Cellular Respiration: Converting carbohydrate into chemical energy without emitting visible light

A knowledge of the relationship between light and the spirit is ancient. According to Proverbs (20:27), “The spirit of man is the candle of the Lord, searching all the inward parts of his being.” The great chemist, Antoine Lavoisier was the first scientist to draw an analogy between respiration and the chemical process of combustion.

Although in 1789, he ended a memoir like so: “One may say that this analogy between combustion and respiration has not escaped the notice of poets, or rather the philosophers of antiquity, and which they had expounded and interpreted. This fire stolen from heaven, this torch of Prometheus, does not only represent an ingenious and poetic idea, it is a faithful picture of the operations of nature, at least for animals that breathe; one may therefore say, with the ancients, that the torch of life lights itself at the moment the infant breathes for the first time, and it does not extinguish itself except at death. In considering such happy agreement, one might sometimes be tempted to believe that the ancients had indeed penetrated further than we think into the sanctuary of knowledge, and that the
myth is actually nothing but an allegory, in which they hid the great truths of medicine and physics.”

J. Robert Mayer, a ship’s physician, originally discovered the First Law of Thermodynamics when he noted in 1840 the color of venous blood is redder in people who live in the tropics than in people who live in colder climates. He wrote, “Observations which I made in the Tropics taught me to recognize the role which the blood corpuscles play in the combustion process in the body. In a sea voyage of 100 days, out of a passenger list of 28 there occurred no serious incidence of sickness. However, a few days after the arrival in Batavia (Dutch East Indies) there broke out an epidemic of an acute catarrhal inflammatory affection of the lungs. In the ample blood-letting which I carried out, the blood from the veins in the arm had an unusually red color, so that if I had judged by color alone I might have thought I had struck an artery.... At this point Mayer realized that in tropical climates there was no need for combustion to heat the body as there is such a need in colder climates, and consequently, there is more unused oxygen in the blood of people who live in tropical climates compared with people who live in colder climates and this is why the venous blood is redder in people who live in tropical climates compared to people who live in colder climates. Mayer also realized that physical work generates heat and that it too must be powered by combustion. Although Mayer was not sure how heat itself caused the muscles to contract.

From this simple observation, Mayer realized that ex nihilo nihil fit. Nil fit ad nihilum. That is, nothing comes from nothing, every effect must be preceded by a cause, and the effect is equal to the cause. He then applied the First Law of Thermodynamics, not only to heating the human body, but to
gravitational energy, radiant energy, chemical energy, kinetic energy, electrical energy and magnetic energy.

In *The Sound of Music*, Maria and Georg sang the song, *Something Good* which contains what I consider to be a truism, consistent with the First Law of Thermodynamics:

*Nothing comes from nothing*

*Nothing ever could*

Last week we reenacted to some degree Michael Faraday’s lecture series on *The Chemical History of a Candle*. Faraday demonstrated the analogy between combustion and respiration by showing that they both produce carbon dioxide and water. Michael Faraday is another scientist who was not trying to replace God with science. In a lecture given at the Royal Institution entitled, *Observations on the Education of the Judgment*, Faraday said, “...the book of nature, which we have to read, is written by the finger of God.”

Last time we observed that the combustion process that occurs in a candle involves **pyrolysis**, which takes place in the dark hollow of the flame, **chemiluminescence**, which can be seen best in the blue region at the bottom of the flame, **incandescence**, which is seen in the brightest portion of the flame, and **oxidation**, which occurs at the outside of the flame ([http://vimeo.com/40271657](http://vimeo.com/40271657)).

The **intracellular combustion process or the respiratory process**, unlike the burning of a candle, does not involve the transformation of chemical energy
into radiant energy and the emission of visible light. So **while the chemical analogy is good, there are limitations.** While **pyrolysis** involves the fragmentation of the fuel by exposing it to temperatures that are high enough to boil our blood, fuel fragmentation occurs very differently in intracellular combustion. How is the fuel fragmented at **ambient temperature** in living cells?

**Louis Pasteur** guessed that **fermentation** is respiration without air, and it not just a **chemical process** but a **vital process** that requires **living organisms.** He wrote, “I am of the opinion that alcoholic fermentation never occurs without simultaneous organization, development and multiplication of cells....” since he was never able to get fermentation to take place **in vitro** in the absence of living yeast. However, **Eduard Buchner** (1897) using a **German beer yeast** instead of a **French wine yeast** was able to obtain fermentation or **anaerobic respiration** **in vitro** when he added sugar to a yeast extract.

Actually this was a **lucky** find, since Buchner was making a health tonic, and only added the sugar as a preservative, when the other antiseptics failed to keep the extract sterile. Buchner’s wife made the suggestion based on her commonsense knowledge that fruit preserves are made by heating fruit in a sugar solution. The sugar acts as a preservative because bacteria cannot grow in high concentrations of sugar (or salt) because the high concentrations of sugar draws water out of the bacteria by osmosis and they dehydrate.
In this way, Buchner discovered the part of the yeast that caused the fermentation of sugar in the absence of air and named the extract **zymase**, from *zyme*, the Greek word for “**yeast**,” and *diastasis*, the Greek word for “break apart.” Willy Kühne named all biocatalysts, **enzymes**, from the Greek words, *en zyme*, which mean “in yeast”.

In the candle, the fuel is broken down in a couple of haphazard steps by heat in a process known as **pyrolysis**. In living cells, the fuel is not fragmented by heat but is broken down in **glycolysis** at **ambient temperatures** in about a dozen sequential and ordered steps as a result of the intervention of **enzymes**. In the process of fermentation, which takes place in the **cytosol**, **hydrogen atoms** in the form of electrons and protons, are removed from the sugar in a process of **oxidation** (**loss of electrons is oxidation**). During the **oxidation process**, a net of **two molecules of ATP** are formed from each sugar molecule. Most of the chemical energy in the original sugar molecule fragmented in glycolysis is left unavailable as lactic acid or ethanol, although we make use of these products in pickling, wine, and beer making.

In the presence of **oxygen**, aerobic respiration takes place where the pyruvate is not turned into lactic acid or ethanol, but **fully oxidized** into **carbon dioxide** and **water**.
The second leg of the oxidation of glucose takes place in **mitochondria** and results in the production of approximately **38 molecules of ATP** per sugar molecule compared with two molecules produced by fermentation alone.

In **aerobic respiration**, the electrons that are removed from the molecules being oxidized are transferred to **NAD⁺ to form NADH**, a molecule that is similar to NADPH, the hydrogen carrier that participates in photosynthesis. The NADH then passes its electrons to an **electron transport chain** composed of **iron-containing cytochromes**, which means “cell color.” This too is similar to the electron transport chain of photosynthesis. After all both processes transform the chemical energy of reduced molecules by oxidizing them. Moreover, as the electrons move from an acceptor with a more negative redox potential to one with a more positive redox potential, they can use the redox energy made available in the electron transfer to transfer protons from the matrix of the mitochondria to the intermembrane space. This **charge separation** is also similar to what happens during photosynthesis. The electrochemical energy of the proton gradient is then used by the coupling factor or ATP synthase to synthesize **ATP** from ADP and Pi.

**All foodstuffs**, including carbohydrates, lipids and proteins are enzymatically combusted so that the energy in their CH bonds can be transformed into the energy of **ATP**. We now know that **ATP is the common intermediate that is used to energize all aspects of life**, including, **mechanical work**, like muscle contraction;
biosynthetic work like sugar, protein and lipid synthesis, and electrical work, like nerve transmission.

In aerobic respiration, the oxygen functions as the ultimate electron acceptor. It is transformed into two water molecules when it gains four electrons and four hydrogen ions (protons). The oxygen gains the electrons transferred to it by cytochrome oxidase, an iron-containing enzyme. This is equivalent to the outermost region of the flame.

The rapid binding of iron to oxygen that took place in the candle when we sprinkled iron powder in the flame or when we struck the flint against the steel took place at a temperature high enough to result in incandescence. On the other hand, the binding of oxygen to iron-containing cytochrome oxidase takes place at ambient temperatures.

Chemically, the formation of water by cytochrome oxidase is a reversal of the oxygen splitting that occurred in Photosystem II of photosynthesis.

Aerobic respiration provides large quantities of energy to the cell. The many small steps involved in intracellular combustion allow some of the energy of combustion to be conserved as the chemical energy of ATP.

The overall equations of aerobic respiration and photosynthesis appear to represent the same reaction proceeding in reverse directions. While there are many similarities between the two reactions that take place in the mitochondria and chloroplasts in terms of generating and using charge separation of electrons and protons to synthesize ATP, respiration and photosynthesis are quite distinct and
irreversible processes. The energy transducing processes of respiration and photosynthesis can be well understood in terms of the **First and Second Laws of Thermodynamics**.

\[ \text{photosynthesis} \quad 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

\[ \text{aerobic respiration} \quad \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy} \]

Photosynthesis, requires an energy input in the form of light, to reduce the entropy of the chemicals involved in photosynthesis. Entropy increases overall however because a portion of the visible wavelengths of light is converted into infrared wavelengths; i.e. heat, thermal energy or entropy. Aerobic respiration, transforms some of the chemical energy of sugar to the chemical energy of ATP, the rest being given off as heat, thermal energy or entropy.

**Wilbur Olin Atwater** treated the human body as a black box with inputs and outputs to gain insight into food, respiration, and mechanical work. In order to do this, he built in 1896 a respiration calorimeter room that measured the amount of oxygen taken up, the amount of carbon dioxide emitted and the amount of heat generated when a person did any kind of mechanical work, for example, peddle a bicycle.
At the time Atwater did experiments, he did not know about how the energy derived by respiration was utilized by muscle contraction. He did not know about ATP and wondered, \textbf{Could it be heat? Or could the electrons transferred from sugar to oxygen be used as an electric current?}

According to the First Law of Thermodynamics, to perform work, you have to ingest (at least) the same number of calories of food. Given the amount of work performed on a daily basis, Atwater recommended that active men and women eat approximately 2000-3000 Calories/day. However, “work” was typically more strenuous 100 years ago before there were cars, computers, washers and dryers.

We measured the ability of a burning \textbf{peanut} to heat water. With a little more sophistication, Atwater burned thousands of foods in a bomb calorimeter to determine their “fuel value.” He found that in general, carbohydrates yield 4 Calories/gram, proteins yielded 4 Calories/gram, and fats yielded 9 Calories/gram. Atwater found that \textbf{meat} and \textbf{cereals} have a fuel value of approximately \textbf{1000 Calories/pound} whereas \textbf{fruits} and \textbf{vegetables} have a fuel value of approximately \textbf{250 Calories/pound} (= 0.55 Calories/gram).
From the **calorimetry perspective alone**, fruits and vegetables did not seem to be very good foods. Modern nutrition theory at the turn of the 20th century based on the **fuel value of food** led to the “**typical American diet**” of white bread, muscle type of meat, potato and sugar. A typical breakfast, lunch and dinner are shown below:

![Typical American diet](image)

We now know that there are other things, such as **vitamins**, **minerals** and **antioxidants** that are important in determining what good food is. We do not eat food for its fuel value alone.

**The China Study** written by T. Colin Campbell (Cornell) presents the gold standard of evidence for the relationship between diet and health.

![The China Study](image)

Thus ends the material for Prelim 1.
We have discussed how candles made of fats or wax can be burned for light. **Coal** is an organic rock produced from **plant products** that we use to generate steam to drive turbines that generate electricity. As a segue to describing coal balls, I will discuss coal itself. **Lignite** and **bituminous** coal are sedimentary rocks, produced from **peat** that grew in **bogs**. Lignite coal was produced during the Tertiary Period (66-2.58 million years ago). It has a high moisture and ash content, low **hydrocarbon** content, and thus low caloric value (60 Calories/gram). Bituminous coal is formed when a lignite-like coal has been subjected to high pressures. It has a higher fuel value than lignite (100 Calories/gram). Bituminous coal was produced about 100-300 million years ago. **Anthracite** coal has the lowest ash and moisture content, the highest hydrocarbon content, and thus the greatest caloric value (120 Calories/gram). This is because anthracite coal is a metamorphic rock that has been subjected to high temperatures and pressures that removed the volatile compounds that would have taken a portion of the thermal energy of the burning coal to volatilize them without producing heat. Anthracite coal was formed during the **Carboniferous Period**, about 359.2-299 million years ago. Notice that all of the coals, because of their high density, have a much higher fuel value than fat (9 Calories/gram).

Coal in relatively stable parts of the lithosphere that have been subjected to very high pressures (5000 MPa) but relatively low temperatures (900 -1300 C) can be transformed into **diamonds**.
While it is the hydrocarbon portion of coal that is burned to turn water into steam, coal also contains other components, including sulfur dioxide (SO₂) that combines with oxygen and water in the atmosphere to cause acid rain (H₂SO₄). Acid rain devastates forests by damaging the leaves of trees and leaching the nutrients from the soil so the roots cannot mine them. Acid rain also dissolves buildings and monuments made from limestone (CaCO₃) and marble, which is composed of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). Marble is metamorphosed limestone.

\[
\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]

The effect of acid rain, resulting from the industrial revolution, was described by Robert Angus Smith (1872), a chemist who lived in the industrial city of Manchester, England, in his book, *Air and Rain: the Beginnings of a Chemical Climatology*. We will talk more about Manchester, England when we discuss the relationship between coal burning, the discoloration of tree bark, and the evolution of the coloration of peppered moths.
Here are some of Smith’s measurements of oxygen and carbon dioxide that may be of interest to you. Note that **candles go out** when the oxygen concentration falls to 18.5%.

The sulfur emissions that are produced by burning coal also **scatter** the sun’s rays just as volcanic dust scatters the sun’s rays, resulting in less sun reaching the earth’s surface and subsequent **global cooling**. Robert K. Kaufmann (2011) noticed that anthropogenic forcing of the global heat load was 0.13 W/m² between 2002 and 2007, which was smaller than the anthropogenic forcing (0.24 W/m²) between 1997 and 2002. Were humans becoming better stewards of the planet? No. Kaufmann suggests that during the latter time period, some of the **global warming** caused by the anthropogenic rise in carbon dioxide (CO₂) was partially mitigated by the doubling
of coal consumption in China between 2003 and 2007, which resulted in an increase in sulfur emissions, and a scattering away of incoming sunlight.

In the past coal gas was distilled from coal to make illuminating gas and the residue, which is known as coal tar, was used as an inexpensive hydrocarbon source to make fabric dyes and pharmaceuticals.

Today we will have a chance to make coal ball peels. Coal balls are found in bituminous and anthracite coal seams. Coal balls are concretions made during the Carboniferous Period, 359.2-299 million years ago, when calcium carbonate infiltrated plant material and it fossilized. The calcium carbonate was probably dissolved from a layer of fossil shells in the strata above the coal. The fossilized material is the same material that makes up the coal, although in the coal balls, its structure is preserved. The coal balls themselves are not coal, they are calcium carbonate rich (76.66%) but not carbon rich (4.95%) and are not burnable.

The coal beds are 10-12 meters thick and formed from many successive layers. Each successive layer represents an individual flood event in the coal swamp.
The flooding occurred during interglacial periods where the continental shelf was covered with shallow seas. During the flood periods, the dead plants did not completely decay but turned into peat. Heat and pressure in the earth transformed the peat into coal. The structures of the plants that were transformed into coal balls were preserved.

Limestone nodules or coal balls, found in the coal seams of Lancashire, were first described in 1855 by Joseph Dalton Hooker M. D., a friend of Charles Darwin, and Edward William Binney Esq., a friend of James Joule. They wrote, “A section of any of these nodules shows a confused mass of decayed and apparently decaying vegetable remains; they present no appearance of these remains having been brought together by any mechanical agency; they appear to be associated together just as they fell from the plants that produced them, and to be rotting remains of a redundant and luxuriant vegetation.”

Binney was a partner in E. W. Binney & Co., who manufactured paraffin wax. In my personal quest to find the connection between all things, I am currently searching for a connection between E. W. Binney (1819-1881) and Binney & Smith, the company that makes Crayola crayons. Here is what I have so far.

E. W. Binney & Company was formed in 1851 by Edward William Binney, James Young and Edward Meldrum. James Young noticed that oil dripped from the roof of a coal mine. Guessing that the oil originated from coal that was exposed to heat, he treated coal with heat and distilled out paraffin oil. Light paraffin oil, also known as kerosene (a term coined by
Abraham Gesner), is used for fuel for lamps and jets, heavy paraffin oil is used for making paraffin wax, which was used for candles. *Keros* (κηρός) is the Greek word for wax.

Joseph Walker Binney (born December 6, 1836), son of Richard and Elizabeth (Cowley) Binney, emigrated from England to upstate New York in 1860 and founded the Peekskill Chemical Works in 1864. I do not know his relationship to E. W. Binney or even if there is a relationship. Joseph Binney used pyrolysis techniques to manufacture charcoal from hardwoods and the pigment lamp black from animal fats and whale oil. In 1885, Joseph’s son Edwin Binney and nephew C. Harold Smith became partners in Binney & Smith, who manufactured carbon black pigment used for car tires that previously were grayish white, and the iron oxide pigment used to paint the red barns seen throughout New York. They used slate to make school pencils (1900) and paraffin to make Crayola crayons (1903). Crayola comes from the French words *craie* for chalk *oléagineux* for oily. In 1958 they introduced the box with 64 colors and a built-in sharpener. I wanted this box all my life. Amy gave me my first one along with the Robert Fulghum’s book, “All I Needed to Know I Learned in Kindergarten: Uncommon Thoughts on Common Things,” in which he wrote,
“Crayolas plus imagination (the ability to create images) - these make for happiness if you are a child. Amazing thing Crayolas. Some petroleum-based wax, some dye, a little binder - not much to them. Until you add the imagination. The Binney Company in Pennsylvania makes about two billion of these oleaginous sticks of pleasure every year and exports them to every country in the United Nations. Crayolas are one of the few things the human race has in common. The green and yellow box hasn't changed since 1937. In fact the only change has been to rename the "flesh" color to "peach". That's a sign of progress.

The way I know about "flesh" and "peach is that when I bought my godson the trainer set, I indulged myself. Bought my very own set of sixty four. In the big four section box with the sharpener built right in. Never had my own set before. Seems like I was always too young or too old to have one. While I was at it, I bought several sets. Got one for the kid's mother and father and explained it was theirs, not his.

What I notice is that every adult or child I give a new set of Crayolas to goes a little funny. The kids smile, get a glazed look on their faces, pour the crayons out, and just look at them for a while. Then they go to work on the nearest flat surface and will draw anything you ask, just name it. The adults always get the most wonderful kind of sheepish smile on their faces - a mixture of delight and nostalgia and silliness. And they immediately start telling you about all their experiences with Crayolas. Their first box, using every color, breaking them, trying to get them in the box in order again, trying to use them in a bundle, putting them on hot things to see them melt, shaving them into waxed paper and ironing them into stained glass windows, eating them and on and on. If you want an interesting party sometime, combine cocktails and a fresh box of Crayolas for everybody.

When you think about it, for sheer bulk there's more art done with Crayolas than with anything else. There must be billions of sheets of paper in every country in the world, in billions of boxes and closets and attics and cupboards, covered with billions of pictures in crayon. Ronald Reagan and Mikhail Gorbachev used crayons, I bet. So did Fidel and the Emperor of Japan and Rajiv Gandhi and Mrs. Thatcher and Mr. Mubarak and maybe even the ayatollah. And just about everyone else you care to name.

Maybe we should develop a Crayola bomb as our next secret weapon. A happiness weapon. A beauty bomb. And every time a crisis developed, we would launch one. It would explode high in the air - explode softly - and send thousands, millions, of little parachutes into the air. Floating down to earth - boxes of Crayolas. And we
wouldn't go cheap, either - not little boxes of eight. Boxes of sixty-four, with the sharpener built right in. With silver and gold and copper, magenta and peach and lime, amber and umber and all the rest. And people would smile and get a little funny look on their faces and cover the world with imagination.

Guess that sounds absurd, doesn't it? A bit dumb. Crazy and silly and wierd. But I was reading in the paper today how much money the Russians and our Congress just set aside for weapons. And I think what those weapons will do. And I'm not confused about what's weird and silly and crazy and absurd. And I'm not confused about the lack of, or the need for, imagination in low or high places. Pass the crayons, please.”

I never found a connection between Edward William Binney, son of Elizabeth (Cross) and Thomas Binney, who supplied Joule’s grandfather with malt, and Binney & Smith Crayons. I did find the following anecdotes.

As reported in the Oxford Dictionary of National Biography, Edward William Binney learned of “the destitution of some artisan mathematicians and botanists” and tried to establish a public society for “the relief and encouragement of scientific men in humble life” (Manchester Guardian, 13 Dec 1843). However, Binney thought that the conditions imposed by Richard Parkinson, a clergyman concerned with the morality of the recipients, would ruin the proposed society’s aims. Consequently, in 1844, Binney set up a private fund where he presented donations at an annual dinner he gave for scientific artisans. James Crowther, a porter, autodidact and amateur botanist, and Richard Buxton, a shoemaker, autodidact, and amateur botanist was supported by Binney’s fund.

Edward William Binney, was, himself, an amateur botanist. Here are some pictures from Binney’s book entitled, Observations on the Structure of Fossil Plants Found in the Carboniferous Strata.
The carboniferous sandstone known as Binney’s Sandstone, was named in honor of Edward Binney by Broadhurst and Simpson (1999) to “commemorate the work of a pioneer in the study not only of the geology of Manchester, but of its building stones as well.”

The carboniferous coal swamp, which included *Lepidodendron*, a tree-like fossil *lycopod*, *Calamites*, a tree-like fossil *horsetail*, and *seed ferns* may have looked like this:

I would like you to know the small living relatives of the tall tree-like plants that gave us coal.
The procedure to make coal ball peels, given below, takes about 25+ minutes.

1. Polish the surface of the coal ball with carborundum (SiC), the second hardest material, for **30-60 seconds** using figure 8 motions.
2. Without touching the surface, rinse the surface with water (catching the carborundum in the tub).
3. Soak the shiny surface of the coal ball in hydrochloric acid (HCl) for **15 seconds** to dissolve the calcite without removing the organic matter that makes up the cell walls. The organic matter should turn white. Gently wash the surface with water (H$_2$O) at an angle.
4. Place the coal ball on its side under a heat lamp on tray of gravel until the water on the surface evaporates and the surface becomes a dull gray. The fan will speed up the evaporation process. This takes about **10 minutes**. Adjust polished surface so that it is horizontal.
5. Cover the surface (and not your clothes) liberally with acetone (CH$_3$)$_2$CO and then gently place an acetate sheet by slightly folding the acetate sheet and applying it from the center to the outside.
6. Wait **30 (15-40) minutes** until the acetate is dry. Then peel the acetate sheet from the coal ball surface and view shiny-side-up with dissecting microscope and take pictures.