohydrate or 1 gram of protein can only store 4 Calories. **One Calorie is equivalent to 4184 Joules**. If we stored the same amount of energy as carbohydrate (4 Calories/gram) or as protein (4 Calories/gram), we would weigh more than we do. Thus "*fat is good*!"

In the early 18th century, the photogenic **Michel Eugène Chevreul**, a chemist interested in the chemistry of soaps and candles, both of which were produced from natural products, determined that all fats are composed of glycerol and fatty acids. Fats, which were solid, had more stearic acid, and oils, which were liquid had more oleic acid. Stearic acid comes from *stear* (στέαρ), the Greek word for tallow, and oleic acid from the Latin cognate (*oliva*) of the Greek word *elaía* (ἐλαία) for olive. Palmitic acid comes from the word palm, and was first isolated from palm oil.

We can use animal fat to make candles. Survivalists make candles out of tallow and they could eat them if it became necessary. Tallow rendered from beef suet is composed primarily of palmitic (16:0), stearic (18:0) and oleic (18:1) acids**.** **Tallow candles allow us to transform life into light**.

Spermaceti candles are made from a **wax** found in the heads of **sperm whales**. Spermaceti wax is composed primarily of the ester of **cetyl alcohol and palmitic acid** ($C_{15}H_{31}COO\text{-}C_{16}H_{33}$). **Spermaceti candles allow us to transform life into light**, and were the original candles used to define one **candlepower** in the British Metropolitan Gas Act of 1860. Whaling is outlawed and our spermaceti was made synthetically.

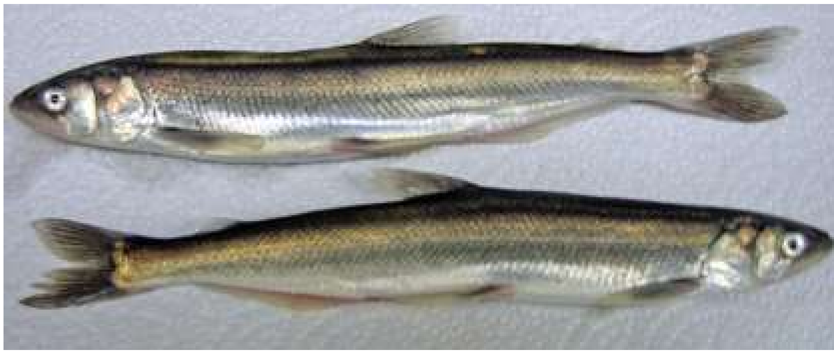



Bayberry candles are made from the green wax that is removed from the surface of the bayberry (*Myrica pensylvanica*). They have a wonderful smell. Bayberry wax is not actually a wax but more like plant tallow made of triglycerides, composed of lauric acid (12:0), myristic acid (14:0) and palmitic acid

(16:0). A true wax is an ester of a long chain alcohol and a fatty acid. **Bayberry candles allow us to transform life into light**.

Beeswax is a true wax made from by **worker bees** by **chewing honey** made from **nectar**. In fact the burning candles smell like honey. The bees use the wax to build honeycomb cells in a hive which the young are raised. The fresh wax is white, but it turns yellow when pollen oils and a resinous substance called propolis that is used to seal the hives is incorporated into the wax. Beeswax candles are chemically complex and are made of many components and allow us to **transform life into light**.

Historically or in parts of the world we do not see often, other organisms are used to turn life into light. For example, the **candlefish** (*Thaleichthys pacificus*) is composed of 15% fat. Indigenous people dry the fish and burn it as a candle!



Candle-wood or **bogwood** formed about 4500 years ago when the climate in Ireland and Scotland changed, perhaps as a result of volcanic dust, by becoming wetter and cooler. The cool water-loving bog plants, including sphagnum moss, heathers, grasses and sedges encroached on the oaks, pines and yews. In the newly formed bogs, the trees died due to lack of oxygen. The lack of oxygen in acidic waterlogged peat provided a reducing atmosphere that prevented the decomposition of the dead trees. Candle-wood or **fatwood** is harvested from the stumps of long leaf pine in Honduras.

As long as the **proportion of hydrocarbons is high**, whether, tallow, spermaceti, bayberry, beeswax, candlefish or candle wood, **the chemical energy produced by life can be transformed into the radiant energy of light**.

Today we will study the **combustion process that occurs in a candle** and that gives rise to a **flame** in order to understand the chemistry of combustion and next time we will **compare and contrast** it to the **combustion process that takes place in living organisms**. Both combustion processes conform to the **First and Second Laws of Thermodynamics** in that **one form of energy is transformed**

into another and that the **transformation only occurs in one direction**. In general combustion processes ***out of the body*** are hot enough to boil water (> 100 C = 373 K) whereas the combustion processes that take place ***in the body*** do so at ambient temperature (37 C = 310 K). **Enzymes** make it possible to perform combustion reactions at ambient temperatures.

The **photosynthetic transformation of radiant energy into chemical energy** that ultimately gives rise to all our food, and to the fats and waxes used in candles, can be looked at as the **closest thing to the "reverse process" of combustion although it is clearly not a reversal of the combustion process** and candle light in not a result of light emission from chlorophyll. When the overall chemical formulae of combustion and photosynthesis make photosynthesis and combustion look like two words for the same reversible process, clearly and consistently with the **Second Law of Thermodynamics**, they are not reversible processes but each **irreversible** and **directional in time**.

In order to understand the combustion process that occurs in a candle, let's first characterize the flame itself. The unknown intensity of the candle flame can be measured with **Rumford's photometer** that compares the darkness of the shadow produced by the light in question to a standard candle. The test light is moved forward or backward until the shadows are equally dark. The relative intensity is calculated from the distances of the two lights to the screen using the inverse square law.

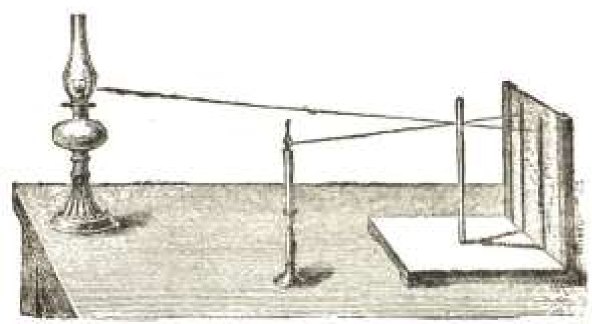


Fig. 262. Rumford's Shadow Photometer.

Intensity of unknown light = Intensity of standard light $\frac{d_{unknown}^2}{d_{standard}^2}$

The unknown intensity of a candle flame can also be measured with **Bunsen's Photometer** where the distance between an unknown light from a piece of white paper with a grease spot is varied until the grease spot seems to disappear because it is equally illuminated on both sides.

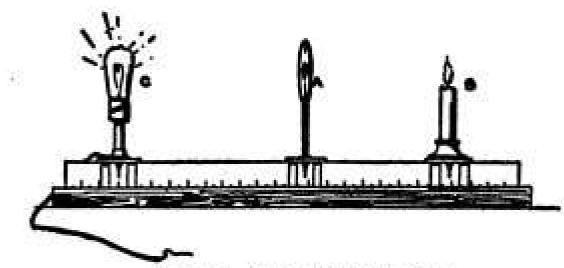


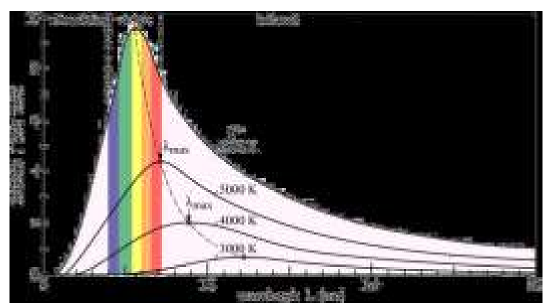
Fig. 32. Bunsen's photometer

Again, the inverse square law, which we learned from geometrical optics and used to estimate the luminosity of the sun, is useful.

$$\text{Intensity of unknown light} = \text{Intensity of standard light } \frac{d_{unknown}^2}{d_{standard}^2}$$

The **temperature** of the flame can be estimated from its luminosity or intensity at a given distance using the formula: $I(r) = \frac{L_{candle}}{4\pi r^2} = \sigma T^4$. The measured **color temperature** of a candle flame is approximately **1850 K**.

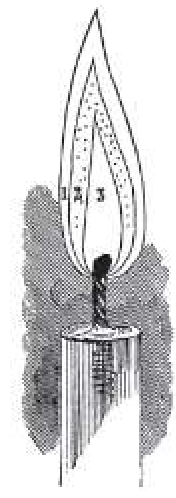
Demonstration: Look at the flame through the spectroscope. Is the spectrum continuous or discrete? Although we cannot see the infrared wavelengths, the peak of the spectrum is closer to the red compared to the peak of the solar spectrum, which you can observe through the pinhole in the window. We can characterize the light emitted by the candle as a continuous spectral distribution produced by a "hot" **incandescent body** using **Max Planck's blackbody radiation law**:



$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)}$$

where λ (in m) is the wavelength of light, k is the Boltzmann constant (k = 1.38 × 10^{-23} J/K), c is the speed of light (c = 2.99 x 10^8 m/s) and h is Planck's constant

($h = 6.626 \times 10^{-34}$ J s). Soon we will **identify the incandescent hot body** that gives rise to the continuous blackbody spectrum.



Look at the virtual image of the flame of a spermaceti candle through the 1 diopter (f = 1 m) and 2 diopter (f = 0.5 m) converging lenses aligned to form a 3 diopter compound lens (f = 0.333 m). A closer look shows that the flame consists of three parts, as described by Worthington Hooker. The **inner part** of the flame appears to be **dark and hollow. The wax is vaporized in the hollow, called region 3**, and passes into **region 2**, the borderland between the fuel in region 3 and the air in region 1.

The brightest part of the flame is caused by the **incandescence** of the **fine solid particles of carbon soot** in region 2. The **incandescent particles are also the cause of the black body spectral distribution**. This region is also very hot. As the carbon particles combine with oxygen, they move away from region 2 as carbon dioxide and water. As the soot particles turn to gas in region 1, the flame dims compared with region 2. The major locus of **heat** generation during the combustion process occurs in region 2 where **the fuel and the air come together**. The highest temperatures however are in the blue region, where the oxygen concentration is high and most of the chemical energy is converted to heat and not light.

What happens to the candle over time? Assuming time exists, the fact that candles get shorter over time as they use up their fuel source made possible candle clocks, which are among one of the most ancient time keepers made by humans. The candle gets shorter as the fuel gets used up. How does the fuel get to region 2

where it will combine with the air? In order to understand the passage of fuel to the combustion zone, let's look at the flame produced by olive oil burning lamps, which have been used at least since biblical times when the Israelites were commanded in Exodus 27:20 "*to bring you clear oil of pressed olives for the light so that the lamps may be kept burning.*"

When we light the wick, the flame travels down the cotton to the olive oil, where the flame is put out. The **liquid oil** itself does ***not*** burn while the flame does continue to burn above the oil at the expense of the oil. The oil can only burn when it gets to the top of the wick where it is vaporized. While the oil is initially vaporized by the heat from the match, the flame of the lamp takes over the role of vaporizer for as long as the lamp is lit. That is, some of the energy of the oil must be used to vaporize the oil.

$$\text{Heat} + \text{liquid} \rightarrow \text{vapor}$$

How does the oil get to the top of the wick? The oil gets to the top of the wick by **capillary attraction**. Capillary action is a result of **electrostatic attraction** that is stronger than the attractive **force of gravity** towards the earth.

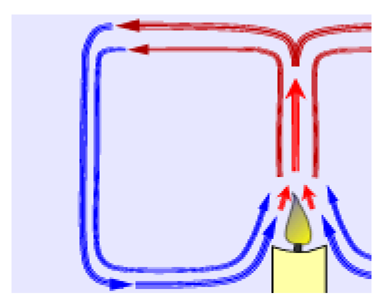
The greater the surface area of the wick, the greater is the amount of electrostatic attraction and the greater the amount of capillary action. The surface area is increased by using many thin treads of cotton to form the wick. Multiple thin filaments are excellent at wicking and they can wick bacteria from a non-sterile area such as the vagina to an axenic area such as the uterus to cause pelvic inflammatory disease. This was the **unintended consequence** of the filaments attached to the Dalkon shield, an **intrauterine**

device (IUD) that caused pelvic inflammatory disease (PID). What is true and good for candles is true and bad for IUDs.

At the top of the wick of an oil lamp, the vaporized oil molecules collide with each other. If the molecules are hot enough, they break each other's bonds when they collide into each other and the molecules literally fragment. At the bottom of the flame you will see a little blue that results from the chemiluminescence of the C_2 and CH fragments, which will combine with sufficient oxygen at the **bottom of the flame** to form invisible molecules of carbon dioxide and water without forming more complicated soot particles. The blue region is the hottest part of the flame. **Above the flame**, the fragments cannot become invisible quick enough because there is not enough available oxygen. Consequently soot particles form. It is these soot particles that incandesce to turn the chemical energy of the CH bonds of olive oil into the radiant black body spectral distribution of lamp light. The soot molecules become invisible when they turn into carbon dioxide and water as they come in contact with oxygen in region 1.

Let's look at a candle, where the fuel is a solid. The flame melts the solid hydrocarbon into a cup-containing liquid. The transformation of solid fuel into a liquid fuel requires heat and some of the chemical energy of the solid fuel is used to drive this solid-to-liquid phase transition.

$$\text{Heat} + \text{solid} \rightarrow \text{liquid}$$

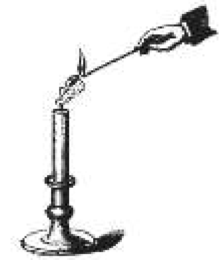


The flame also causes the current of air to move upward as a result of the flame heating the air since the heated air expands and becomes less dense. This results in a low pressure region above the flame and the air moves from regions of high pressure to regions of low pressure. The **upward flow of air cools the sides of the candle** and makes a cup to hold the melted wax that is not cooled by the air.

The candle flame, like the oil lamp flame, is separated from and is above the liquid wax. The temperature at which the candle wax melts (transformed from a solid to a liquid) is known as its **melt point**. The melted hydrocarbon, like the olive oil, also moves up the wick against the force of gravity to make a flame by **capillary action**. The greater the number of strands and the thinner they are in a wick, the greater the surface area, the greater the electrostatic attraction, and the greater the rate of ascent of the liquid. Lower molecules are attracted to the climbing molecules and also get pulled up to the flame where the liquid hydrocarbon is evaporated, vaporized and turned into a gas. The temperature at which the liquid wax is vaporized (transformed from a liquid to a gas) and it is able to ignite and burn is known as its **flashpoint**. The transformation of liquid fuel into a fuel vapor requires heat and some of the chemical energy of the solid fuel is used to drive this liquid-to-vapor phase transition.

Wax	**Approx. formula**	**H/C**	**melt point (F)**	**flashpoint (F)**
Beef Tallow	$C_{16}H_{32}O_2$	2	104	512
Bayberry	$C_{12}H_{24}O_2$	2	118	230
Beeswax	$C_{15}H_{31}COOC_{30}H_{61}$	2	144-147	399.9
Paraffin	$C_{31}H_{64}$	2.06	115-154	395
Spermaceti	$C_{32}H_{64}O_2$	2	210	500

Vaporized hydrocarbon is a fuel that can burn. You can see this by blowing out the candle and looking at the vaporized fuel as a white smoke. You can light this smoke two or three inches above the wick. When the **vapor ignites it will cause the wick to relight**.



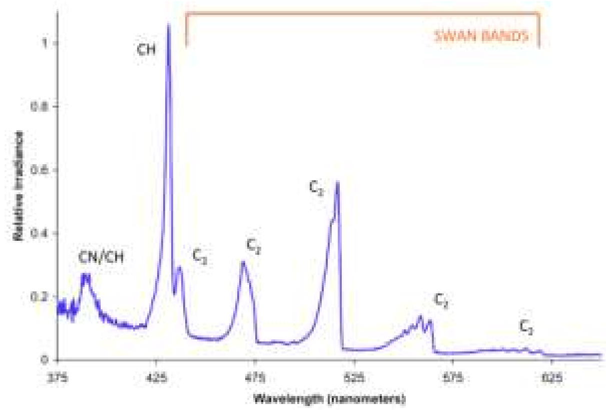
We can show that this **vaporized fuel** is in region 3, the **dark inner hollow of the flame**. We can examine the dark region 3 by inserting a bent glass tube into this region. The vapor that comes out of the end of the tube can be ignited and the flame of the candle can be produced at a distant place. When I raise the tube to **region 2**, t**he bright part of the flame, there is nothing to ignite.** In region 2, the vapor has already been burned and the result is the production of a black smoke that is composed of soot particles. Region 2 is where the combustible vapor and the oxygen in the air have combined to make incandescent light.

We can see where the soot particles that incandesce are localized in the flame in an unusual way. When the candle is illuminated by the lamp of a slide projector, one sees that the brightest region of the flame casts a shadow on the screen. Thus **the soot particles, which are opaque and cast a shadow are in the brightest region of the flame**. Surrounding the dark shadow is a lighter shadow and surrounding that is a bright region that is a diffraction artifact resulting from the light that diffracts from the particles that make the shadow. (Next time you are

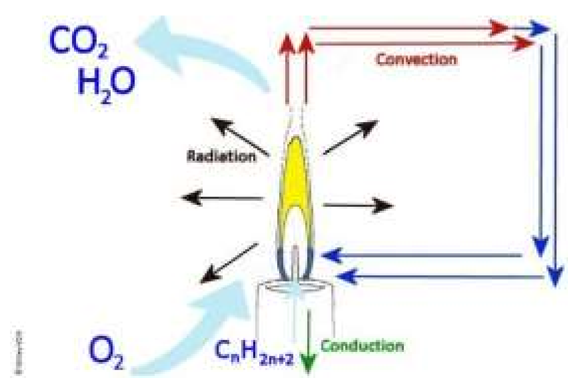
looking at your own shadow on a sunny day you will see that your shadow too is surrounded by a bright halo).

In the middle of the flame is the combustible vapor and on the outside of the flame is the oxygen that is necessary to combust the vapor. **In between these two regions is the reaction zone where the oxygen and the vapor interact to form incandescent soot particles and heat**. This is the hottest region of the flame above the wick. Region 2 can be visualized with a piece of paper because it is hot enough to produce a ring on a piece of paper that results from the caramelization of the top of the filter paper and soot deposited on the bottom of the filter paper.

In region 3, where oxygen is limiting, the hot vaporized fuel molecules collide with each other and break into smaller molecules such as C_2 and CH. This **oxygen-limited process** is known as **pyrolysis**, which means heat-induced breakup in the absence of oxygen. It also results in the production of free radicals. The newly formed molecules transform some of their excitation energy into light energy in a process known as **chemiluminescence**. Chemiluminescence of C_2 and CH gives rise to the blue in the flame. **The blue exists throughout the flame** but is dimmer than the continuous spectral distribution of light resulting from **incandescence**. Below are pictures of a candle flame taken with quartz lens and a filter that only lets ultraviolet light pass (l), a filter that only lets visible light pass (c) and a filter that only lets infrared light pass (r).



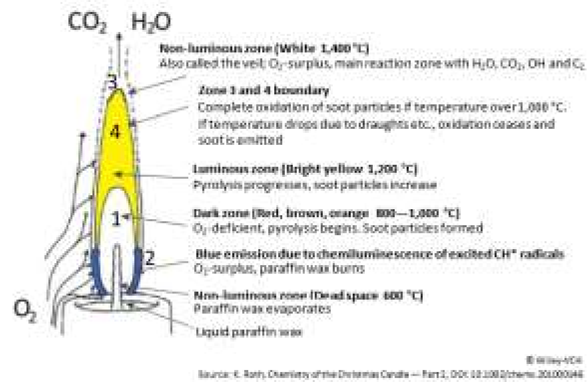
In the absence of oxygen, the pyrolytic fragments get a chance to form complicated soot particles in region 2 that can incandesce. When these soot particles are exposed to enough oxygen as they reach region 1, they turn into the invisible molecules of carbon dioxide and water, causing region 1 to be less bright than region 2.



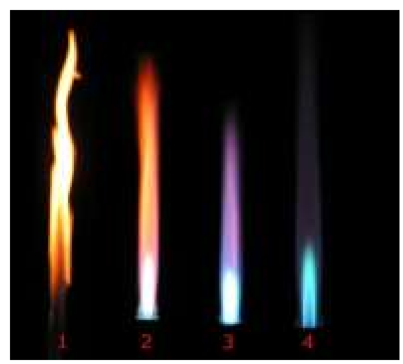
At the bottom of the flame, the pyrolytic fragments will quickly combine with the readily available oxygen to form invisible molecules of carbon dioxide and water without forming more complicated soot particles which would incandesce. Thus the chemical energy is mostly converted into thermal energy. Above the flame, the pyrolytic fragments cannot become invisible quick enough because there is not enough available oxygen. Consequently soot particles form. It is these soot particles that incandesce to turn the chemical energy of the CH bonds of the fuel into the radiant black body spectral distribution of candle light. The soot molecules become invisible when they turn into carbon dioxide and water as they come in contact with oxygen.

Fresh air is necessary for combustion to proceed. When we place a candle in a bell jar, the flame is extinguished after a minute or two.

Since the heat of the candle results in an upward draft of fresh oxygen-containing air, the **bottom of the reaction zone** has the most oxygen resulting in the complete combustion of the products of pyrolysis without the intermediate production of soot. In this region, **chemiluminescence** is ***not*** overwhelmed by the **incandescence of the soot particles** and the flame appears **blue**.



The flame in a **gas stove, propane torch or a Bunsen burner**, has sufficient oxygen for the oxidation of the products of pyrolysis without the intermediate formation of soot. **Under these conditions, more energy is emitted as heat than as visible light**. The flames shown on the right result from increasing availability of oxygen.



Complete combustion without producing sooty intermediates allows us to cook our food efficiently and cleanly, but there is not enough light produced by this process to provide light. Ever think that soot could be romantic?

Soot production occurs when there is not enough oxygen to burn the initial pyrolysis products directly into carbon dioxide and water. The perfect amount of incomplete combustion produces a yellowish flame. The **wick** too is important in determining the quality of the flame. Too little combustion occurs when a wick is so big that it delivers too much fuel for the amount of oxygen available and a black sooty smoke is produced. When the wick is too small, combustion is also limited because there is not enough fuel.

Incandescence results from the oxidation of soot particles produced by the incomplete combustion of the products of pyrolysis. **Any finely divided solid, which has a large surface to volume ratio, can incandesce.** Each *Lycopodium* spore vaporizes producing soot particles that become incandescent when they oxidize. **The large surface to volume ratio maximizes the amount of oxygen that can interact with the spore and minimizes the amount of heat that can be carried away**. **The result is the transformation of chemical energy into light**. The incandescence produced by ignited *Lycopodium* spores was used to produce a **flash of light by photographers** in the early days of photography. *Lycopodium* spores are used by magicians to create a clean-burning jet of fire known as dragon's breath.

Iron particles (Iron powder) also become **incandescent** when placed in a flame. Incandescence occurs because their large surface to volume ratio maximizes the amount of oxygen that can interact with the iron but minimizes the amount of heat that can be carried away. A **cast iron skillet** does not incandesce because it has a much smaller surface to volume ratio than the iron powder. Unlike the *Lycopodium* spores, the iron powder remains a solid and incandesces without vaporizing. Iron has a high affinity for oxygen. We often see rust. In order for iron to rapidly bind to oxygen though, it has to be **heated** to high temperatures or acted on **enzymatically** at ambient temperatures.

Incandescent iron can be seen when you hit a nail with a hammer. The nail becomes hot enough to combine with oxygen and bits of iron fly off due to the explosion. The spark is incandescent iron oxide formed by the burning of iron!

Electrical energy can be converted into thermal energy when a 9V battery is touched to the finely spun iron in **steel wool** that has been fluffed up. This can be used to make a fire when camping. https://www.youtube.com/watch?v=xbwNJhJwnSs

Likewise, on a camping trip, mechanical energy can be converted into thermal energy with a magnesium fire starter. https://www.youtube.com/watch?v=Cz7md8ArN60

Incandescent iron is formed by **flint and steel lighters**. The incandescent iron oxide particles produced by rubbing flint on steel can be used to ignite **charcloth** (pure carbon) and start a fire. The charcloth is made by heating cotton or linen in limited oxygen in a tinderbox for about five minutes. This lowers the ignition temperature of the fabric by eliminating the volatile components that would drain away heat necessary for volatilizing these components from the fire.

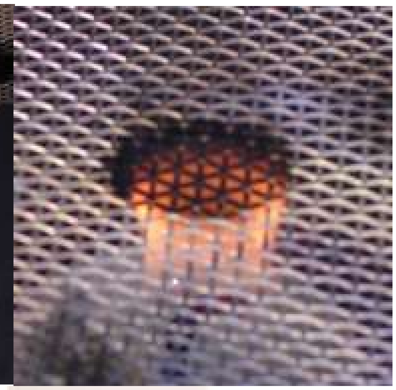
This process of heating wood ($C_{42}H_{60}O_{28}$) in the absence of oxygen (**pyrolysis**) is used to make **charcoal** ($C_{16}H_{10}O_2$). The same process is used to make **biochar**, which can be used to amend soils.

$$2C_{42}H_{60}O_{28} \rightarrow 3\ C_{16}H_{10}O_2 + 28\ H_2O + 5\ CO_2 + 3CO + C_{28}H_{34}O_9$$

The carbon-rich solid charcoal has too little oxygen to form a flame, which is why **charcoal glows or incandesces** while **wood burns or produces a flame**.

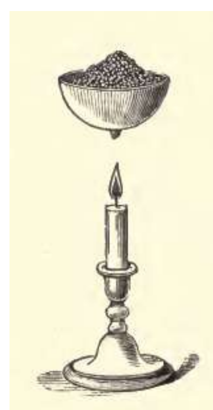
Approximately 30,000-32,000 years ago, Cro-magnon man used charcoal to produce beautiful drawings in the caves of Grotte Chauvet Pont d'Arc, which was rediscovered by moderns in 1996.

The surface to volume ratio of an **iron mesh** causes it to carry off the heat of a flame without incandescing white. The decrease in the temperature prevents the combustion of soot particles and the flame cannot go through the mesh and is quenched. This is why a wire mesh is placed in front of your fireplace and around a **Davy safety lamp** invented by **Humphry Davy**, Michael Faraday's predecessor at the Royal Institution and used by miners to see in coal mines.



The products produced by a candle flame can be captured in a **fire balloon**. They are ***not*** sooty, but transparent or invisible. The soot particles are formed as a result of incomplete combustion. Incandescence does not continue when there is sufficient oxygen. So when there is sufficient oxygen, as there is in region 1 at the margin of the flame, the carbon that makes up the soot is transformed into something else that is **gaseous and invisible**.

One of the products that formed in the flame is **water**. We can condense the gas produced by the candle flame (or from our breath) on the bottom of a dish containing ice and salt into a liquid to see if it is water. Water is the only gas that will become a liquid close to 0 C. Water is not initially in the candle. **The water formed by combustion is made of two substances, one provided by the candle and one provided by the air**.



The other product that is formed in the flame is **carbon dioxide**. Carbon dioxide can be tested with **limewater**, which is an aqueous solution of calcium hydroxide. Limewater was used as a whitewash in **buon fresco painting**. Historically, it is known as the paint whitewash. The chemical reaction of carbon dioxide gas with aqueous limewater results in the production of solid calcium carbonate and water. A cloudy appearance of the limewater solution caused by the calcium carbonate indicates that the sample gas, whether from the candle or our breath, contains carbon dioxide.

$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

Carbon dioxide is not initially in the candle. **The CO_2 formed by combustion is made of two substances, one provided by the candle and one provided by the air**.

Carbon dioxide can also be identified by testing a gas' ability to **extinguish fire**. The gas emitted by the candle flame is able to extinguish a match. Carbon dioxide acts a **fire extinguisher** by displacing oxygen and can be used in putting out fires where there is no source of oxygen.

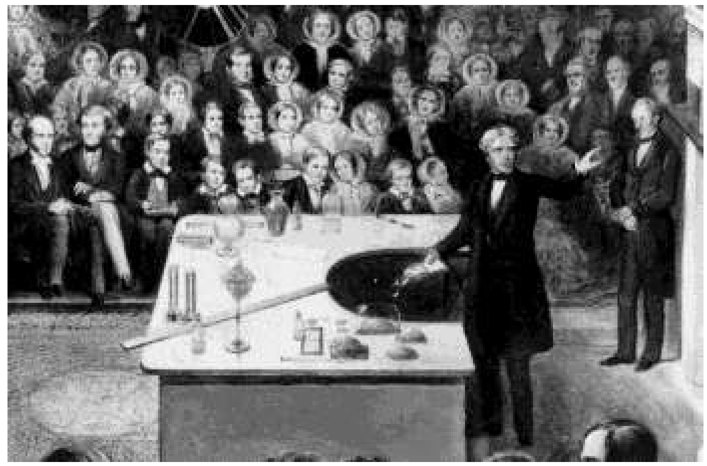
Now I want to show you that an unsalted dry roasted peanut can be used for a fuel to make a flame. We can also estimate the amount of thermal energy it produces when it burns by placing the burning peanut under a tin can that has been filled with 0.1 kg of water (m). After weighing the peanut (0.5-1 gram), we measure the temperature of the water with an **infrared thermometer probe**. Then we light the peanut, and measure the rise in the temperature (ΔT) of the water. The amount of heat produced by the peanut is given by the following formula:

$$\text{Thermal energy} = c\ m\ \Delta T$$

where c is the heat capacity of water and is equal to 4186 J/(kg C) or 1 Calorie/(kg C). The ratio of 4.186 to 1 is the ratio of the **mechanical equivalent of heat** to the specific heat determined by **James Joule** with his **paddle wheel** in the **basement of the brewery**. The thermal energy of a peanut measured in this crude way is about 4186 J or 1 Calorie. If the difference in the initial weight and final weight of the peanut was 0.5 g, then the energy content of the peanut would be about 2 Calories/gram. This is an underestimate since much of the heat is radiated away by the metal can. How could we be more accurate?

Next time we will look at **ancient fossils** found in the **coal beds** of America to get an idea of fossil fuels and of geological time. The plant fossils still contain the carbon that they fixed photosynthetically so many years ago. The fossil fuels are mostly and most likely hydrocarbon rich deposits of ancient organisms that we combust to release thermal energy today. We will also discuss more about respiration in living organisms that occurs at ambient temperatures.

Michael Faraday ended his lecture series on *The Chemical History of a Candle* by saying, "*...you see the analogy between respiration and combustion is rendered still more beautiful and striking. Indeed, all I can say to you at the end of these lectures (for we must come to an end at one time or other) is to express a wish that you may, in your generation,* ***be fit to compare to a candle****;* ***that you may, like it, shine as lights to those about you; that, in all your actions, you may justify the beauty of the taper by making your deeds honourable and effectual in the discharge of your duty to your fellow-men****.*"



Light, to the **luminaries** who created the **Enlightenment** such as Thomas Jefferson, is freedom from ignorance. As **Thomas Jefferson** said in a letter to Tench Coxe in 1795, "***Light and liberty go together***" and in a letter to Cornelius Camden Batchly in 1822, "***I look to the diffusion of light and education as the resource most to be relied on for ameliorating the condition, promoting the virtue, and advancing the happiness of man.***"

Hans Christian Anderson wrote a fairy tale and a short story that relates to today's lecture. Hans Christian Anderson's first fairy tale, which was discovered in 2012, was entitled, *The Tallow Candle*.

"*It sizzled and fizzled as the flames fired the cauldron. it was the Tallow Candle's cradle - and out of the warm cradle came a flawless candle; solid, shining white and slim it was formed in a way that made everyone who saw it believe that it was a promise of a bright and radiant future – promises that everyone who looked on believed it would really want to keep and fulfil.*

The sheep – a fine little <u>*sheep*</u> *– was the candle's mother, and the melting pot its father. Its mother had given it a shiny white body and an inkling about life, but from its father it had been given a craving for the flaming fire that would eventually go through its marrow and bone and shine for it in life.*

That's how it was born and had grown; and with the best and brightest anticipation cast itself into existence. There it met so many, many strange creations that it became involved with, wanting to learn about life – and perhaps find the place where it would best fit in. But it had too much faith in the world that only cared about itself, and not at all about the Tallow Candle. A world that failed to understand the value of the candle, and thus tried to use it for its own benefit, holding the candle wrongly; black fingers leaving bigger and bigger blemishes on its pristine white innocence which eventually faded away, completely covered by the dirt of a surrounding world that had come much too close; much closer than the candle could endure, as it had been unable to tell grime from purity – although it remained pristine and unspoiled inside.

False friends found they could not reach its inner self and angrily cast the candle away as useless.

The filthy outer shell kept all the good away – scared as they were to be tainted with grime and blemishes – and they stayed away.

So there was the poor Tallow Candle, solitary and left alone, at a loss at what to do. Rejected by the good, it now realised it had only been a tool to further the wicked. It felt so unbelievably unhappy, because it had spent its life to no good end – in fact it had perhaps sullied the better parts of its surroundings. It just could not *determine why it had been created or where it belonged; why it had been put on this earth – perhaps to end up ruining itself and others.*

More and more, and deeper and deeper, it contemplated – but the more it considered itself, the more despondent it became, finding nothing good, no real substance for itself, no real goal for the existence it had been given at its birth. As if the grimy cape had also covered its eyes.

But then it met a little flame, a tinder box. It knew the candle better than the Tallow Candle knew itself. The tinder box had such a clear view – straight through the outer shell – and inside it found so much good. It came closer and there was bright expectation in the candle – it lit and its heart melted.

Out burst the flame, like the triumphant torch of a blissful wedding. Light burst out bright and clear all around, bathing the way forward with light for its surroundings – its true friends – who were now able to seek truth in the glow of the candle.

The body too was strong enough to give sustenance to the fiery flame. One drop upon another, like the seeds of a new life, trickled round and chubby down the candle, covering the old grime with their bodies.

They were not just the bodily, but also the spiritual issue of the marriage.

And the Tallow Candle had found its right place in life – and shown that it was a real candle, and went on to shine for many a year, pleasing itself and the other creations around it."

https://www.youtube.com/watch?v=lBk9qSxn390

Hans Christian Andersen's first short story was entitled, *The Tinder Box*.

https://www.youtube.com/watch?v=GFURBFg1VoA