

CHM 101 GENERAL CHEMISTRY

FALL QUARTER 2008

Section 2

Lecture Notes – 11/19/2008

(last revised: 11/19/08, 4:00 PM)

6.5 Present Sources of Energy (We covered the following parts of this section in the [previous lecture](#).)

- **But First, a Little History:**
 - **Solar Power – The Ultimate Source of All Energy:**
 - **The Pre-Industrial Age:**
 - **The Industrial Revolution:**
 - **Petroleum:**
 - **Sources of Energy in the USA Since 1850:**
- **Petroleum and Natural Gas:**
 - **Natural Gas:**
 - **Petroleum:**

(This is the point where we left off last time.)

- **Coal:** Coal has formed over geological time from buried biomass. Depending on the age of the biomass deposit and the pressures and temperatures it has encountered over that time, it has by now been converted to (in order of the extent of transformation) lignite, subbituminous coal, bituminous coal, or anthracite. This is also their order of carbon content, as the transformation processes tend to eliminate carbon, hydrogen, and oxygen. See Table 6.5, where I have included the mass elemental composition of wood (assumed to be the same as cellulose) for comparison purposes.

TABLE 6.5 Elemental Composition of Various Types of Coal

Type of Coal	Mass Percent of Each Element				
	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1
Wood (CH ₂ O)	40	7	53		

- **Uses of Fossil Fuels:** Let's return to Figure 6.11 and talk about sources *and uses* of energy in the USA over time.

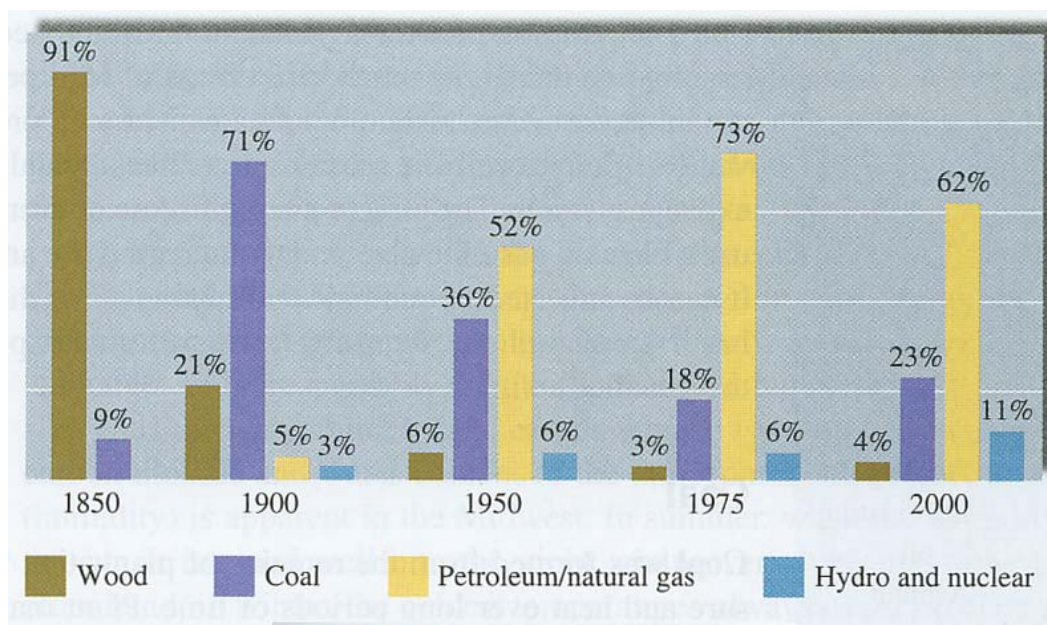


FIGURE 6.11
Energy sources used in the United States.

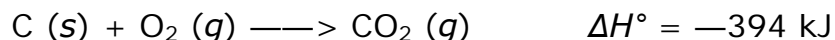
In 1850, the USA derived nearly all its energy from wood. Some of it went into transportation to drive wood-powered steam locomotives and inland steamboats, but I expect most of it went for domestic heating.

By 1900, the USA had become a leading manufacturing power, and coal had mostly displaced wood as the predominant energy source. Coal had become the principal fuel for transportation, directly by powering the steam engines that drove trains and ships, and indirectly, by generating the electricity that powered urban streetcars and interurban railways. Coal and wood shared the domestic heating market. In manufacturing, coal-fired steam

engines produced mechanical power that would be distributed through a plant by a system of belts, pulleys, and rotating shafts. The lighting market was shared by coal and petroleum, coal after conversion to electricity (typically sold by the street railway utility) or to coal gas (a mixture of H₂ and CO), petroleum in the form of kerosene fuel for oil lamps.

In more modern times, since around 1950, we see that petroleum (together with natural gas) has become our dominant source of energy. It now powers nearly all of our transportation, cars, trucks, airplanes, ships, and even our railroads. (When the railroads converted from steam to diesel in the 1940's and 1950's, their energy efficiency increased by a factor of 4.) The only significant market remaining for coal is electric power generation; coal accounts for about half of this market.

- **Problems with Fossil Fuels – Supply:** If we refer back to Figure 6.11 (repeated here), we see that we derive most of our current energy consumption from petroleum (including natural gas). Indeed, it is said that the USA consumes some 30% of the world's petroleum production, and much of this must be imported, as we possess only about 3% of the world's known petroleum reserves. Moreover, our petroleum reserves peaked in the early 1970's and have declined ever since, despite vigorous exploration for new oil fields. Some politicians advocate expanded exploration for petroleum, but government studies indicate this will do little to expand supplies. More ominously, some experts warn that world petroleum production capacity may soon peak, causing demand to exceed supply, with skyrocketing oil prices being the consequence.
- **Problems with Fossil Fuels – Pollution:** In an ideal world, coal would be 100% carbon and would burn completely to produce energy, carbon dioxide, and nothing else:



Of course, the world is not ideal, and coal combustion produces several unwanted effects:

- **Incomplete Combustion:** Incomplete combustion produces toxic soot and carbon monoxide.
- **By-Products:** The high temperatures reached during combustion promote the reaction of nitrogen and oxygen in the combustion air to form various oxides of nitrogen. (Recall our discussion about acid rain in Section 5.10.)

- **Impurities:** Any sulfur present in the coal will be oxidized to sulfur dioxide. Other impurities present in the coal (even uranium!) can be vaporized or they can be converted into fine particulates.

These various unwanted products of coal combustion tend to be swept into the stream of exhaust gases, and unless they are trapped in some way, they will pass into the environment, where they can cause tremendous pollution problems. (Think Pittsburgh in the early 1900's or Eastern Europe during the Communist Era.)

These kinds of problems are not unique to coal:

- **Gasoline:** Photochemical smog from the unburnt hydrocarbons and nitrogen oxides in car exhaust.
- **Diesel Oil:** Soot and sulfur dioxide from diesel engines.
- **Wood:** Wood smoke. Need I say more?

The above discussion is limited to problems that occur at the point of use. Pollution also can occur at the point of extraction, during transport, and during processing. Some examples:

- **Oil Spills at Sea**
- **Toxic Releases from Oil Refineries**
- **Open Pit Coal Mining**
- **The Greenhouse Effect:** The sun radiates copious amounts of energy that impinges on the earth, mostly in the form of visible light. Let's examine what happens to this energy:
 - **Reflection by the Atmosphere:** About 30% of solar energy gets reflected back to space by the atmosphere (mostly by cloud tops).
 - **Photosynthesis:** Plants absorb light and use its energy to convert CO_2 and H_2O to sugars and other biomass.
 - **Hydrological Cycle:** Solar energy powers the hydrological cycle by evaporating water (mostly from the sea).
 - **Heating:** Most of the solar energy reaching the surface becomes absorbed by soil, rocks, and water and increases the temperature at the surface.

Reradiation from the Surface: What happens to solar energy absorbed at the earth's surface?

- **Atmospheric Heating:** Some of the energy absorbed at the surface goes into heating near-surface air and causing it to rise. Thus this energy sets the atmosphere into motion and drives our weather.
- **Infrared Radiation:** Most of the energy that goes into heating the earth's surface is reradiated back toward space in the form of infrared radiation. Not all of it gets there. Several atmospheric gases such as carbon dioxide, water vapor, and methane are opaque to infrared and absorb it, only to reradiate it. The process is illustrated in Figure 6.12:

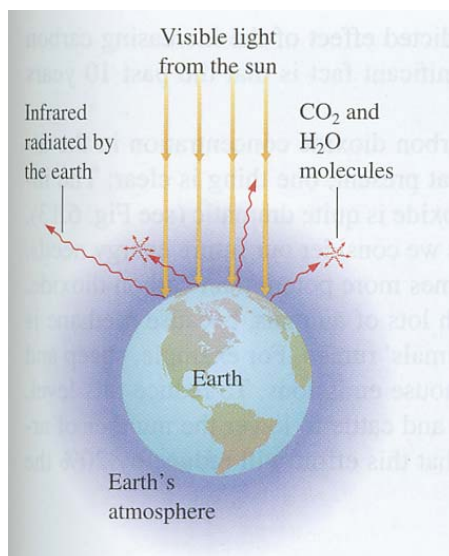


FIGURE 6.12

The earth's atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth's surface is strongly absorbed by CO₂, H₂O, and other molecules present in smaller amounts (for example, CH₄ and N₂O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

The result is that the earth's surface and the lower atmosphere are significantly warmer than they would be, were there no infrared absorption by atmospheric gases. The role of these gases is analogous to the role of the glass in a greenhouse, thus the phenomenon is called the *greenhouse effect*, and the infrared-absorbing gases are called *greenhouse gases*.

- **Carbon Dioxide and Global Warming:** Water vapor and carbon dioxide are the principal contributors to the greenhouse effect. Since infrared absorption is proportional to concentration, fluxuations and long-term changes in the atmospheric contents of these gases should be of concern.
 - **Water Vapor:** The concentration of water vapor in the atmosphere has a marked effect on heat retention. Indeed, under conditions of high humidity (high atmospheric moisture content), there is little cooling at night, and we experience warm, muggy weather conditions. In contrast, cooling is extensive on low-humidity nights when the air is clear. Fortunately, the amount of water vapor in the atmosphere is controlled by the hydrological cycle, and although it fluxuates over short periods of time, it does not change in the long run.
 - **Carbon Dioxide:** The carbon dioxide content of the atmosphere shows only small, short-term fluxuations. But what about the long run? Figure 6.13 shows a significant long-term increase in the CO₂ content of the atmosphere since 1750. This increase is thought to have come about from humankind's use of fossil fuels starting at the dawn of the Industrial Revolution around 1750.

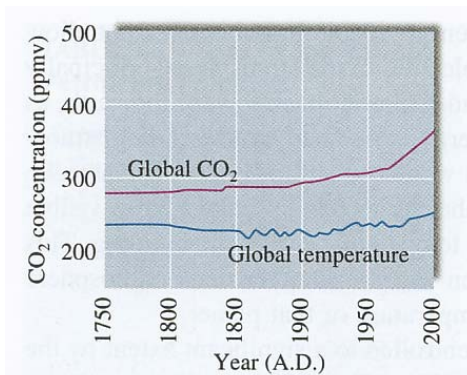


FIGURE 6.13

The atmospheric CO₂ concentration and the average global temperature over the last 250 years. Note the significant increase in CO₂ concentration in the last 50 years.

(Source: National Assessment Synthesis Team, *Climate Change Impacts on the United States: The Potential Consequences of Climate, Variability and Change, Overview*, Report for the U.S. Global Change Research Program, Cambridge University Press, Cambridge, UK, p. 13, 2000.)

- **Global Temperature Trends:** [The Wikipedia article on global warming](#) shows a graph of global temperatures for the period 1850-2008. The trend is unmistakably toward rising temperatures; increases of 0.8 C° since 1850 and 0.4 C° versus the global mean for 1961-1990.
- **Cause and Effect:** Although global warming has been a controversial subject, and although increases in atmospheric carbon dioxide are not its only cause, nearly all scientists now agree that carbon dioxide emissions from use of fossil fuels are a significant cause of global warming, and that humankind needs to curtail these emissions in order to forestall catastrophic further increases in global temperatures.

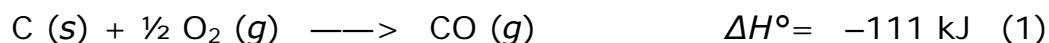
6.6 New Energy Sources: Our present energy economy, based primarily on petroleum, is unsustainable in the long run. World oil shortages approach, and if we are to continue to supply enough energy to meet future demand, we need to look elsewhere than petroleum. But even if petroleum were in unlimited supply, the threat of global warming would still force us to curtail our exploitation of fossil fuel resources unless and until we can develop technology for sequestering CO₂ before it can enter the atmosphere.

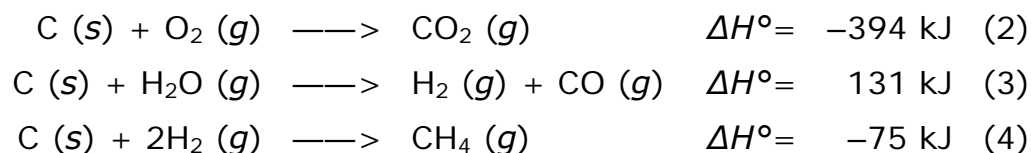
- **Practicalities**

- **Pollution**
- **Technical Feasibility**
- **Energy Efficiency**
- **Ease of Distribution**

- **Coal Conversion:** Coal creates environmental problems at every stage of its production, refinement, transport, and use cycle, at least while it remains a solid. Is it possible to control some of these problems by using it a feedstock to produce a liquid or a gas fuel?

- **Gasification:** Coal gasification is hardly a new process. The earliest gas utility companies in the latter half of the 19th century produced their gas from coal, but later switched to natural gas, as long-distance pipelines enabled it to be distributed. The most important chemical reactions in the process are:

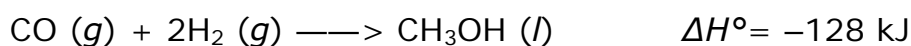




The feedstocks are coal, air, and water. Some of the coal is burned in reactions (1) and (2) to supply energy to make steam and drive the endothermic reaction (3) which produces a desirable product stream, a mixture of hydrogen and carbon monoxide (and air) called *synthetic gas, syngas* for short, or originally, *water gas*. Often, some of the hydrogen from the syngas stream is used to treat additional carbon to produce methane (4).

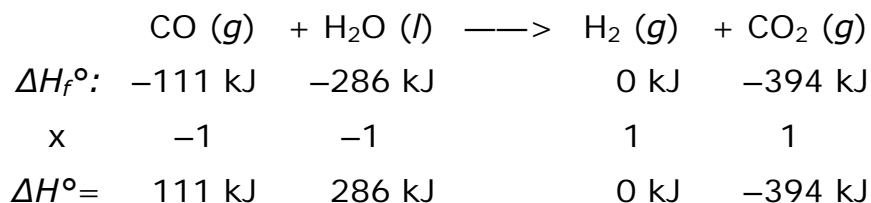
Under carefully controlled conditions, the process runs without requiring additional inputs of energy. The process, however, has some disadvantages. Carbon dioxide is an unavoidable by-product of generating the energy needed to drive the process. See reaction (2). And direct use as fuel of the gases produced by reaction (3) is complicated by the presence of air in the mixture. This product stream is sometimes called *low BTU (for British Thermal Unit) gas* because it has only about 30% the energy content of natural gas. Moreover, the toxicity of CO is also of concern.

- o **Liquefaction:** Syngas can be directly converted to the useful fuel, methanol:



The process is already commercial; about half the motor vehicle fuel used in South Africa is syngas-based methanol.

The reaction, however, does not consume all of the CO in the feed stream. Would it be feasible to use it to generate additional methanol? On paper, one might consider reacting it with steam. We can look up the heats of formation of the components in Appendix A4 to compute the enthalpy of this reaction:



$$\Delta H^\circ = \quad \quad \quad 3 \text{ kJ}$$

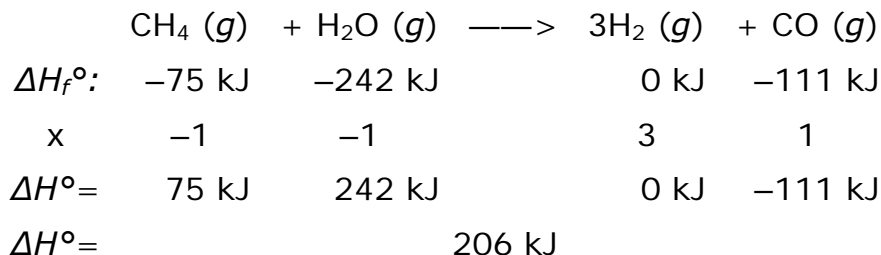
I have no information concerning whether it gets put to use, but it does look like an energy-neutral way to convert a potentially unwanted by-product into something useful.

- **Hydrogen as a Fuel:** Many people advocate using hydrogen as a clean, CO₂-free fuel. It's combustion reaction looks very attractive. It produces lots of energy and absolutely no carbon dioxide:

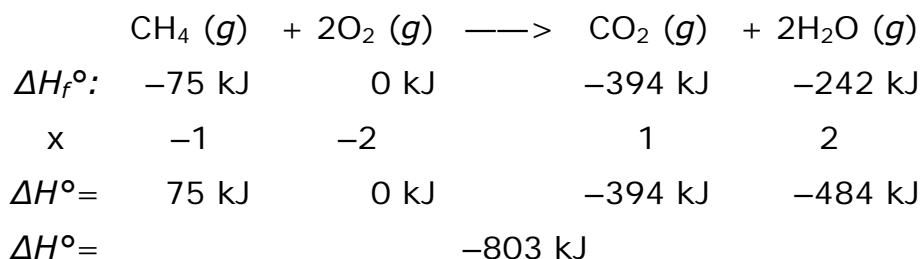


However, there are some little (I mean big.) problems.

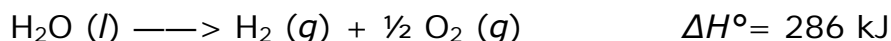
- o **Supply and Production:** There is very little naturally-occurring hydrogen gas. The standard manufacturing process is by reacting methane with steam:



This reaction is highly endothermic. Using the methane directly as fuel would be much more energy efficient:



Now one might argue that there is all the hydrogen we need. All we need to do is extract it from water, using the reaction:



The fallacy in this is that we must as much energy into this reaction as we can get out of the hydrogen it produces. Even though water is an abundant source of hydrogen, there is no energy to be gained by turning it into hydrogen.

However, this reaction is potentially useful as a means of *storing energy*. It is quite possible to convert solar energy into electricity by capturing it in photovoltaic panels. We could use this electricity as it is produced, or we could use it to charge a storage battery, or we could use it to electrolyze water to make hydrogen gas and oxygen gas. Now the hydrogen is available for us to use as a fuel.

Indeed, Iceland is now in the beginning stages of building infrastructure for using hydrogen as a means of storing geothermal energy for use as an automotive fuel.

- **Energy Density:** The energy content of hydrogen gas appears to be high. One mole has a mass of just over 2 grams and a combustion energy of -286 kJ/mol.

Comparison with Gasoline: This works out to -143 kJ/g compared to -48 kJ/g for gasoline (computed as octane). But gasoline is a liquid at room temperature, whereas one needs to cool hydrogen to -253 °C in order to liquefy it. Even then its density is less than 10% that of gasoline (0.07 g/cm³ versus 0.8 g/cm³). So a given volume of gasoline contains about 3 times the energy of an equal volume of liquid hydrogen.

Comparison with Methane: We just computed the molar heat of combustion of methane to be -803 kJ/mole. Now one mole of methane occupies the same volume as one mole of hydrogen under equal conditions of temperature and pressure, but the molar heat of combustion of hydrogen is only -286 kJ/mol. Thus methane contains nearly 3 times the energy as an equal volume of hydrogen.

- **Reactivity with Metals:** Hydrogen gas will dissolve in certain metals and react to form metal hydrides. Since metal hydrides tend to be much more brittle than the original metals, if one makes a storage tank out of such a metal and tries to use it for hydrogen, the tank will become brittle and may rupture. (Maybe I should have said, "**GO BOOM!**")

- **Wind Power**
- **Solar Power**
- **Biomass**