CE 170

Energy, Earth & Humans

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First DRAFT

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To Joanna, My Patient Wife,
And My Children:
Lucas, Sophie and Julie

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Preface

The Bridge Builder

An old man, going a lone highway,
Came at the evening cold and gray,
To a chasm, vast and deep and wide,
Through which was flowing a sullen tide.
The old man crossed in the twilight dim-
That sullen stream had no fears for him;
But he turned, when he reached the other side,
And built a bridge to span the tide.

“Old man,” said a fellow pilgrim near,
“You are wasting strength in building here.
Your journey will end with the ending day;
You never again must pass this way.
You have crossed the chasm, deep and wide,
Why build you the bridge at the eventide?”

The builder lifted his old gray head.
“Good friend, in the path I have come,” he said,
“There followeth after me today
A youth whose feet must pass this way.
This chasm that has been naught to me
To that fair-haired youth may a pitfall be.
He, too, must cross in the twilight dim;
Good friend, I am building the bridge for him.”

- By Will Allen Dromgoole (1860 – 1934)
In Memory of Dean Arthur Richard Newton (1951 – 2007)

1.1 Executive Summary

My goal in this course is to assemble a large, intricate puzzle from simple but numerous pieces. The puzzle will show a clear, I hope, picture of the possible and impossible paths of supplying humanity with energy and the environmental costs of following some of these paths. Individual pieces of the puzzle will be contributed by science. Economics, which usually is more of a philosophical or religious belief than science will play a supporting role.

The major difficulty of this course is not the intricacy of any of the pieces, but their large number and multiple connections. The simplistic and usually incorrect models of biomass-biofuel systems ignore many of the pieces and most of the connections.

The main findings of this course may be summarized as follows:

1. The finite Earth carries too many humans who are too greedy, and are destroying her largest life-supporting systems (atmosphere, oceans, rivers, streams, lakes, swamps, aquifers, tropical forests and green land) at the highest rate ever.
2. We need to stop growth and decrease level of global human population.
3. In particular, we need to stop growth and decrease level of US population.
4. We need to significantly reduce the rate of degradation of valuable energy resources into chemical waste and heat. This degradation process is popularly and incorrectly[1] called *energy consumption*.
5. What we really consume is *not* energy, but *free* energy of pure, highly structured resources.
6. Ecosystems we degrade so cavalierly are also high free energy resources that protect our lives[2].
7. In then follows that one cannot ignore the Second Law of thermodynamics in any meaningful discussion of energy supply systems. Thus far, the Second Law has been missing from almost all analyses[3] of biomass-biofuel systems[4].
8. The Unites States has an economy that is at least 94% unsustainable. About 63% of US economy is based on crude oil and natural gas. Roughly 60% of the oil and 20% of the gas are imported.

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[1] A corollary to the First Law of thermodynamics states clearly that energy *cannot* be created or destroyed. The Second Law of thermodynamics states that *structures* of the high free-energy natural resources are *degraded* to ultimately stable waste products and heat. Although this process is spontaneous, its rate has been accelerated by human activities from billions to hundreds of years, i.e., 100,000,000 times.

[2] It is a testament to our narcissistic arrogance that only *some* of us strive to "protect the environment," while in reality it is the environment that protects *all* of us.

[3] *Analysis* comes from Greek *analyein* = to break. Analysis is an examination of a complex, its elements, and their relations (Webster, 1993).

[4] Some of these analyses also violate the First Law of thermodynamics.

9. In the United States, we need to halve energy “consumption” in the next 10 years, and then halve it again, regardless of the population growth.
10. While at it, we need to change our economic paradigm from the unlimited economic “growth” to a steady-state economy.
11. It is impossible to match the current rate of degradation of fossil fuel resources with biomass and liquid transportation fuels generated from plants.
12. Our use of ecosystems to produce fuels at a disproportionately high rate will destroy us long before we destroy life on the Earth.
13. You must not wait for governments and parents to lead in the preservation of human kind and the planet that keeps us alive. Not only they will not lead, but they are mindlessly and selfishly contributing to the decline of your and future generations.

1.2 Prior Knowledge

Energy, Earth & Humans strives to be a self-contained course. As such, it does not require you to know anything beyond rudimentary college physics, chemistry, biology and mathematics. Clarity of your thinking and length of attention span are probably most important in following this course and book.

1.2.1 Useful Physics

It will be useful for you to know some mechanics and wave motion (*Physics 7A in Berkeley*); heat (*Physics 7B in Berkeley*); and a touch of electromagnetism and quantum physics (*Physics 7C in Berkeley*).

1.2.2 Useful Biology

Some knowledge of biochemistry, cell structure and function, plant and animal development, form and function, ecology, and evolution is useful, but not necessary. (Elements of *Biology 1A and 1B in Berkeley*).

1.2.3 Useful Chemistry

You cannot be hurt by knowing a little about stoichiometry of chemical reactions, quantum mechanical description of atoms, the elements and periodic table, chemical bonding, real and ideal gases, thermochemistry, introduction to thermodynamics and equilibrium, acid-base and solubility equilibria, and introduction to oxidation-reduction reactions (*Chemistry 1A in Berkeley*).

It would be even better, if you knew introductory chemical kinetics, electrochemistry, properties of the states of matter, binary mixtures, and thermodynamic efficiency and the direction of chemical change (*Chemistry 1B in Berkeley*).

1.2.4 Useful Mathematics

The mathematical tools you will need are rudimentary algebra, derivatives, partial derivatives, chain rule, integration, infinite sequences and series, and first-order ordinary differential equations. (mostly *Mathematics 1A and 1B in Berkeley*).

1.3 What is Still Missing

The pdf file with the Class Reader is a living document. I do *not* encourage you to print out all of it (I have not printed a single page yet). We will be printing some of the material in the Reader as we go.

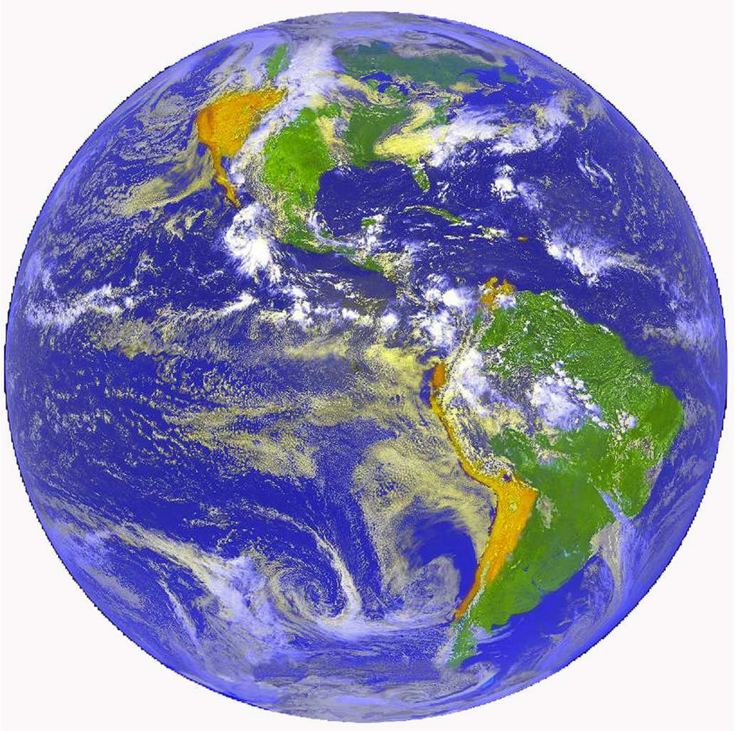
The Reader already contains almost all of the thermodynamics I plan on ever using. The subjects still missing from the Reader are:

1. Energy Availability (exergy): Maximum work, Maximum useful work, Free energy, Irreversibility (Guoy-Stodola Law)
2. Thermodynamics of continuum open systems
3. Maximum biomass production in the US
4. First and Second Law analyses of the corn-ethanol biofuel cycle
5. First Law analysis of soybean biodiesel cycle
6. Second Law analyses of biofuel production from tropical biomass: cellulosic ethanol, Fischer-Tropsch biodiesel, ethanol from sugarcane
7. First Law analysis of fuel cell efficiency
8. First and Second Law analysis of photovoltaics
9. Thermodynamic efficiency of CO_2 sequestration from power stations
10. Thermodynamic efficiency of an in situ thermal recovery and upgrade process in a tar sand
11. Thermodynamic efficiency of an in situ oil shale kerogen conversion process

Many of these subjects have been covered in my various publications.

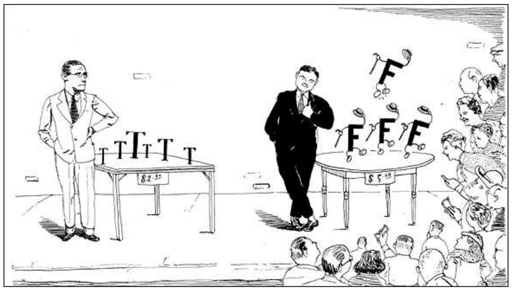
Chapter 2

The Finite Earth



We cannot immunize the continents and the oceans against our contempt for small places and small streams. Small destructions add up, and finally they are understood as large destructions.

— Wendell Berry
Contempt for Small Places (2004)



"In reading the history of nations, we find that, like individuals, they have their whims and their peculiarities; their seasons of excitement and recklessness, when they care not what they do. We find that whole communities suddenly fix their minds upon one object, and go in mad pursuit; that millions of people become simultaneously impressed with one delusion, and run after it, till their attention is caught by some new folly more captivating than the first." (CHARLES MACKAY, *Memoirs of Extraordinary Popular Delusions*, 1841, Volume I, page 1.)

A human can live for only 5 minutes without air, 3 days without water, and 30 days without food. In other words, our biological survival[1] depends on the uninterrupted, high quality services of the Earth's ecosystems (Odum, 1998), **see Figure 2.1**. These ecosystem services are taken for granted and their willful obliteration proceeds at an ever accelerating pace, despite ample evidence that we are committing suicide (Diamond, 2004). For example, the deforestation that subsidized the development of all Mediterranean cultures over roughly 2000 years was equal in area to the deforestation of the Amazon forest over the last 20 years. Unfortunately, the Earth has not expanded 100-fold in the meantime.

Just like bacteria, fungi, and higher animals, humans will always seek new sources of cheap, accessible organic carbon. From the soil and crop carbon, through the wood carbon in forests, coal, petroleum, and natural gas, humans have developed an insatiable appetite for power from the ever more abundant and fungible sources of carbon energy.

Faced with the looming depletion of the easily accessible, plentiful sources of petroleum carbon, and desperately clinging to our energy-rich lifestyles, we now pretend that returning to plant carbon that is produced in annual cycles will somehow replace ancient carbon sources. Consequences of this self-delusion will be tragic for humanity and the life-giving ecosystems.

The quest for new energy resources cannot be posed in separation from the Earth systems in which we exist. We use most of fossil energy in our homes, on food, and while driving to work and shops. The development of

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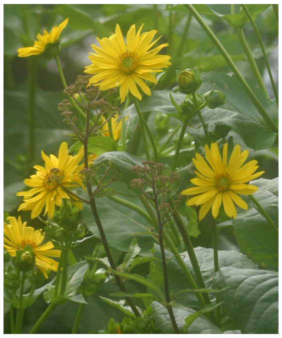
[1] "The poisonous stench came from a mix of petrochemical waste transported by a Panamanian-registered tanker chartered by the Dutch firm Trafigura. The pitch-black sludge found its way from Amsterdam – via Estonia and Nigeria – to Ivory Coast aboard the Korean-built and Greek-managed Probo Koala. And it was later illegally dumped, in the dead of night, by a local company called Tommy at open-air sites all over Abidjan. Trafigura said in a statement that tests performed on the waste in Holland proved it was not toxic. Yet almost a dozen people have died. Dozens more have been hospitalized, and more than 100,000 have sought medical treatment." Source: *Ivory Coast Tragedy Exposes Toxic Flow to Poor*, by OFEIBEA QUIST-ARCTON, NPR, Oct. 20, 2006.

Figure 2.1: Six-month-old Salam Oudrawogol of Abidjan, Ivory Coast, has been covered with sores since he was exposed to toxic waste in August 2006.

energy-efficient, compact cities, intertwined with the local water, crop, animal, and biofuel supplies, and complete waste recycling is the necessary condition to start shrinking our runaway energy consumption. Once we develop the thriving, local, low-energy community centers, time will come to reform medical care, and schooling, which will be tied to the communities they serve. Note that this vision requires an almost complete decentralization of most social activities, with the ensuing political and administrative consequences. Of all countries on the Earth, the US is perhaps most removed from the walking-distance low-impact lifestyles, while consuming more energy than anyone else. The US will have to change its ways if we want to avoid collapse and, perhaps, bringing all humanity down with us.



"The Highway Department says that 100,000 cars pass yearly over this route during the three summer months when the *Silphium* is in bloom. In them must ride at least 100,000 people who have 'taken' what is called history, and perhaps 25,000 who have 'taken' what is called botany. Yet I doubt whether a dozen have seen the *Silphium*, and of these hardly one will notice its demise. If I were to tell a preacher of the adjoining church that the road crew has been burning history books in his cemetery, under the guise of mowing weeds, he would be amazed and uncomprehending. How could a weed be a book?" ALDO LEOPOLD, *A Sand County Almanac, and Sketches Here and There*, 1948, Oxford University Press, New York, 1987, pp. 44-46.

The Earth and her crust are made of stellar matter, and the current abundance of each chemical element and its compounds (minerals, ores, etc.) results from chemical composition of that primordial matter and geologic evolution of the Earth. The Sun powers the Earth; life has evolved her atmosphere, stabilized the climate, and made all fossil fuels, coal, crude oil, natural gas, gas hydrates, oil shale, etc. The deposition and transformation rates of these fossil fuels are *very* slow (Patzek and Pimentel, 2006). It is the unimaginable length of deposition time, measured in hundreds of *millions* of years, that accumulated large quantities of these fuels, see **Figure 2.2**. In a few *hundred* years, a geological blink of an eye, humans will practically exhaust the fossil fuels.

All resources that feed our civilization: the highly concentrated or pure ("low-entropy") compounds (Georgescu-Roegen, 1971) – clean water, clean air, pure minerals, finished metals, high-quality fossil fuels, wood, uncontaminated food –, as well as the self-sustaining ecosystems that let us live by cleaning our waste, come from the Earth's crust and the biosphere (Odum, 1998).

The limited high quality resources from the environment are the ultimate inputs to our civilization and economics (Daly, 1977). The low entropy embedded in these resources can only be used *once* (Georgescu-Roegen, 1971; Patzek, 2004).

Many American economists and politicians disregard this fundamental physical limitation of economy, and talk about the unfettered economic growth, unrestricted future payments for the Social Security, medical care, and military spending. This thinking was best captured by a Nobel Laureate economist ROBERT SOLOW: "... the world can, in effect, get along without natural resources ... at some finite cost, production can be freed of dependence on exhaustible resources altogether..." (his 1974 lecture to the American Economic Association).

The low environmental entropy exists in two forms: an accumulation or *stock* – as in a coal deposit – and *flow* – as in inflow of solar energy to the biosphere, and outflow of heat from the Earth to the Universe (Patzek, 2004) –, see **Figure 2.3**. The Earth's stock is of two kinds: resources accumulated only on geological time scale (all the *nonrenewable* fossil fuels listed above), and resources accumulated on human time scale (the *renewable* biomass). The Earth's nonrenewables are limited in the total amount available, just how a water bottle can only hold a certain amount of water. The Earth's renewables are also limited in the total amount available and can be exhausted[2]. When exploited at a rate that can be sustained by nature, the renewable resources are *funds*, whose rates of return, crops, are very much limited by the rate of

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[2] An old-growth forest can only be clear cut once in tens of human generations and is *de facto* a geological deposit of organic carbon.

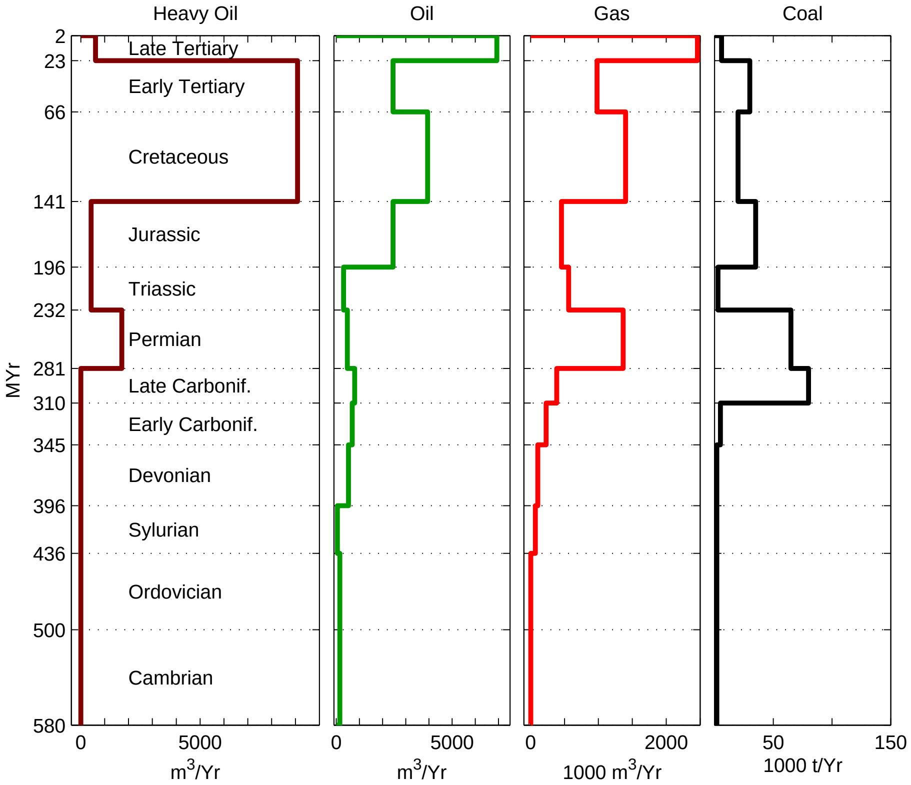

Figure 2.2: The average rates of accumulation of fossil fuels in the Earth over geological time. The average rates of heavy oil deposition are from Demaison (1977). The average rates of oil and gas deposition are from Bois et al. (1982). The coal deposition rates are from Bestougeff (1980). Note the almost imperceptible global annual deposition rates of fossil fuels, and the unimaginably long duration of their deposition processes. These rates were scaled up by factors 3-8 to reflect the best current estimates of fossil fuel endowments: Heavy Oil $= 12 \times 10^{11}$ m^3, Oil $= 8 \times 10^{11}$ m^3, Gas $= 3.5 \times 10^{14}$ sm^3, Coal $= 2 \times 10^{13}$ tonnes.

conversion of solar energy to biomass and the availability of aqueous nutrients in high quality soils. Finally, the sun is a practically unlimited source of energy, but the rate of flow of solar energy is *low*.

> All physical inputs into a human economy are limited in size and/or rate.

Humans need air, water, food, and energy to survive. Clean air is an in-

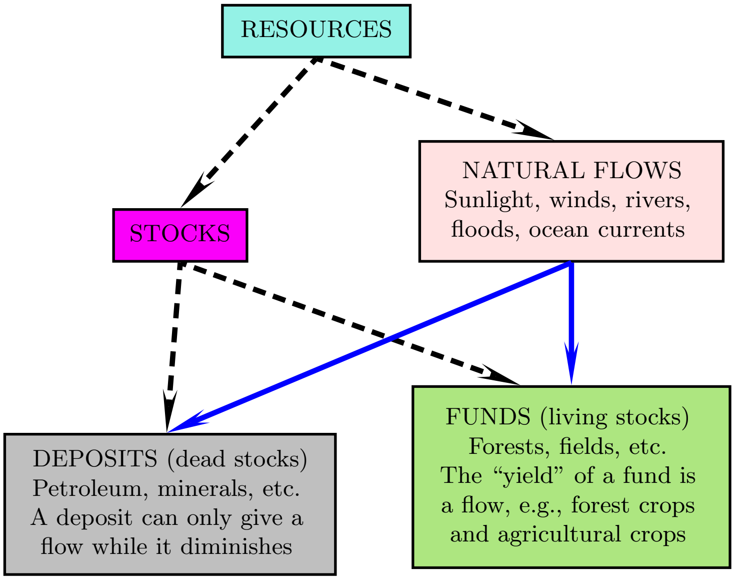

Figure 2.3: A physical resource classification.

creasingly rare natural resource in industrialized nations[3]. Much of drinking water must now be *manufactured* in the energy-intensive chemical purification factories[4]. Uncontaminated food is increasingly more difficult to get, even in seemingly pristine ecosystems[5]. Industrial agriculture and forestry for food and fuels are funded from massive fossil fuel subsidies and, in good part, groundwater mining. As such, they are unsustainable (Patzek, 2004; Patzek and Pimentel, 2006).

As new energy resources are tapped[6] and substitute the old ones[7], they remain subject to the same laws of physics, and are limited in total volume and rate of production.

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[3] In recent decades, increased aerosol loadings (soot and other particles from burning coal, oil, wood, etc.) were at least partially responsible for the observed decreases in global radiation and direct radiation, the clearness index, and the monthly percentage of possible sunshine duration over much of China (Che et al., 2005).

[4] As of now, MTBE has been detected in 1861 water systems in 29 states, serving more than 45 million Americans. Per customer of United Water in Woodbury, Conn., it costs $500 in the first year and $125/yr thereafter to produce drinking water free of MTBE. A. Barrionuevo, *A Dirty Little Footnote to the Energy Bill*, NYT, 4/15/2005, pp. C1-C4.

[5] Health officials urged that children and women of child-bearing years avoid eating a half-dozen species of fish caught in the Adirondack and Catskill Mountain regions. The fish are feared to be contaminated with mercury. L. W. Fodebaro, *Caution Urged in Eating Fish from Mountains of New York*, NYT, 4/16/2005, p. A11.

[6] The new fossil fuel resources are tar sands, ultra heavy oil, oil shale, tight-rock gas, and coal-bed methane. The new biomass resources are wood, sugarcane stems and bagasse, corn grain and stover, soybeans, palm oil, rape seed oil, various plant and animal plants abbreviated as "waste," etc.

[7] The classical fossil fuels are coal, conventional crude oil, and conventional natural gas.

If we bring more technology to produce these resources, their depletion will occur faster, and the environmental destruction their production and use bring about will be more severe.

So the question most relevant to energy supply for the living is as follows: *Not* can we produce more energy (we can), but what will be the consequences of doing so for the Earth's life-support systems on which we depend for breathing, drinking, eating, and enjoyment of life? It appears that the U.S. and China[8], the largest consumers of energy and the environment on the Earth, will have to answer this question first.

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[8] China's wholesale destruction of its rich and diverse environment has more than offset its economic growth (Diamond, 2004), Chapter 12.

Chapter 3

Energy Primer

> *[We are reluctant] to recognize our limitations in relation to space, to time, and to matter and energy*
>
> — Nicholas Georgescu-Roegen
> *The Entropy Law and the Economic Process* (1971, p. 6)

3.1 What Are You Going To Learn?

You will learn about the fundamental units of work and power, heats of combustion, fuel heating values, and about energy use in the United States.

3.2 Why Is It Important?

In order to compare different energy supply technologies that use different fuels, we need to construct a physically sound and consistent analytical framework. Unfortunately, even the first steps in this construction lead to confusion and error. Thus, it is important to know why the so-called *high heating values* of fuels allow for their consistent comparison and the commonly-used *low heating values* do not. The high heating values can be used to calculate how much energy is used annually in the US. It is important to comprehend just how much fossil energy is consumed each year in the US. Otherwise, we may be tempted to think that biofuels or other renewable sources might replace fossil fuels at today's levels. This, however, is utterly impossible for more than a year or two.

3.3 Preliminaries

I have decided to introduce you to *primary energy* use in the US before you actually learn what "primary energy" is, why you cannot convert coal to electricity with a 100% efficiency, what the "high heating value" is, etc. To accomplish this task, I will follow the early descriptive thermodynamics and thermochemistry taught in the 1880 – 1900's. The thermodynamics of processes described here will be treated in more detail in Chapters 7 – 11.

3.3.1 Units of Energy

For the unit of energy we will use 1 joule (J). It is a fairly small amount of energy. A little more than 4 joules are necessary to heat one teaspoon of water by one degree on the Celsius scale. For the unit of power we will use one joule per second (J/s) or 1 watt (W). On average, an adult sedentary human needs about 100 W continuously to live and function. This requirement makes a human equivalent to one 100 W bulb operating continuously.

Larger energy units are the powers of 1 joule. We use kilo joules (kJ), mega joules (MJ), giga joules (GJ), tera joules (TJ), peta joules (PJ), and exa joules (EJ).
Here is the list of these derived energy units:

1kJ is 1 000 or 10^3 joules

1MJ is 1 000 000 or 10^6 joules

1GJ is 1 000 000 000 or 10^9 joules

1TJ is 1 000 000 000 000 or 10^{12} joules

1PJ is 1 000 000 000 000 000 or 10^{15} joules

1EJ is 1 000 000 000 000 000 000 or 10^{18} joules

During one year, the U.S. population requires approximately

$$100 \frac{\mathrm{J}}{\mathrm{s} \times \mathrm{person}} \times 300\,000\,000 \text{ persons} \times 3600 \times 24 \times 365 \text{ s/year} \approx 1 \text{ EJ/year} \tag{3.1}$$

as food.

The amount of energy required to feed the entire U.S. population for one year, 1×10^{18} J or 1 EJ, is the fundamental unit in which all other energy flows in the U.S. economy will be described.

Another unit of energy is 1 kWh (kilo watt-hour); it is equal to 3.6 MJ. An average household electricity bill is about 1000 kWh/month, or 3.6 GJ/month. To produce this electricity with an overall efficiency of 0.32, we need to burn 11.25 GJ/month of a fossil fuel, or 135 GJ/year. This amount of energy is equivalent to the total energy in 2.9 metric tonnes of gasoline. So each household in the U.S. is responsible to burning almost 3 metric tonnes of gasoline equivalents per year to obtain the needed electricity.

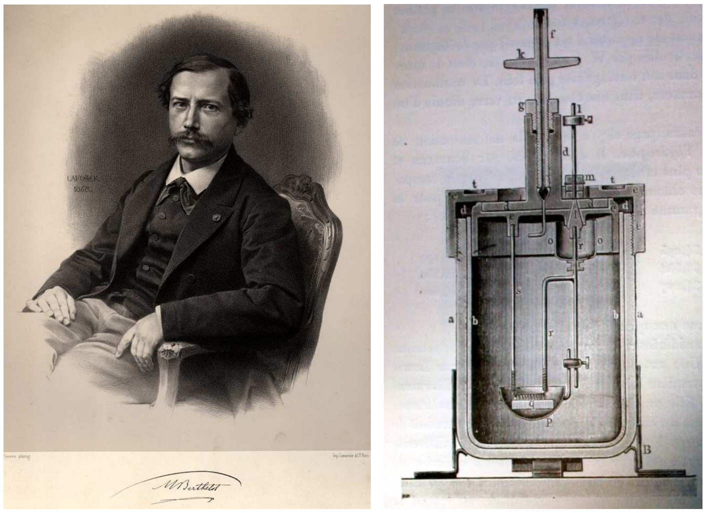

Figure 3.1: Pierre Eugène Marcellin Berthelot (1827 – 1907), proved with thousands of experiments that all chemical phenomena depend on the action of physicochemical forces which can be determined and measured. He also introduced the bomb calorimeter, see his *Thermochimie* (1897).

3.3.2 Bomb Calorimeter

A *calorimeter* is a device used to measure the heat of a physical process or chemical reaction. For fuel combustion reactions, we often enclose all reactants in an explosion-proof steel container, called the *bomb*, whose volume does not change during combustion. Subsequently, the bomb is submerged in water or another liquid that absorbs the heat of the spontaneous combustion reaction initiated with an electric discharge. The heat capacity of the bomb plus its contents is measured using the standard techniques of calorimetry. Such an instrument is called a *bomb calorimeter*, and its application is called the *bomb calorimetry*, see **Figure 3.1**.

Calorific Value of Sucrose

Here are the results of a hypothetical calorimetric bomb experiment to determine the *calorific value*, or the *heat of combustion* (with liquid produced water), or the *high heating value* of sucrose.

Since volume does not change, a bomb calorimeter measures heat evolved under constant volume

$$Q = \Delta U = C\Delta T \tag{3.2}$$

where Q is the heat of combustion (J); ΔU is an increase of the internal energy of calorimeter content (J); C is the heat capacity of calorimeter content ($\mathsf{J\ K^{-1}}$), and ΔT is the calorimeter temperature increase (K). Here are the steps of our thought experiment:

1. When a 10-watt ($\mathsf{J/s}$) heater is used to heat a bomb calorimeter, its temperature increases by 3 K in 5 min. Calculate the heat capacity of the calorimeter.

   Solution: The constant electrical power used over 5 minutes generates a quantity of heat,

   $$\begin{aligned} &Q = 10\ \mathsf{J\ s^{-1}}\ \times 5 \times 60\ \mathsf{s}\ = 3000\ \mathsf{J}.\text{ Therefore, the heat capacity is} \\ &C = \frac{3000\ \mathsf{J}}{3\ \mathsf{K}} = 1000\ \mathsf{J\ K^{-1}} \end{aligned} \tag{3.3}$$

   Answer: The heat capacity of this bomb calorimeter is 1000 $\mathsf{J\ K^{-1}}$.

2. The same bomb calorimeter is used to measure the heat of combustion in air from 0.303 g of sucrose, $C_{12}H_{22}O_{11}$(s). (Why is one molecule of water missing from the formula?) The bomb is charged with enough air to allow for full combustion of the sucrose. The measured temperature increase during combustion is 5 K. Calculate the heat actually released, and the amounts of heat released by 1 gram and 1 mole of sucrose. (Note that in this energy balance we start from, say, 25^0 C and calculate the heat released relative to this temperature.)

Solution:

$$Q = C\Delta T = 1000 \text{ J K}^{-1} \times 5 \text{ K} = 5000 \text{ J} \tag{3.4}$$

The amount of heat released by 1 g of sucrose would be $5000/0.303 = 16.5$ kJ g^{-1}. Since the molecular weight of sucrose is 342.3 g mol^{-1}, the amount of heat released by 1 mol would be

$$Q = 16.5 \text{ kJ g}^{-1} \times 342.3 \text{ g mol}^{-1} = 5648 \text{ kJ mol}^{-1} \tag{3.5}$$

Answer: The heat released by one mole of sucrose combusted in a bomb calorimeter is 5648 kJ mol^{-1}.

3. Calculate the enthalpy of combustion per mole of sucrose.

By definition, the enthalpy of combustion, ΔH, is equal to the heat released at constant pressure, whereas ΔU is equal to the heat released at constant volume. These two quantities are related by the defining equation:

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + RT\Delta n \tag{3.6}$$

Here we have applied the *equation of state* of an *ideal gas* $pV = nRT$, and Δn is the number of moles of gas in the products minus the number of moles of gas in the reactants. The final temperature of the products is equal to the initial temperature of the substrates, $\Delta T = 0$.

Solution: The balanced chemical reaction equation is

$$\mathrm{C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)} \tag{3.7}$$

i.e., the produced water vapor is condensed. The total number of moles of gases, 12, before the reaction is the same as that after the reaction and $\Delta n = 0$. Therefore,

$$\Delta H = \Delta U + 0 = 5648 \text{ kJ mol}^{-1}. \tag{3.8}$$

Answer: The molar enthalpy of combusting sucrose is equal to the amount of heat released during its combustion at constant volume. The amount of 5648 kJ mol^{-1} (16.5 MJ kg^{-1}) is the *maximum amount of energy*, or the *high heating value*, released when 1 mole of sucrose is metabolized.

3.3.3 Heating Values of Fuels

For a thorough discussion, please read Ulf Bossel's paper (Bossel, 2003b). What follows is a summary of this paper.

Lower Heating Value of Fuel

The *Lower Heating Value* (also known as *net calorific value* or LHV) of a fuel is defined as the amount of heat released by combusting *in air* a specified quantity of the fuel initially at 25^0 C, and returning the temperature of the combustion products to 150^0 C.

The lower heating value assumes that the latent heat of vaporization of water in the reaction products is not recovered. Historically, LHV was created in the late 1800's when it became obvious that condensation of water vapor or sulfur oxides in smoke stacks lead to excessive corrosion and destruction of exhaust systems. As it was technically impossible to condense flue gases of sulfur-rich coal, the heat below 150^0 C was considered of no practical use and therefore excluded from energy considerations. Therefore, there is no scientific justification for the LHV, just an obsolete practical justification.

Higher Heating Value of Fuel

The *Heat of Formation* (HOF) is experimentally determined in a bomb calorimeter by charging it with a stoichiometric mixture of fuel and oxidizer (e.g., two moles of hydrogen and one mole of oxygen) at 25^0 C. When hydrogen and oxygen are combined, water vapor emerges at a high temperature. Subsequently, the vessel and its content are cooled down to the original temperature and the HOF of water is determined by measuring the heat released between identical initial and final temperature of 25^0 C.

By definition, the HOF includes all sensible and latent heats of a chemical reaction between the initial state at 25^0 C and the final state, also at 25^0 C. For energy engineering applications oxidation reactions with air are of prime importance. Therefore, engineers prefer the term *Higher Heating Value* (HHV). Its definition is derived from the Heat of Formation, but it represents the heat released by oxidation of a fuel with air.

The HHV and LHV values are tabulated for fossil fuels from different sources, as well as synthetic chemical substances such as carbon monoxide or hydrogen, see **Tables 3.1** and **3.2**.

The difference between the two heating values depends on the chemical composition of the fuel. In the case of pure carbon or carbon dioxide, both heating values are almost identical, the difference being the small sensible[1] heat content of CO_2 between 150^0 C and 25^0 C. For hydrogen the difference is much more significant as it includes the sensible heat of water vapor between 150^0 C and 100^0 C, the latent heat of condensation at 100^0 C and the sensible heat of the condensed water between 100^0 C and 25^0 C. All in all, the HHV of hydrogen is 18.2% above its LHV or, in absolute values, 142 MJ kg^{-1} vs. 120 MJ kg^{-1}. For hydrocarbons the difference depends on the hydrogen content of the fuel. For

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[1] *Sensible* heat interaction causes a change of temperature. In contrast, *latent heat* is added or subtracted in phase changes at constant temperature; examples are heat of evaporation or heat of fusion of water.

Table 3.1: Higher and lower heating values of some fuels (Castorph et al., 1999)

Fuel	HHV(MJ/kg)	LHV(MJ/kg)	HHV/LHV	LHV/HHV
Coal[a]	34.1	33.3	1.024	0.977
CO	10.9	10.9	1.000	1.000
Methane	55.5	50.1	1.108	0.903
Natural gas[b]	42.5	38.1	1.115	0.896
Propane	48.9	45.8	1.068	0.937
Gasoline[c]	46.7	42.5	1.099	0.910
Diesel[d]	45.9	43.0	1.067	0.937
Hydrogen	141.9	120.1	1.182	0.846

[a] Anthracite, average
[b] Groningen gas field in The Netherlands
[c] Average gas station fuels in Germany
[d] Average gas station fuels in Germany

gasoline and diesel the HHV exceeds the LHV by about 10% and 7%, respectively, for natural gas about 11%.

Ton of Oil Equivalent (toe)

The metric tonne of oil equivalent (toe) is a unit for measuring heating value of crude oil. Since there are different definitions in the literature, here we will adopt the IEA/OECD definition: 1 toe equals 10 Gcal (thermochemical) or 41.868 GJ or 5.80 MBtu/bbl (Anonymous, 1995a) (forgive my not rounding off the IEA definition from five to two significant digits). It is the standard amount of heat that would be produced by burning one metric ton of crude oil, presumably its LHV. The HHV of oil equivalent is obtained by increasing the LHV value by 7%. Since different crudes differ in chemical composition and generate varying amounts of heat when burnt, the toe energy unit is a convention. The heat content of crude oil from different countries varies from about 5.6 MBtu per barrel to about 6.3 MBtu (Anonymous, 1995b), with the arithmetic mean of 5.8 MBtu per barrel.

Crude density also varies considerably, see **Table 3.3**. For 1993, EIA reported values ranging from below 760 $\mathrm{kg\ m^{-3}}$ for some countries of origin to over 880 $\mathrm{kg\ m^{-3}}$ for others (Anonymous, 1995b). For the US, the average density of crude was 840 $\mathrm{kg\ m^{-3}}$. This average, together with the nominal equivalence of 5.80 MBtu per barrel of crude, corresponds to an average heating value (presumably LHV?) of US crude oil of 44.8 $\mathrm{MJ\ kg^{-1}}$.

Table 3.2: Average high and low heating values of some fossil fuels from (Castorph et al., 1999; Bossel, 2003c; Spiers, 1961). Other sources are listed in the footnotes.

Fuel	Density kg/sm^3	HHV[a] MJ/kg	LHV[a] MJ/kg	HHV[a] MJ/kg	LHV[a] MJ/kg	Source[i]
Oil equivalent	760 – 880[o]	44.769[p]	41.868[q]			
Coal equivalent		29.3[q]	29.3[r]			
Gasoline	720 – 800	46.7[b]	42.5[b]	46.8	43.6	Table 339
Diesel fuel	840	45.9	43.0	45.3	42.3	Table 350
Methane	0.66[d]	55.5[c]	50.1[c]	55.1(g)		Table 347
LPG[e]	0.58	50.0	46.0			
NG[f]	0.84	48.7	43.9			
Ethanol	787[h]	29.7[g]	26.7[g]	29.6	26.8	Table 353
Corn grain dry		18.8[j]				
Corn stover[k]		17.7	16.5			
Corn stalks[l]		15.8	14.8			
Corn meal[m]		16.0				
Corn oil[n]	909.5	39.5	38.8			

[a] HHV = High Heating Value; LHV = Low Heating Value

[b] Average of gas station fuels, I choose the mean density of 740 kg m^{-3}, The leftmost gasoline, diesel fuel, LPG, and NG data are from (Castorph et al., 1999)

[c] From Bossel, Table A, (Bossel, 2003c)

[d] (Lide, 1994), 6-25

[e] A mixture of propane and butane, C_3H_8 and C_4H_{10}

[f] An average of natural gas compositions from Groningen, Orenb., Ekofisk, and Leman Bank

[g] http://bioenergy.ornl.gov/papers/misc/energy_conv.html

[h] (Lide, 1994), 15-46

[i] (Spiers, 1961)

[j] Based on the mean of the values reported by Schneider & Sprague (1955), p. 496, 2033 kcal lb^{-1}; and Miller (1958), p. 639, 2059 kcal lb^{-1}. 1 thermochemical kcal = 4.184 kJ

[k] The mature corn stalks of corn from which the ears have been removed. (Domalski et al., 1987), p. 16

[l] (Domalski et al., 1987), p. 17

[m] *Zea mays*, 11.79% moisture (Domalski et al., 1987), p. 93

[n] Liquid vegetable oil (Domalski et al., 1987), p. 223

[o] >8 bbl/tonne to <7 bbl/tonne (Anonymous, 1995b). US average was 840 kg m^{-3} in 1993

[p] 1 kgoe = 1.00×10^7 cal (IT) = 41.868 MJ = 39.68 kBtu (IT) (Anonymous, 1995a)

[q] 1 kgoe = 1.07×10^7 cal (thermochemical) = 44.769 MJ = 42.46 kBtu (thermochemical) (Häfele, 2003)

[r] 1 kg of coal (equiv) = 29.3 MJ = 27.8 kBtu (Häfele, 2003)

3.3.4 Higher or Lower Heating Values?

Often we are interested in how much primary energy from different sources is used to obtain a given chemical fuel (chemical energy carrier): gasoline, pure

Table 3.3: Densities of petroleum fluids

Fluid	Density $\mathsf{kg\ m}^{-3}$
Aviation gasoline[a] @ 60^0 F	722
Crude oil[b], 48^0 API @ 60^0 F	790
Crude oil[b], 40^0 API @ 60^0 F	825
Crude oil[b], 35.6^0 API @ 60^0 F	847
Crude oil[b], 32.6^0 API @ 60^0 F	862
Crude oil[b], California @ 60^0 F	915
Crude oil[b], Mexican @ 60^0 F	973
Crude oil[b], Texas @ 60^0 F	873
Diesel fuel oil 20 to 60 @15^0 C	$820 - 950$
Fuel oil[b] @ 60^0 F	890
Jet fuel[b] (kerosine) @ 60^0 F	818
Residual oil[a] (No. 6) @ 60^0 F	960

[a] Wikipedia
[b] http://www.simetric.co.uk/si_liquids.htm

natural gas, heating oil, coal dust, corn ethanol, biodiesel, or hydrogen. We are also interested in what the cumulative emissions of greenhouse gases[2] are when we produce this fuel. The primary energy sources to obtain the fuel of interest are different fossil fuel resources[3], nuclear fission, biomass, or solar energy captured as light, wind, water behind a dam, waves, tides, etc.

1. In the simplest case, we compare different energy conversion technologies that all use the same chemical fuel. This fuel may come from from different sources and be supplied via different routes. The analysis is reduced to a comparison of energetic efficiencies according to the First Law of thermodynamics and to a summation of greenhouse gas emissions at various stages of the energy chain. As long as the same source fuel is used (natural gas, heating oil, gasoline, coal, or hydrogen), the results are informative and meaningful. Different gasoline engines, different gas furnaces, or coal fired steam power plants from different manufactures may be compared with other products of the same category.

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[2] The main greenhouse gases are: H_2O vapor, CO_2, N_2O, NO_x, SO_x, methane, hydrocarbon vapors, ammonia, halogenated hydrocarbons, etc. The greenhouse effect will be discussed in Chapter 16.

[3] The important primary sources of fossil energy are crude oil in a subsurface formation, coal in a deposit, natural gas in a gas field or coal seam, biodegraded petroleum in a tar sand, kerogen in oil shale, etc.

For energy equipment using the same fuel, the comparison may be based on either its Higher Heating Value (HHV) or the Lower Heating Value (LHV).

2. A meaningful analysis involving different chemical fuels must be based on the true energy content or the Higher Heating Value (HHV) of all fuels considered, not on the Lower Heating Value (LHV).

The one and only proper and physically exact reference would be the Heat of Formation (HOF) of a chemical fuel. The HHV is the closest practical measure of the HOF of the fuel.

3.3.5 Conclusion

Only the *Higher Heating Values* should be used to compare different fuels. In the biofuel literature, the *Lower Heating Values* are used instead, leading to the first of the numerous misunderstandings.

3.4 Primary Energy Use in US

Now we are ready to apply our knowledge to the estimation of primary energy use in the US.

3.4.1 Data Sources

- The main source of energy and price data is the U.S. Department of Energy Energy Information Agency (EIA), www.eia.doe.gov.
- The solar cell data can be obtained from EIA and from www.solarbuzz.com.
- The wind turbines are thoroughly discussed in *The True Cost of Electricity from Wind Power and Windmill "Availability" Factors* by GLENN R. SCHLEEDE,

  www.mnforsustain.org/windpower_schleede_costs_of_electricity.htm

3.4.2 Electricity

In 2003, the U.S. electricity consumption was 3 883 185 million kWh, or 14.0 EJ/year.

Fifty one percent of electricity was generated in coal-fired power plants, 20% in nuclear power plants, 17% in natural gas-fired power plants, 7% in hydro power plants, and 3% each by oil-fired on other power plants, see **Figure 3.2**. Solar electricity generation was only 0.02 % of the total, and wind electricity generation was 0.13 % of the total. In other words, only 2 parts in 10000

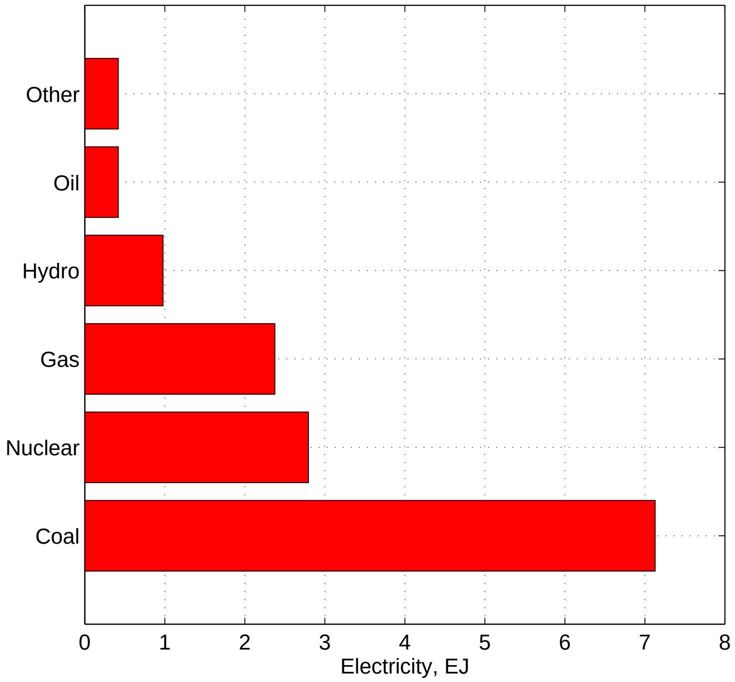

Figure 3.2: Electricity generated in the U.S. in 2003 by source. The "Other" category consists almost entirely of burning biomass to generate electricity. Wind and solar-generated electricity are not noticeable at this scale.

of electricity generated in the U.S. in 2003 came from solar cells and solar collectors/concentrators. Only 1 part in 1000 came from wind turbines.

The largest power plants in the U.S are:

Grand Coulee Hydro Dam located 28 miles north east of Coulee City in Grant and Okanogan Counties on the Columbia River. It is the largest concrete structure in the USA. The plant is owned and operated by the U.S. Bureau of Reclamation. The dam is used as a peaking facility, and its newly upgraded turbines develop power of 805 MW each. The power plant is now capable of generating 6795 MW of electricity. The lake holds 1.6×10^9 m^3 of water and has the surface area of 101 million m^2. The power density delivered by the lake/dam system is 67 $\mathsf{W/m}^2$ of lake surface. The Columbia River drains a 670 000 km^2 basin that includes territory in seven states in the U.S. and a Canadian province. The power density of the dam/drainage basin system is 0.01 $\mathsf{W/m}^2$ of the drainage basin.

Center Point Energy Houston Elec in W. A. Parish, near Thompson, TX, generates 3766 MW of electricity. This plant is on 1975 hectares, has 4 gas-fired and 4 coal-fired steam generators. The power density delivered by the plant is 190 W/m^2, just below the time-averaged insolation of the ground surface in the U.S. of about 200 W/m^2.

Palo Verde Nuclear run by Arizona Public Service Co. has the electrical power of 3733 MW and the area of 1640 hectares. The power density is 230 W/m^2, above the time-averaged insolation of the ground surface.

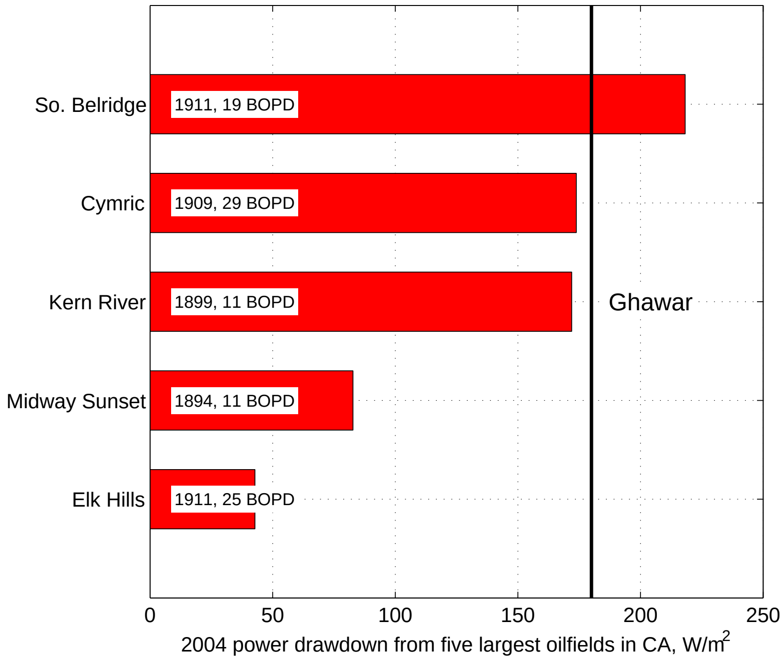

Figure 3.3: The power density of petroleum extraction from 5 largest oilfields in California. These giant fields are among the 10 largest oilfields in the US. The discovery dates and current average production rates in barrels of oil per well are also shown. The vertical line is the power density of oil and gas condensate extraction from the largest oilfield in the world, Ghawar in Saudi Arabia with the expected ultimate recovery of 100 billion boe.

For comparison, a good wind farm may achieve a power density of 1.2 W/m^2, up to 4 W/m^2 in those rare sites, which have strong wind that blows from the same direction. A photovoltaic (solar cell) farm may achieve the time-averaged power density of 10-20 W/m^2.

For a limited time[4], the specific power drawdown from a large oil field is of the order of 100 W m^{-2}, see **Figure 3.3**.

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[4] Fifty years of production might be typical at these power drawdown rates.

3.4.3 Petroleum

In 2003, the U.S. consumed 20 034 000 barrels of petroleum per day. *Consumption* refers to petroleum products supplied, which is equal to field production, plus refinery production, plus imports, plus unaccounted for crude oil, minus stock change, minus crude losses, minus refinery inputs, minus exports.

One barrel of petroleum, or 42 U.S. gallons, can hold approximately 134−136 kilograms of good quality crude. If this crude is burned, it can generate at most (high heating value) 45 − 48 MJ/kg. So, in 2003, the U.S. used at least 44.8 EJ/year of primary energy as crude oil. Fifty six percent of all crude oil consumed in the U.S. was imported. In 2003, the total U.S. expenditure on crude oil was $202 billions at wellhead ($27.56/barrel), of which $113 billions were spent on the imported crude oil. In 2004, this cost was at least 30% higher, and it was still higher in 2005 (on February 1, 2005, the crude oil price was about $50/bbl).

In 2003, the U.S. burned 519.171 billion liters of gasoline with an average density of 0.74 kg/L and the high heating value of 46.7 MJ/kg. Thus, the annual use of gasoline amounted to 17.9 EJ of primary energy (only $\ll$20% of this energy was converted into shaft work of moving automotive vehicles).

3.4.4 Coal

In 2003, the U.S. used 967 millions of metric tonnes of coal (almost one trillion tonnes). With the average high heating value of coal equal to 27 MJ/kg, the amount of primary energy in the coal was 26.1 EJ/year. The average coal producer price was $19.8/metric tonne, so $19 billions were spent on coal in 2003.

3.4.5 Natural Gas

In 2003, the U.S. used 22 375 billion standard cubic feet of natural gas. The standard conditions refer to the pressure of 1 atmosphere and room temperature. This volume of gas is equal to 633.6 billions of standard cubic meters. The standard density of natural gas is 0.84 kg per standard m^3 and its high heating value is 48.7 MJ/kg. Therefore, in 2003, the U.S. purchased 25.9 EJ/year as primary energy from natural gas at the mean producer price of $4.88 for 28 standard m^3 of gas (1000 scf), or $109.19 billion in total.

3.4.6 Nuclear Energy

In 2002, the U.S. generated 780 064 million kWh of electricity from nuclear power plants with 104 operable reactors. This amount of electricity is equal to 2.8 EJ/yr, and the amount of heat (primary energy) that was used to generate this electricity is roughly 3 times higher, or 7.8 EJ/yr.

3.4.7 Summary

Primary energy uses in the US in 2003 and 2004 are summarized in **Tables 3.4** and **3.5**. About ninety five percent of primary energy in the US comes from fossil fuels and fission of uranium. Liquid transportation fuels, produced almost exclusively from petroleum and natural gas, account for 1/3 of primary energy use in the US, see **Figure 3.4**. The renewable sources of primary energy are tiny and dominated by hydropower[5] and biomass burning for electricity and heat. To the extent that US uses fossil energy and outdated nuclear reactors, its economy is at least 94% *irreversible* and *unsustainable*. Irreversibility and sustainability or lack thereof will be defined in Chapter 10. The US population uses over 100 times more primary energy than we need as food. If were to metabolize this amount of energy, each one of us would be a 15 m long sperm whale weighing 40 tons. There are probably less than 360,000 sperm whales worldwide (Baker and Clapham, 2004) and 833 times more Americans. A statistical child born in the US impacts the world energy resources ∼1000 times more than an adult male sperm whale.

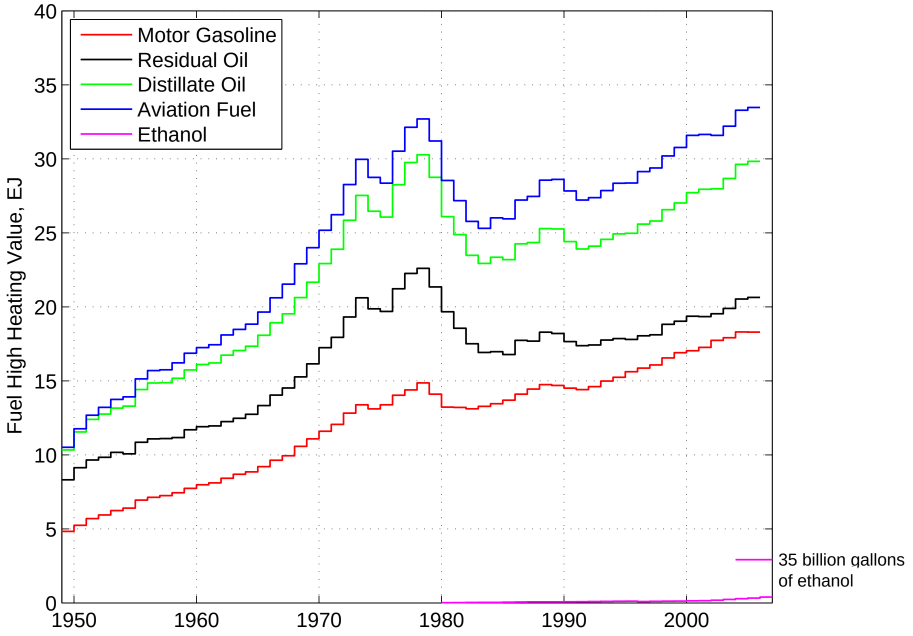

Figure 3.4: Transportation fuel use in the US from 1949 to 2006. Sources: Fuel volumes from EIA and RFA, fuel densities and HHVs from Tables 3.2 and 3.3. Each curve represents the fuel HHV increment above the curve below it.

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[5] Because of silting, hydropower is not renewable on a time scale of century. Dams have other negative impacts on soil erosion, soil inundation, and aquatic animals.

Table 3.4: Annual use of energy in the U.S. in the year 2003. Sources: U.S. DOE Energy Information Agency, www.eia.doe.gov; Section 3.3.3

Source	Use EJ/year	Comments
Petroleum	41.8	Primary HHV[a]
Coal	26.1	Primary HHV
Natural Gas	25.9	Primary HHV
Nuclear	7.8	Primary
Biomass	2.0	Primary
Hydro	1.0	Primary
TOTAL	**104.6**	**Primary energy**
Food	1	Food products to live
Gasoline	18	All uses
Electricity	14	All sources
Nuclear	2.8	Electricity
Biomass	0.4[b]	Electricity
Wind	0.04[c]	Electricity
Photovoltaics	0.002[d]	Electricity

[a] HHV= High Heating Value, see Section 3.3.3

[b] The EIA data seem to be inconsistent. The summary statistics table lists biomass as the source of 3% (0.4 EJ/yr) of all electricity produced in the U.S. The detailed statistics list 37 and 22.9 billion kWh from wood and other biomass respectively (0.22 EJ/yr).

[c] The wind electricity was 10 260 150 000 kWh/year in 2002 or 0.04 EJ/yr according to www.mnforsustain.org/windpower_schleede_costs_of_electricity.htm, if the windmills operated with a 25% capacity factor (accessed March 5, 2005)

[d] The solar electricity was 0.003 EJ/yr in 2003 according to www.solarbuzz.com/-StatsMarketShare.htm (accessed March 5, 2005)

3.4.8 Energy Costs

In 2003, the total cost of primary energy (at producers' prices) was approximately \$260 billions (I have included \$3.6 billion for the electricity *cost* of \$0.0046/kWh from nuclear power plants). The energy cost to the customers was 2-3 times higher. For example, in 2003, the cost of gasoline exceeded the wellhead price of crude oil by a factor of 2.3-2.7. The average cost of electricity to the consumer, 0.084 \$/kWh, exceeded the average production cost by a factor of 5, see **Figure 3.5**. Similarly, natural gas costs the consumer about 2 times the production cost.

3.4.9 Problems

1. Express these energy fluxes in $\mathsf{W\ m^{-2}}$ or $\mathsf{MW\ m^{-2}}$, etc.:

Table 3.5: Annual use of energy in the U.S. in the year 2004. Sources: U.S. DOE Energy Information Agency, www.eia.doe.gov; Section 3.3.3

Source	Use EJ/year	Comments
Petroleum	44.8 (41%)	Primary HHV[a]
Coal	24.9 (23%)	Primary HHV
Natural Gas	25.6 (23%)	Primary HHV
Nuclear	8.7 (8%)	Primary
Biomass	3.1 (3%)	Primary
Hydro	2.8 (3%)	Primary
TOTAL	**109.9** (100%)	**Primary energy**
Food	1	Food products to live
Gasoline	18.3	All uses
Electricity	14.0	All sources
Coal	7.1	Electricity
Nuclear	1.7	Electricity
Hydro	1.0	Electricity
Wind[b]	0.1290	Peak Electricity
Solar	0.0645	All sources

[a] HHV= High Heating Value, see also (Patzek, 2004)

[b] Actual power is perhaps 1/4 of the peak power. See Footnote c in Table 3.4

(a) 11 700 calories per square centimeter during one month

(b) 254 BTU per square foot per minute

(c) 2MW of electricity per 130 acres of solar collector

(d) 1/2 cord (find out on Google what 1 cord of wood is) of white oak wood per acre per year. The calorific value of dry oak wood is 19 MJ/kg and its density is 590 - 930 kg/m^3 of dry wood. Use the mean density.

In reality, the energy of 1 cord of wood will be at least 30% less than the calculation above, because the pieces of wood cannot be packed tightly, and the pile will have a considerable porosity.

2. Find out primary energy use in the US in 2005. Also find the average costs of petroleum, natural gas, coal, and electricity in 2005 and 2006. Put your results in a table identical to **Table 3.4**. Also list your source numbers from EIA in their original units. For example, in 2004, EIA reported the numbers listed in **Table 3.6**.

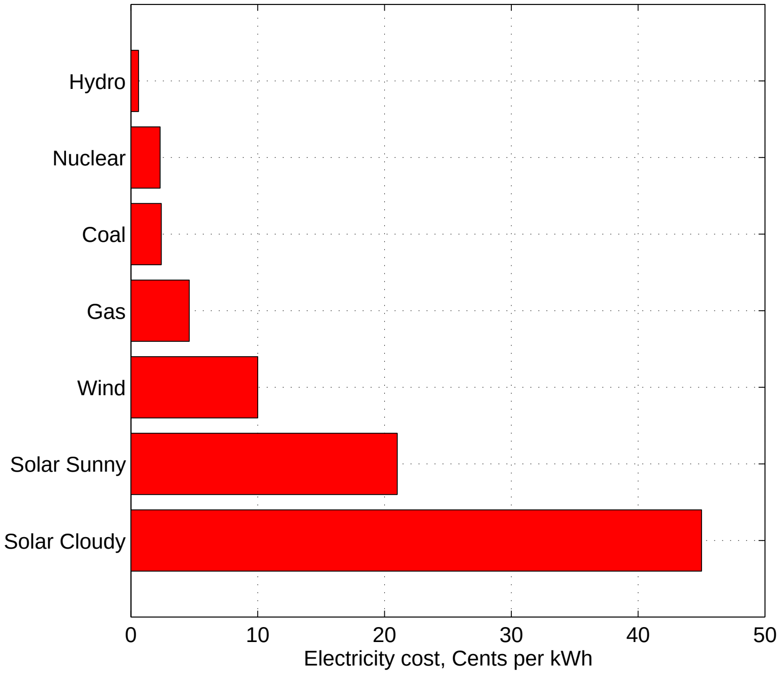

Figure 3.5: Unit cost of electricity generation in cents per kWh. The wind electricity costs are highly uncertain. The January 2005 average solar electricity prices were obtained from http://www.solarbuzz.com.

3. As you may know, Poland has recently joined the European Union, and there is increased pressure to deliver electricity from renewable sources. To adhere to the Kioto Protocol, Poland must deliver 7 percent of its primary energy use from biomass (wind turbines and photovoltaic cells are still completely insignificant as energy sources).

   The new corporate owners of a large, 8 × 220 MW coal-fired power plant in Polaniec[6] have decided to do something about it using the existing regulations to their advantage. Here are the details of their story:

   (a) The price of fossil fuel-derived electricity in Poland is 80-90 zl/MWh (Polish zloty/megawatt-hour), but for renewable electricity producers may charge 250-300 zl/MWh, or over three times more.

   (b) In 2005, wood for paper pulp sold in Poland for 80-90 zl/m^3 of wood with, say, 15% of moisture by mass.

   (c) Wood has the highest heating value of all biomass, equal to 19.0 MJ/kg of bone-dry wood. The heating value of moist wood is ap-

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[6] See www.electrabel.pl/content/corporate/aboutelectrabel/electrabel_ polaniec_ EN.asp- ?timstp=1125262687885

Table 3.6: Annual use of energy in the U.S. in the year 2004 in EIA units[a]

Quantity	Units
20731000	bbl of crude oil/day
22375×10^9	scf/year of natural gas
1094.7×10^6	short tons per year of coal
$3883185 \times 10^6 \times 0.2$	kWh of nuclear power
2.72515×10^{15}	Btu/year of hydropower
2.845×10^{15}	Btu of wood, chips, ethanol, etc.
3883185×10^6	kWh of all electricity
0.1223×10^{15}	Btu/year of wind power
6.1170×10^{13}	Btu/year of solar power
9105000	bbl of motor gasoline/day

[a] Later, EIA updated these numbers and converted the fuel volumes into energy, see their stb0101.xls – stb0103.xls spreadsheets. The conversion appears to have been done using the fuel LHV's. Consequently, I have multiplied the EIA fuel energy estimates by the factors of HHV/LHV for crude oil, natural gas, and coal+coke

proximately equal to the mass fraction of dry wood multiplied by its heating value (0.85×19.0 MJ/kg moist wood).

(d) The Polish Forest Service sells about 26–27 million cubic meters of wood each year, but this wood is also used for lumber, transportation crates, paper making, etc.)

(e) Polaniec contracted as much paper wood as they could get and offered to pay for it 130 zl/m^3.

Your task is to calculate how much wood Polaniec will use if they want to burn it to power 1,2,. . . ,8 of its turbines.

(a) Assume that the overall thermodynamic efficiency of the Polaniec power plant is 35%, i.e. it takes 220/0.35 MW of fossil energy (here wood) to generate 220 MW of electricity from a single turbine.

(b) Assume that the power plant operates 24 hours a day, 330 days per year. One month is devoted to maintenance.

(c) For simplicity, assume that all wood has the density is 750 kg/m^3 of slightly moist wood sold with 15% of moisture.

(d) If it turns out that Polaniec must also use the higher quality wood, assume that the wood price will increase all the way up to 200 zl/m^3. Will the wood-burning still make "economic" sense?

Those of you who are particularly curious may think about the ash and slag content of the wood, and emissions of other elements in the wood, such as sulfur and nitrogen oxides. Do a Web search to find out a little about these problems. in particular, try to find out if the slag is a toxic material or not.

4. (**Bonus**) Given the body mass distribution of US males and females of all races, **Table 3.7**, and the projections from the US Census in 2000 summarized at wonder.cdc.gov/WONDER/help/populations/population-projections/ProjectionsStateAgeSex2005.html#Summaries, estimate the calorific value of food needed to sustain the entire US population for 1 year.

   Hint: Pick year 2005 for the census projections. Assume 2700 kcal/day per 78 kg male and 2000 kcal/day per 64 kg female. Scale the metabolic rates as $2700 \times (m_{\text{avg}}/78)^{1/4}$ for males, and $2000 \times (m_{\text{avg}}/64)^{1/4}$ for females (both in kcal/day). Here m_{avg} is the average body mass at the midpoint of an age group. Assume constant mean body mass for males and females above 74 years of age. Note that this scaling treats the serious obesity problem in the US population as a nutritional requirement. In other words, overweight people eat too much and continue to be overweight, but we treat their excessive calorie consumption as a nutritional necessity.

   A different way of scaling the overall nutritional needs of males and females comes from a study by the Food, Nutrition, and Poverty Program of the United Nations University (UNU), with the support of the United Nations Development Program (UNDP). For example, it is assumed that an average working adult male in India needs 2800 kcal day^{-1} and average working female needs 2360 kcal day^{-1}. Then the calorie requirement factors in **Table 3.8** are applied to a population distribution.

   Answer: Using the 2005 population projection by USCB, the calorific value of food required to feed the US population is approximately 1.0 EJ/year using Table 3.7, and 0.83 EJ/year using Table 3.8. The actual per capita food supply and consumption in the US are shown in **Figure 3.6**. Notice that the 2250 kcal/day per person consumed in 1970, can be translated into 1900 kcal day^{-1} per average female and 2670 kkcal day^{-1} per average male. Also notice that the US per capita food consumption, adjusted for losses, increased by 19% between 1983 and 2000. No wonder, so many of us are obese!

5. (**Bonus**) Find the specific power drawdown in W m^{-2} from coal production in a major deposit in Wyoming or South Dakota.

   Hint: Find annual production and the deposit's productive or currently developed area.

Table 3.7: Average body mass and standard deviation for all males and females in US[a]

Age Group	Mean Age (yr)	Mean male mass (kg)	std (kg)	Mean female mass (kg)	std (kg)
0.5 to 1	0.75	9.4	1.3	8.8	1.2
1 to 2	1.50	11.8	1.9	10.8	1.4
2 to 3	2.50	13.6	1.7	13.0	1.5
3 to 4	3.50	15.7	2.0	14.9	2.1
4 to 5	4.50	17.8	2.5	17.0	2.4
5 to 6	5.50	19.8	3.0	19.6	3.3
6 to 7	6.50	23.0	4.0	22.1	4.0
7 to 8	7.50	25.1	3.9	24.7	5.0
8 to 9	8.50	28.2	6.2	27.9	5.7
9 to 10	9.50	31.1	6.3	31.9	8.4
10 to 11	10.50	36.4	7.7	36.1	8.0
11 to 12	11.50	40.3	10.1	41.8	10.9
12 to 13	12.50	44.2	10.1	46.4	10.1
13 to 14	13.50	49.9	12.3	50.9	11.8
14 to 15	14.50	57.1	11.0	54.8	11.1
15 to 16	15.50	61.0	11.0	55.1	9.8
16 to 17	16.50	67.1	12.4	58.1	10.1
17 to 18	17.50	66.7	11.5	59.6	11.4
18 to 19	18.50	71.1	12.7	59.0	11.1
19 to 20	19.50	71.7	11.6	60.2	11.0
18 thru 24	21.50	73.8	12.7	60.6	11.9
25 thru 34	30.00	78.7	13.7	64.2	15.0
35 thru 44	40.00	80.9	13.4	67.1	15.2
45 thru 54	50.00	80.9	13.6	68.0	15.3
55 thru 64	60.00	78.8	12.8	67.9	14.7
65 thru 74	70.00	74.8	12.8	66.6	13.8

[a] National Center for Health Statistics, 1987, M.F. NAJJAR and M. ROWLAND, Anthropometric Reference Data and Prevalence of Overweight, United States 1976-1980, Data from the National Health Survey Series 11, No. 238, DHHS Publication No. (PHS) 87-1668, US Public Health Service, US Government Printing Office, Washington, DC, October 1987

Table 3.8: Calorie requirement factors for different age groups using adult males as the standard [a]

Age	Males	Females
0 – 1	0.43	0.43
1 – 3	0.54	0.54
4 – 6	0.72	0.72
7 – 9	0.87	0.87
10 – 12	0.97	0.93
13 – 15	1.03	0.80
16 – 19	1.02	0.75
20 – 39	1.00	0.71
40 – 49	0.95	0.68
50 – 59	0.90	0.64
60 – 69	0.80	0.51
70+	0.70	0.50

[a] www.unu.edu/Unupress/food/8F082e/8F082E02.htm, accessed January 28, 2007. Tables 1 and 2 in the contribution by C. H. Shah, Gujarat Institute of Area Planning, Ahmedabad, India

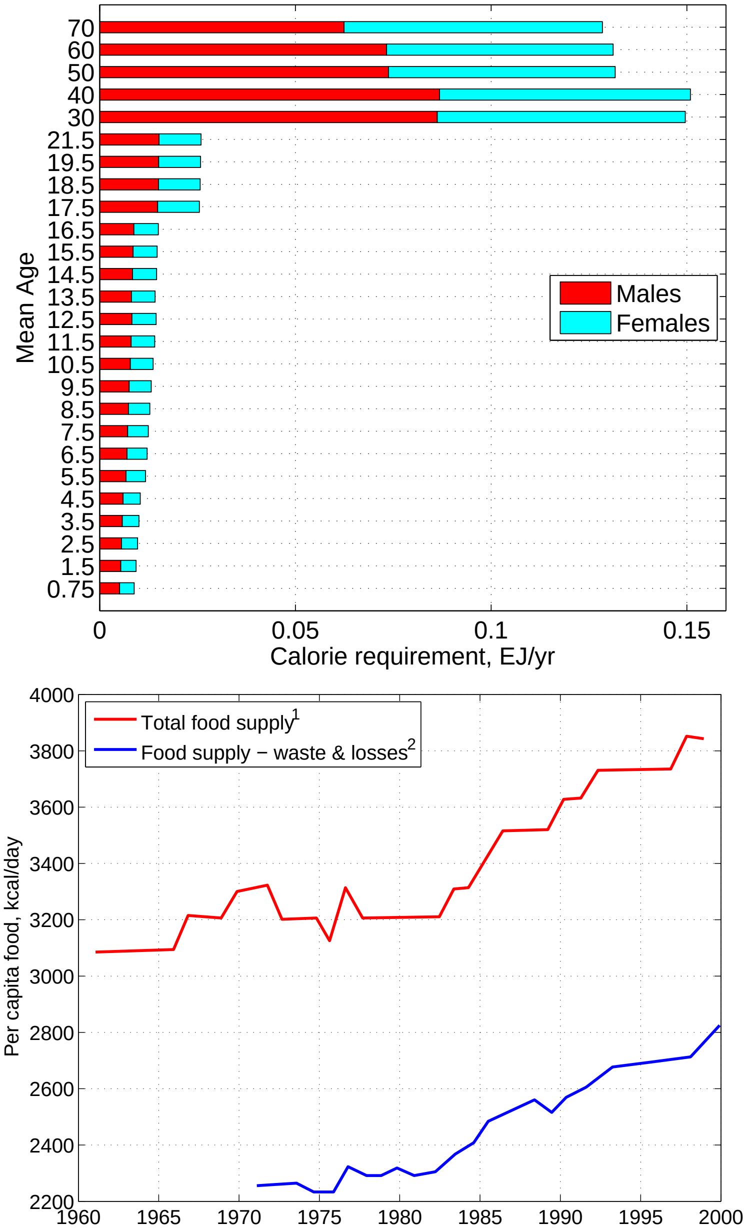


Figure 3.6: Food calorie requirements by in the US. **Top**: The US Census Bureau projections for July 2005 have been linearly interpolated against the age groups in Table 3.7. The 2006 US food energy requirement is 1.005 EJ/yr, in remarkable agreement with my rough estimate of 100 W per average person. **Bottom:** [1]Total food supply available for consumption; rounded to the nearest hundred. [2]Food supply adjusted for spoilage, cooking losses, plate waste and other losses; not calculated for years before 1970. Sources: USDA's Center for Nutrition Policy and Promotion, and USDA's Economic Research Service.

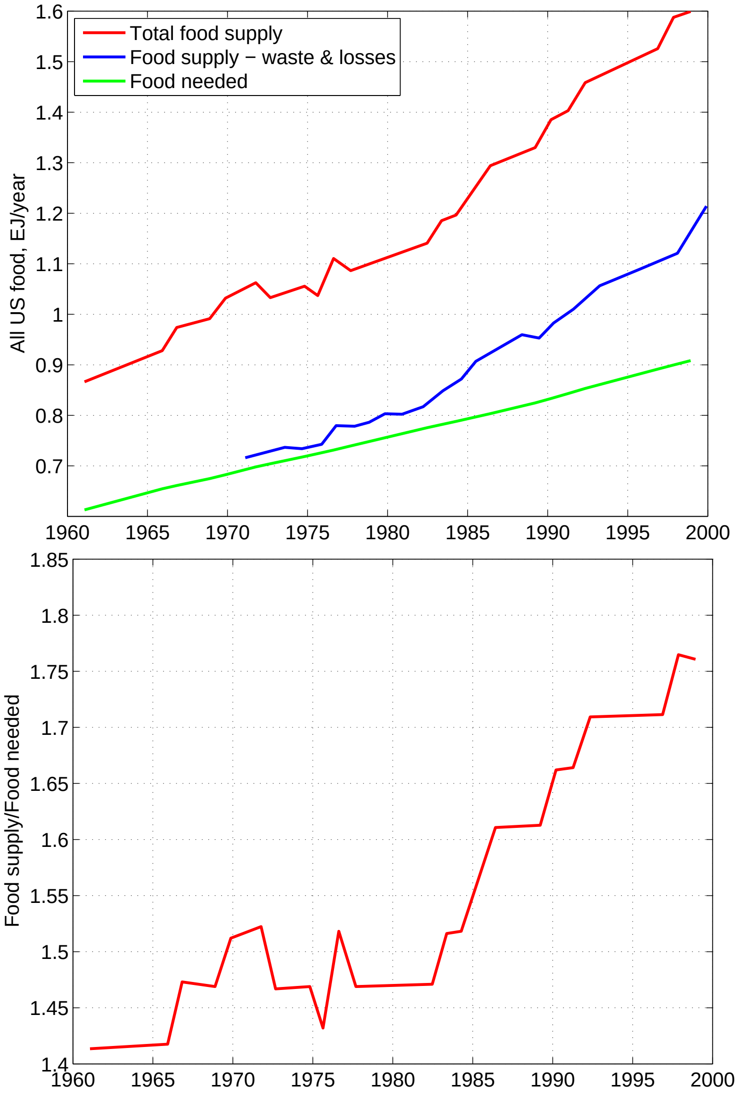
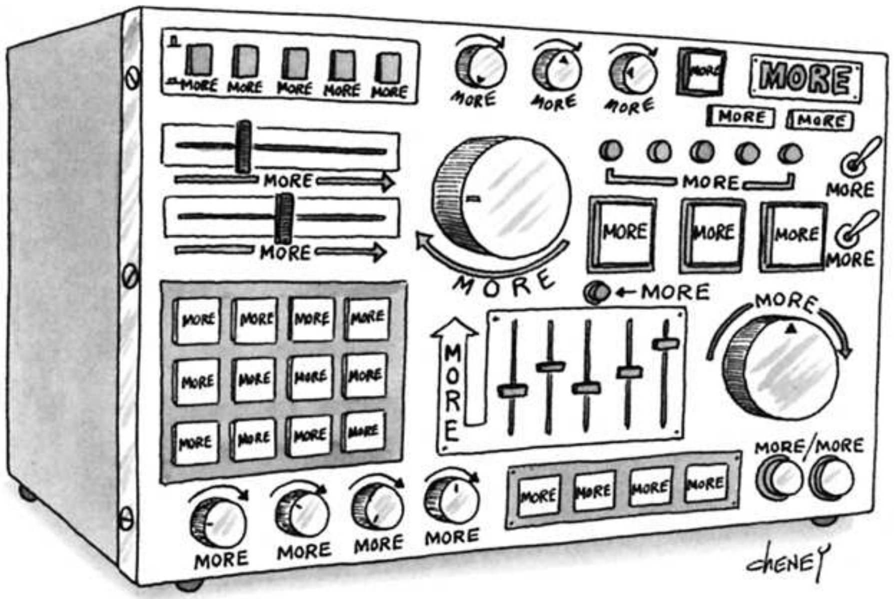


Figure 3.7: **Top:** Total food supply and consumption in the US, scaled to 1EJ per 300 million people per year. The calculations are based on Figure 3.6. Note that soon after Nixon's agriculture "reform" in 1973, the food need and consumption started to diverge. **Bottom:** The historical ratio of the energy in US food supply to the energy need to feed US population. The conspicuous consumption of the early 80s started an unsettling trend of wasting food, fattening the US population, and damaging the environment - all to increase profitability of agricultural and food-processing corporations.

Chapter 4

Economics



> *The decadent international but individualistic capitalism in the hands of which we found ourselves after the war is not a success. It is not intelligent. It is not beautiful. It is not just. It is not virtuous. And it doesn't deliver the goods.*
>
> — John Maynard Keynes
> *Collected Writings* (1971-80)

4.1 What Are you Going to Learn?

You are going to learn about the concept of *steady-state economy*, that is about an economy that maintains a constant stock of people and their artifacts.

4.2 Why Is It Important?

As you have learned in the Introduction, our planet is finite and is endowed with finite amounts of raw materials and a finite capacity to regenerate herself. Therefore, boundless economic growth is fundamentally incompatible with anything sustainable. If we want to talk about sustainability, we must first understand the concepts of natural limits and zero-growth. Otherwise, you may stop reading now and go shopping, see **Figure 4.1**.

Figure 4.1: In a steady-state economy (SSE), this new personal Cessna Mustang ($2.7 millions) and Bugatti ($1.45 million) will not be made to your order. But not to worry, in the SSE, you will not be taking home an $83 million December bonus for the contributions to raping and pillaging the world and people.

4.3 Background

This chapter has been greatly influenced by two seminal books, *Steady-State Economics* by Herman E. Daly (Daly, 1977), and *The Entropy and the Economic Process* by Nicholas Georgescu-Roegen (Georgescu-Roegen, 1971), see **Figure 4.2**.

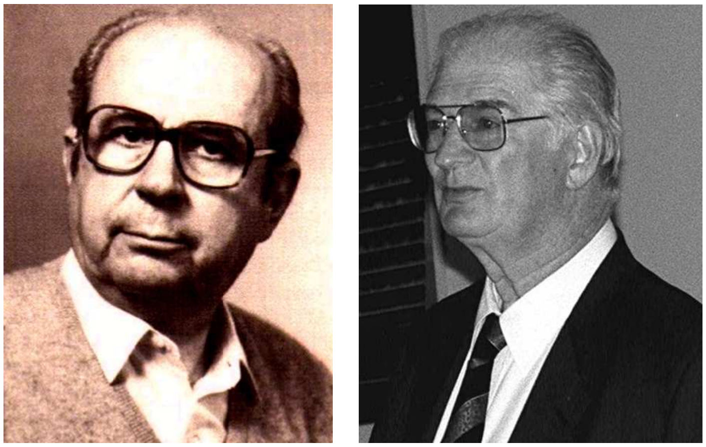


Figure 4.2: The two greatest proponents of a sustainable economy (if it can exist at all): Nicholas Georgescu-Roegen (1906-1994, left) and Herman E. Daly (Professor at the School of Public Policy at the University of Maryland, College Park, right).

Definition 1 A sustainable, steady-state economy (SSE) consists of a constant number of people, and a constant number of their possessions (physical wealth). Both populations are maintained at optimal levels by a minimal throughput of babies and raw materials. Thus, the steady-state economy is an extension of a stationary population to include not only the human bodies but also their manifold physical extensions. Equally important is to list what is *not* held constant: genetic inheritance, knowledge, goodness, wellness, etc., embodied in the humans. For details, see (Daly, 1977), pp. $16 - 17$. □

The concept of no-growth is so alien to our economic indoctrination that the SSE requires more explanation. First, it is a *physical concept*, not a *mathematical abstraction*. How does this physical concept relate to "economic growth"? As currently measured by the Gross Domestic Product (GDP), **Figure 4.4**, which is a value index of a physical flow, economic growth is strictly tied to the flow of physical objects and raw materials. Even services are measured as the use of something or somebody for a period of time, and these things and people require physical maintenance; more of them requires more maintenance. In contrast, the SSE is defined through constant stocks, not flows. GDP is a flow and as such it is irrelevant to the SSE. In fact, minimizing flow of natural resources through the

SSE leads to minimizing GDP! The steady state point of view seeks to maintain a desired level of stocks with a minimum throughput, and if minimizing the throughput leads to a reduction in GDP, so be it, see p. 18 in (Daly, 1977).

4.4 A Crash Course on the SSE

Economics has to do with deciding *how* and from *what* we produce things and services, and with the reasons *why* we produce these things and services. The fundamental problem with economics is that it operates only in the middle of the means-ends spectrum shown in **Figure 4.3**, while claiming that it encompasses the whole spectrum. In other words, economists almost never speak about the Ultimate Means, the low-entropy, pure and valuable resources[1] we extract from the Earth and Society. They also almost never speak about the Ultimate End, the reasons for our very existence and labors of our lives. Instead, economists focus on the middle of the means-ends spectrum and talk about allocating intermediate means (products and services we buy) in the service of intermediate ends (food, comfort, entertainment, education,...).

As Professors Georgescu-Roegen and Daly have shown, this undelineated but limited focus has been the main source of confusion about "economic growth."

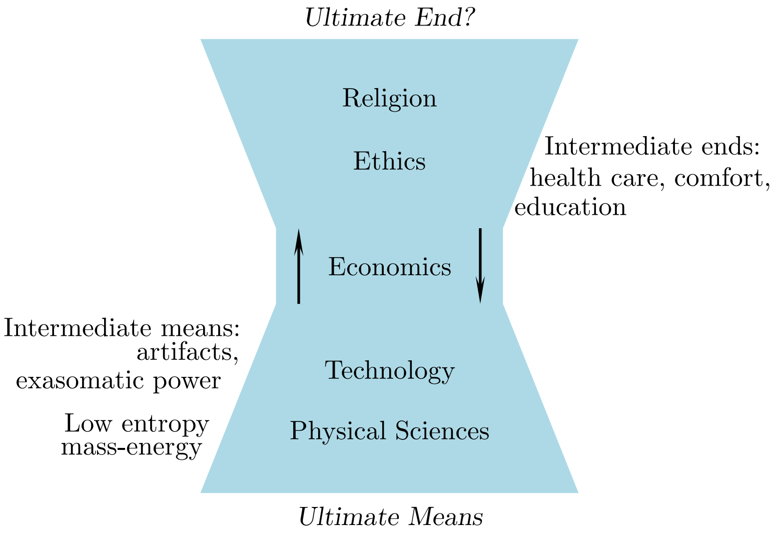


Figure 4.3: The context of economics, adapted from Figure 1, in Daly (1977), p. 19.

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[1] These resources do include clean water, clean air, fertile soil rich in the life-saving minerals, virgin forests, clean beaches, healthy human population, educated and productive population, competent governments, etc.

Consider Figure 4.3. The labels inside the two funnels indicate steps in the ends-means continuum. Each such step is an end with respect to lower categories and a means with respect to higher categories. From this point of view, intermediate ends are means in the service of the Ultimate End, and intermediate means are ends that are served by Ultimate Means. Only at both ends do we have that which is pure end or pure means.

- The Ultimate End is that which is intrinsically good regardless of anything we may produce or serve and it cannot be used as a tool to reach any other end. This end may be thought of as salvation and eternal life by religious people, or ultimate scientific or artistic enlightenment by some others.
- Ultimate Means is that which is useful or necessary for serving human ends, but cannot be created by human beings, and thus cannot be the end of any human activity.

By looking only at the middle range of the ends-means spectrum economics has not dealt with ultimates and absolutes, and has falsely assumed that the intermediate solutions and substitutions among scarce means and ends are representative of the whole spectrum. Absolute limits are absent from most economic theories because these limits can only be encountered by confronting them with the very ultimates that have been excluded. Most economists forget about extremes because they are not interested in ethics and are not schooled in natural sciences. Linear programming is not a substitute for life's complexity.

Definition 2 If one remembers about the finite resources on the Earth, economic growth can be defined as the conversion of ever more ultimate means (natural resources) into ever more intermediate means (market products) for the purpose of satisfying ever more intermediate ends (wants) whatever they might be, see Figure 4.1. □

4.5 Global Population

Population growth has continued more less unabated since our ancestors learned how to farm and live shorter, unhealthy and unhappy lives, but have more children (Cavalli-Sforza and Cavalli-Sforza, 1995). The human population grew rather slowly from times immemorial to about 1650, see **Figure 4.5**. The comfortable antiquity supported more humans – with the number of people reaching 400 millions at the time of Christ, and dropping down by 50 percent 500 years later when the Roman Empire fell. In Medieval times, the estimated human population was roughly constant. It is thought that England in A.D. 1086[2] had less than one-half of the population she supported during Roman times. The year 1650[3] seems to be a threshold of the much-increased rate of

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[2] The *Domesday Book* census of England and Wales by William the Conqueror.

[3] 1650 was the year of the Civil War in England and CROMWELL's victories. GALILEO GALILEI died in 1642, just before birth of Isaac Newton, in January 4, 1643 or December 25,

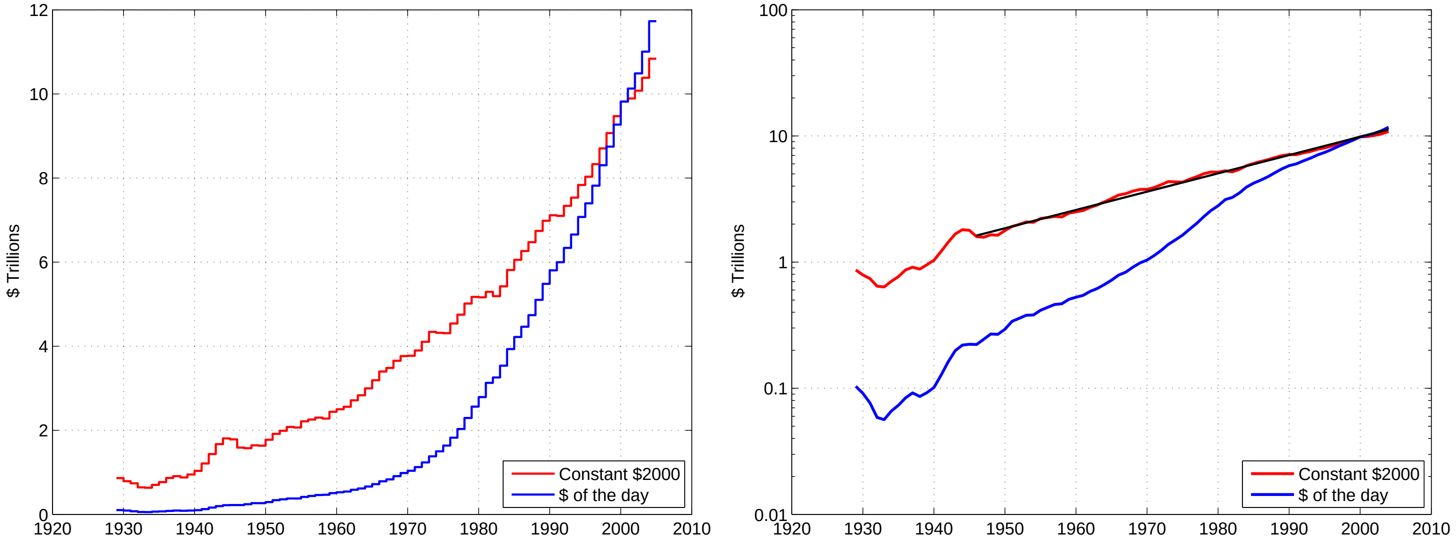

Figure 4.4: Since 1950, the US Gross Domestic Product (GDP) has been growing exponentially at 3.3% per year (the slope of the black line on the right). The faster growth in 1940-1945 was caused by the unmatched prosperity during World War II. By the war's end, if you didn't have to fight and die on Iwo Jima or in Normandy, you should have had the best time of your life. The severe peacetime crash of 1945 led to the now permanent re-militarization of US economy. The GDP growth is unlimited and, therefore, GDP must be non-physical on the finite Earth. Source: The U.S. Department of Commerce, Bureau of Economic Analysis, www.bea.gov/bea/dn/home/gdp.htm.

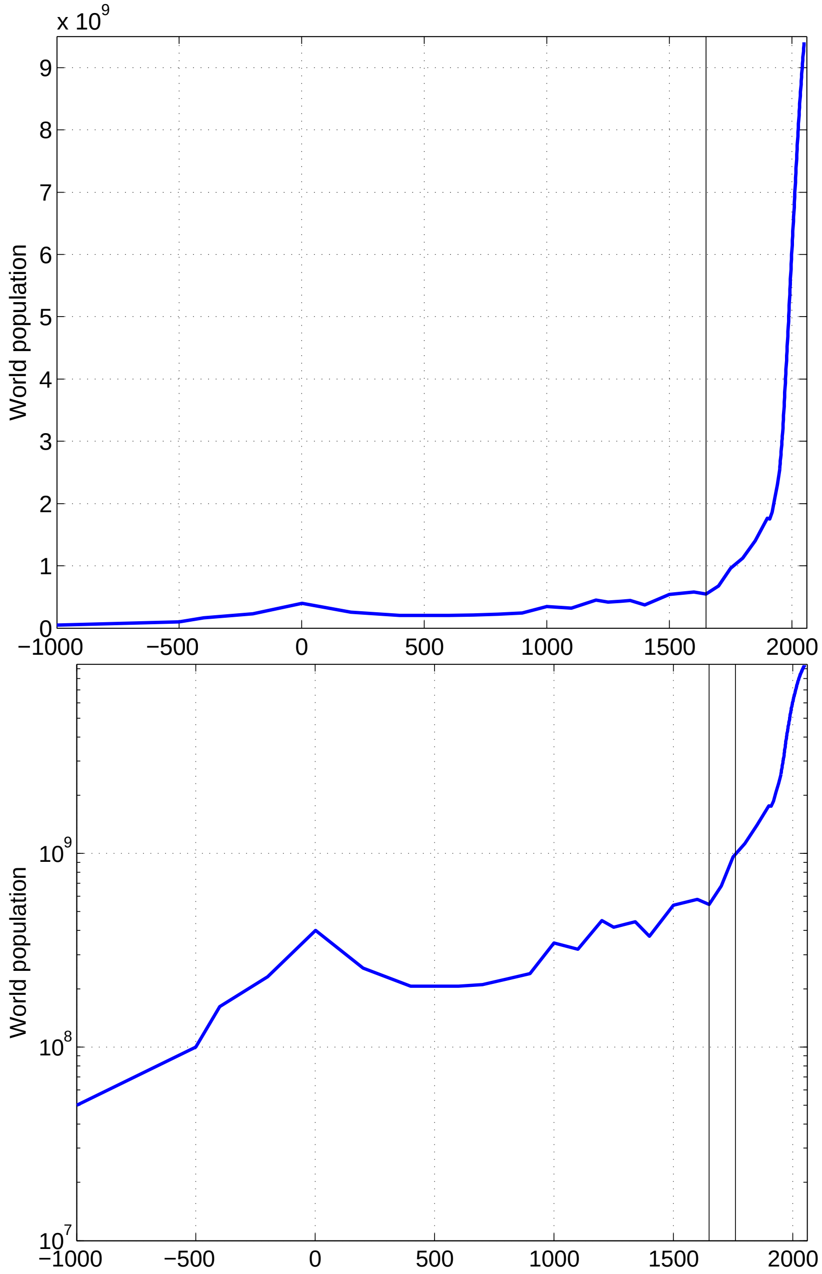

Figure 4.5: The historical and projected world population on linear and semi-logarithmic scales. Note the explosive population growth since 1650. Imagine yourself standing on the population high in 2050 and looking down. Also note that at the onset of Industrial Revolution (ca. 1760), the world population was about 1 billion people. Today it is 6.6 times higher. Source: US Census Bureau.

human population growth. By 1750, at the onset of Industrial Revolution in Europe, the population doubled to almost 1 billion people. Sometime between 1750 and 1800, the number of humans exceeded 1 billion. It took over 130 years (until 1925 or so) to double the human population to 2 billion people, and just 50 years to double it again (in 1974). It is anticipated that another doubling will happen in 50 years hence, by the year 2025.

With the number of humans growing exponentially and demanding ever more resources from the finite Earth, a sustainable economy is impossible. So something must be done to limit the number of people devouring the planet that gave them life.

4.6 US Population

The US population has been increasing rather vigorously since reliable records were established in 1790 or so, see **Figure 4.6**. The number of people has grown from roughly 10 millions in 1825 to 100 millions in 1915, 200 millions in 1968, and 300 millions in 2006. In the next 40 years the US population might grow by another 120-150 million people! The projected future US population, if it materializes, will exert an unbearable pressure on the Earth resources and will crush our current prosperity.

4.7 Population Control

In order to have an SSE, human population must be held constant at a certain level. But how to achieve and maintain this level without forced abortions? The idea of transferrable birth licenses was first put forward in 1964 by KENNETH BOULDING[4] (Boulding, 1964) pp. 135 – 136. Although widely ridiculed, it still remains the best plan yet offered. The plan is to issue equally to every person (or perhaps to every woman, because only maternity is certain) and amount of licenses that corresponds to replacement fertility. Thus each woman would receive 2.1 licenses. The licenses would be divisible in units of 0.1 ("deci-child"). Possession of 10 deci-child units would confer right to legal birth of one child. The licenses would be freely transferrable by sale or gift. Thus equity of distribution is achieved by the original distribution, and allocation efficiency is achieved through the market.

4.8 Problems

1. In 1860 or so, WILLIAM STANLEY JEVONS described the phenomenon of resource degradation and dilution as follows: "The expression "exhaustion

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1642, depending on the calendar. WILLIAM SHAKESPEARE was born in 1642. In short, modern science and literature had arrived.

[4] An extraordinary economist, who also said: "Anyone who believes exponential growth can go on forever in a finite world is either a madman or an economist."

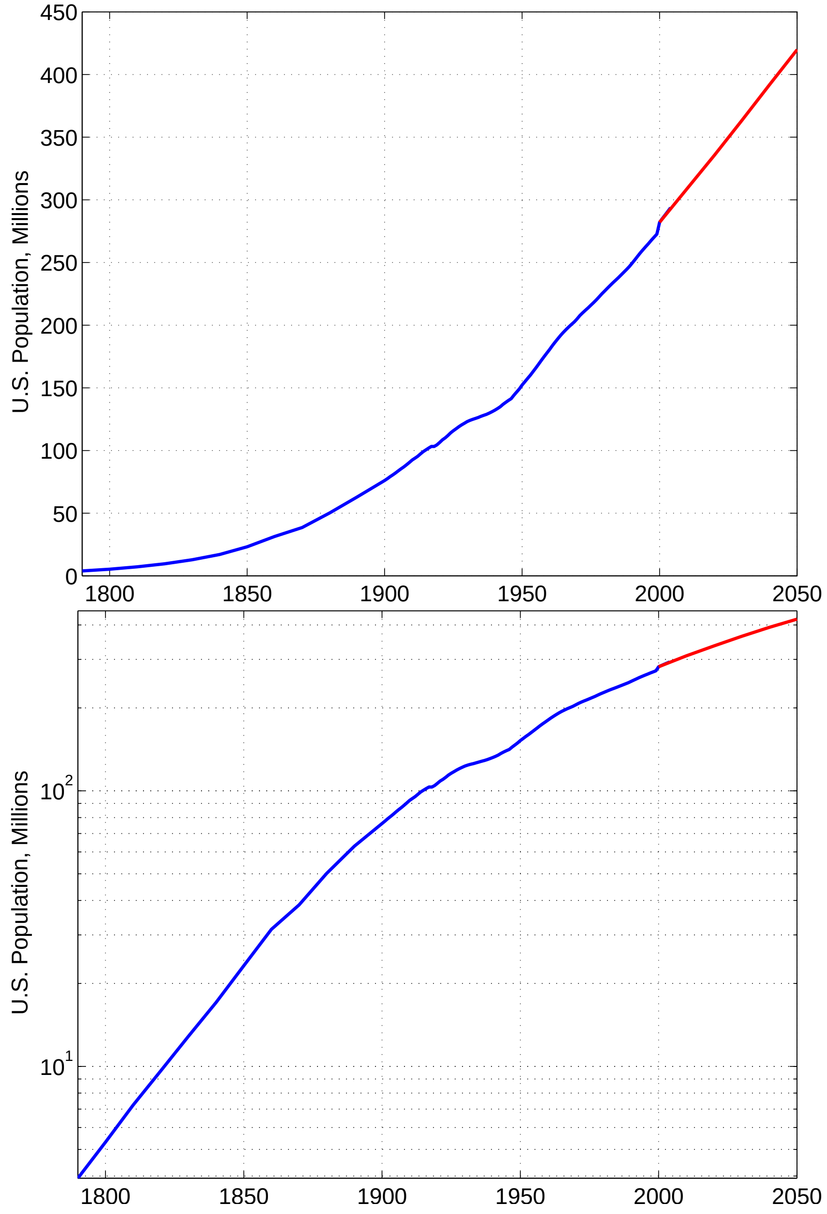

Figure 4.6: The historical and projected US population on linear and semi-logarithmic scales. Note the instantaneous addition of about 10 million illegal aliens in the 2000 US census. Also note that another 120 million people will be added in the next 40 years. If the current US rate of resource consumption is maintained, these new people will face very harsh conditions of living. Source: US Census Bureau.

of our coal mines," states the subject in the briefest form, but is sure to convey erroneous notions to those who do not reflect upon the long series of changes in our industrial condition which must result from the gradual deepening of our coal mines and the increased price of fuel. Many persons perhaps entertain a vague notion that some day our coal seams will be found emptied to the bottom, and swept clean like a coal-cellar. Our fires and furnaces, they think, will then be suddenly extinguished, and cold and darkness will be left to reign over a depopulated country. It is almost needless to say, however, that our mines are literally inexhaustible. We *cannot get* to the bottom of them; and though we may some day have to pay dear for fuel, it will never be *positively* wanting[5]"

Of course later we found two more convenient substitutes for coal: petroleum and natural gas. And most economists said: "Aha! Resource substitution is driven by the market and is always successful."

Summarize briefly the circumstances at which these economists' reasoning is either incorrect or irrelevant. How can you reduce the fundamental economic assumption of resource substitution to an absurdity?

2. Why is the following statement by two prominent economists not only silly and pompous, but also fundamentally wrong?

   "Advances in fundamental science have made it possible to take advantage of the uniformity of energy/matter – a uniformity that makes it feasible without preassignable limit, to escape the quantitative constraints imposed by the character of the earth's crust. . . . Nature imposes particular scarcities, not an inescapable general scarcity." (Barnett and Morse, 1963), p. 11. Note that the same thinking was present in Robert Solow's infamous remark cited in Introduction.

   Hint: Use the principles of physics and chemistry in your argument. You may also think about producing gold from lead, or some other element transmutations.

3. Why is the following statement by two geographers fundamentally wrong?

   "An examination of the prices of resource commodities (both in deflated dollars and in actual inputs of labor) reveals a downward rather than upward trend. The Malthusian view [of absolute resource scarcity] is so oversimplified that it is completely wrong. The data presented do not prove, but do strongly support the notion that technology can overcome increasing shortages of natural resources *ad infinitum*." (Burton and Kates, 1964). Note that the same silly argument was used with great success to discredit Professor Paul Ehrlich. What famous bet am I referring to? What were the consequences?

4. Present scientific arguments for/against the following statement: "But what's really striking is the advancement in the technology of molecular

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[5] (Jevons, 1866), *Preface*, pp. vi-vii, my italics.

transformation. Remember back in the Middle Ages, you had kings who employed alchemists to turn lead into gold? That's a useful metaphor for what you can do today, with molecular science becoming so advanced. You hear about things every day on the biological side – genetic engineering, wondrous pharmaceutical development. In the energy business, we're in range of the same thing: the ability to take any kind of feedstock and synthesize the fuels you want." DON PAUL, Chevron's CTO, *Spinning Straw into Black Gold*, by SAHELI S. R. DATTA, Business 2.0 Magazine, CNN, Feb. 13, 2007.

5. In view of Definition 2, describe briefly the direct physical damage to the Earth inflicted daily by our Consumer Economy. Use examples to illustrate your points.
6. How would you attempt to set the desired levels of human population? On the Earth? On each continent? For each country?
7. Suggest ways of cheating around birth license allocations. Suggest countermeasures.
8. By fitting a parabola to the semi-logarithmic plot of US population in Figure 4.6, predict maximum of the population and the year when it occurs. **Hint:** Use the Census Bureau data between 1880 and 2050.

Chapter 5

Exponential Growth?

When an executive decides to take action for reasons of social responsibility, he is taking money from someone else – from the stockholders in the form of lower earnings or from the consumer in the form of higher prices.

— Milton Friedman (Nobel Laureate Economist)
The Social Responsibility of Business Is to Increase Its Profits (New York Times Magazine, 13 Sept. 1970, 32ff.)

5.1 What Are You Going To Learn?

You will learn about the fundamental dichotomy between the fuzzy illusion of monetary economics, which we consider to be the hard truth, and the cold facts dictated by the finiteness of the Earth that we disregard.

5.2 Why Is It Important?

If the United States wants to share a peaceful world with others, we will not be able to continue what we do now: use 1/4 of all energy produced from the Earth without thinking much about it. You need to understand why exactly our current energy use cannot be maintained for much longer.

5.3 Growth Rates

As shown in **Figure 5.1**, the rate of production of anything on the finite Earth may follow as a function of time one of the three major patterns: normal (Gaussian), S-shaped, or exponential, At early times, these three patterns are practically indistinguishable and some may think that production rates of exhaustible resources (coal, oil, natural gas, iron ore, copper ore, etc.) can grow exponentially. In reality, these rates first grow and then decline. Some people think that annual yields of renewable resources (corn, soybeans, trees, etc.) can too grow without bounds. At best, these yields follow the S-shaped curves. More often than not, however, crop yields decline with time because of the exhaustion of soil minerals, destruction of soil texture, disappearance of topsoil through wind and water erosion, salt deposition, salty water invasion, emergence of specialized parasites[1], etc., see **Figure 5.2**. If this happens, the yield history of a crop follows a normal curve characteristic of a nonrenewable resource. In contrast, economic “growth” knows of no bounds because of the “law” of compound interest, see **Figure 4.4**.

Examples of exponential growth of the rates of resource production are common. Between 1880 and 1970, the global rate of crude oil production doubled, on the average, every 10.8 years, or at an average annual rate of increase of just above 6.6 percent, see **Problem 3**. The cumulative production also doubled every 10 years. The amount of oil produced between 1857 and 1984 was almost exactly equal to all the oil produced between 1984 and 2006, see **Figures 5.3** and **5.4**.

US oil production first grew exponentially and increased almost 1000-fold over 70 years, see **Figure 5.5**. US gas production also increased exponentially for 80 years and grew 100-fold, see **Figure 5.6**.

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[1] For example, the decline of the Mayan civilization may be traced to nematodes, small earth worms. Agriculture in Mesopotamia and countless other areas of the world declined because of soil salination and erosion.

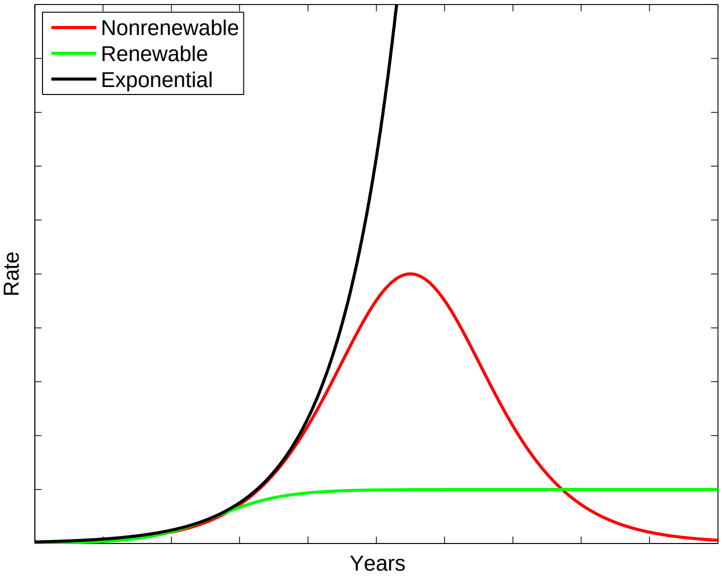
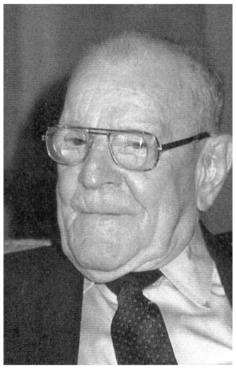


Figure 5.1: Production rate of a *nonrenewable* resource must go through a peak and decline to zero. Production rate of a *renewable* resource must stabilize at the maximum production capacity of the biome that supports the renewing of that resource. An *exponential* production rate (as in annual growth of the U.S. Gross Domestic Product) is without bounds and, therefore, non-physical after passage of enough time. Note that early on all three processes may have similar rates of growth and some economists have gotten confused.

5.4 King Hubbert



M. KING HUBBERT was born in San Saba, Texas in 1903. He attended the University of Chicago, where he received his B.S. in 1926, his M.S. in 1928, and his Ph.D in 1937, studying geology, mathematics, and physics. He worked as an assistant geologist for the Amerada Petroleum Company for two years while pursuing his Ph.D. He joined the Shell Oil Company in 1943, retiring in 1964. He reorganized and led Shell Development Company, indisputably the best *ever* research organization in the oil industry. Because of Hubbert's vision and stature, Shell Development attracted the following pioneers of earth sciences: W. R. PURCELL - capillarity; G. E. ARCHIE - modern petrophysics; M. A. BIOT - modern geophysics; John HANDIN - rock physics, and several others; and "graduated" the following well-known faculty and researchers: E. CLARIDGE, R. CLARK, G. HIRASAKI,

Figure 5.2: Visible soil salt deposits on the former bed of the Aral Sea. Source: Wikipedia.

L. Lake, Ch. Matthews, I. G. Macintyre, P. van Meurs, C. Miller, L. Orr, G. Pope, D. G. Russell, L. E. Scriven, G. Stegemeier, M. Prats, E. C. Thomas, R. Uber, H. Vinegar (still with Shell), M. H. Waxman, . . . , W. Chapmann, Ch. White,. . . , and T. W. Patzek. After Hubbert retired from Shell, he became a senior research geophysicist for the United States Geological Survey until his retirement in 1976. He also held positions as a professor of geology and geophysics at Stanford University from 1963 to 1968, and as a University Professor at Berkeley from 1973 to 1976. He died on October 11th, 1989.

Hubbert made several contributions to geophysics, including a mathematical demonstration that hot rock in the Earth's crust, because it is also under immense pressure, should exhibit plasticity, similar to clay. This demonstration explained the observed deformations of Earth's crust over time. He also studied the flow of underground fluids.

Hubbert is most well-known for his studies on the production capacities of oil and gas fields. He predicted that the petroleum production from all oil & gas fields in a petroleum province, such as the U.S., over time would resemble a bell curve, peaking when half of the petroleum has been extracted, and then falling off.

At the 1956 meeting of the American Petroleum Institute in San Antonio, Texas, Hubbert made the prediction that overall oil production would peak in the United States in the late 1960s to the early 1970s. He became famous when this prediction came true in 1970, see **Figure 5.7**. The curve he used in his analysis is known as the *Hubbert curve*, and the peak of the curve is known as

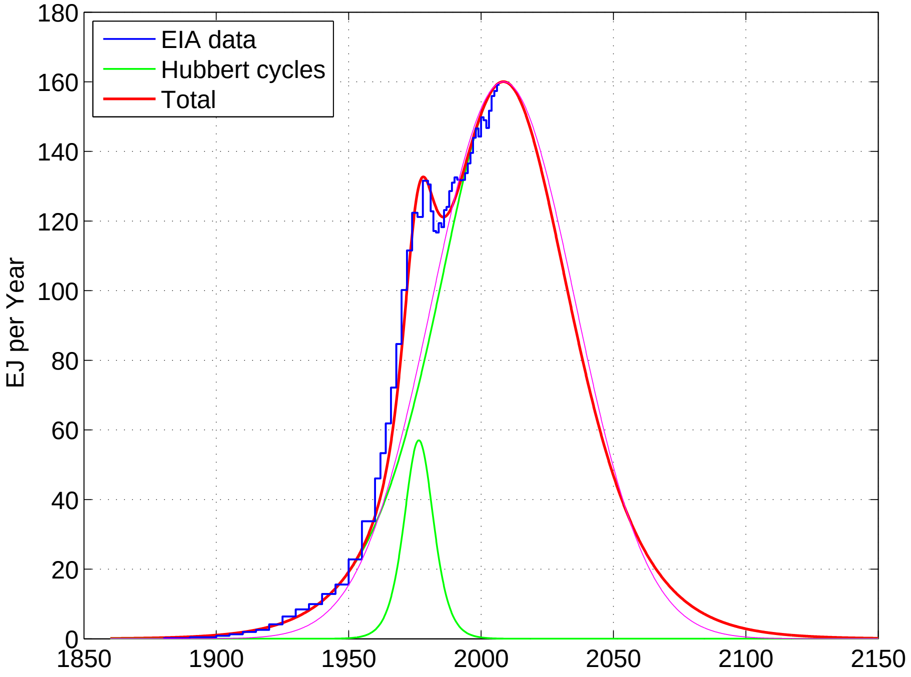


Figure 5.3: World crude oil production between 1880 and 2006, and the corresponding Hubbert cycles. The predicted ultimate oil recovery is 1.9 trillion barrels of crude oil, not counting condensate.

the *Hubbert peak.*

Between October 17, 1973, and March 1974, the Organization of Petroleum Exporting Countries (OPEC) ceased shipments of petroleum to the United States, causing what has been called the 1973 energy crisis. In 1975, with the United States still suffering from high oil prices, the National Academy of Sciences confirmed their acceptance of HUBBERT's calculations on oil and natural gas depletion, and acknowledged that their earlier, more optimistic estimates had been incorrect. This admission focused media attention on HUBBERT.

5.5 What Did Hubbert Teach Us?

During a 4-hour interview with STEPHEN B. ANDREWS, on March 8, 1988, Dr. HUBBERT handed over a copy of the following, which was the subject of a seminar he taught, or participated in, at MIT Energy Laboratory on Sept 30, 1981.

> The world's present industrial civilization is handicapped by the coexistence of two universal, overlapping, and incompatible intellectual systems: the accumulated knowledge of the last four centuries

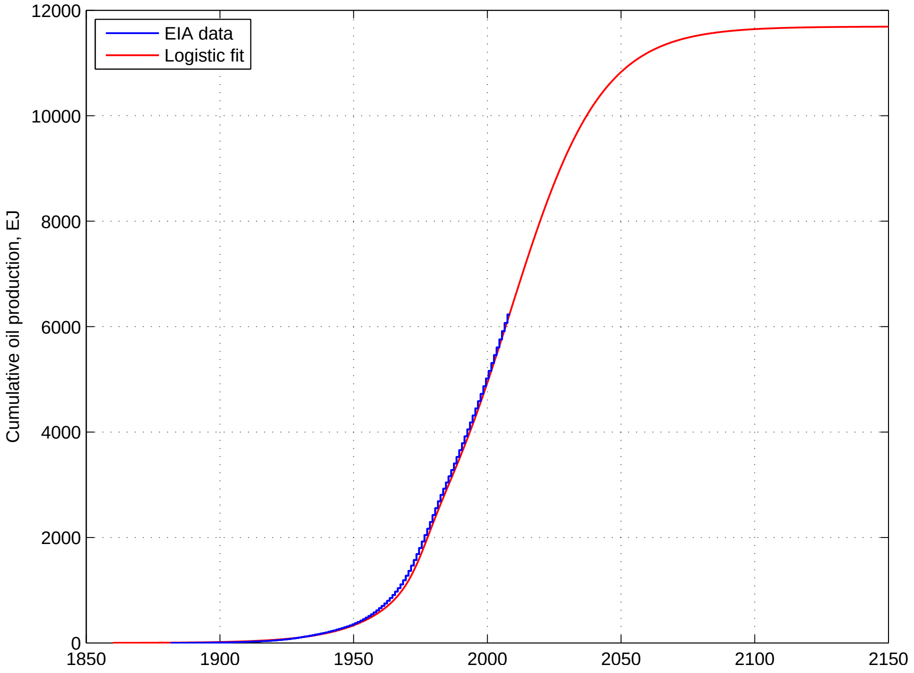


Figure 5.4: Cumulative oil produced worldwide between 1880 and 2006, and the corresponding Hubbert curve. We are already at the peak oil production!

of the properties and interrelationships of matter and energy; and the associated monetary culture which has evolved from folkways of prehistoric origin.

The first of these two systems has been responsible for the spectacular rise, principally during the last two centuries, of the present industrial system and is essential for its continuance.

The second, an inheritance from the prescientific past, operates by rules of its own having little in common with those of the matter-energy system. Nevertheless, the monetary system, by means of a loose coupling, exercises a general control over the matter-energy system upon which it is superimposed.

Despite their inherent incompatibilities, these two systems during the last two centuries have had one fundamental characteristic in common, namely, exponential growth, which has made a reasonably stable coexistence possible.

But, for various reasons, it is impossible for the matter-energy system to sustain exponential growth for more than a few tens ($\log 1000/\log 2 \approx 10$ *doublings to grow by a factor of 1000, TWP*) of doublings, and this phase is by now almost over (*see* ***Figures 5.5*** *and* ***5.6****, TWP*).

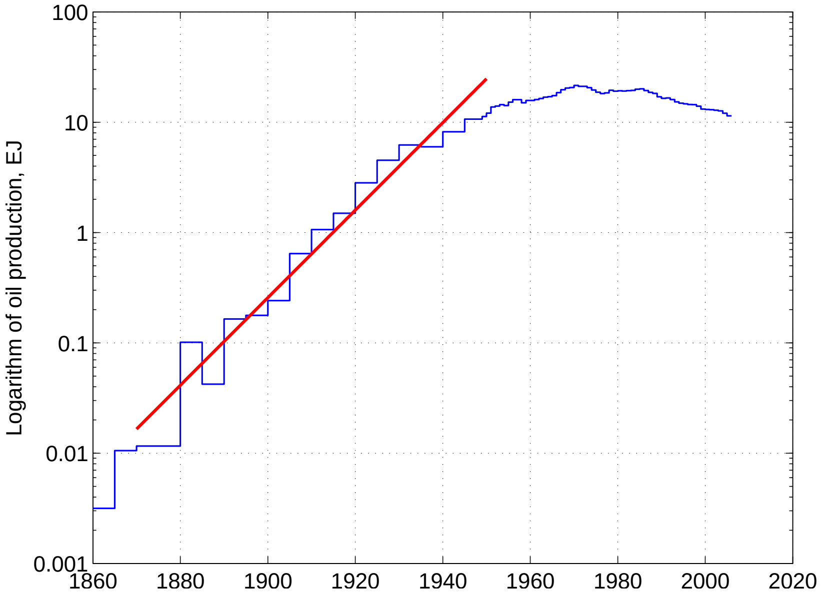


Figure 5.5: Between 1880 and 1940, the annual production rate of oil&condensate in the US was increasing 9% per year!

The monetary system has no such constraints, and, according to one of its most fundamental rules, it must continue to grow by compound interest. This disparity between a monetary system which continues to grow exponentially and a physical system which is unable to do so leads to an increase with time in the ratio of money to the output of the physical system. This manifests itself as price inflation. A monetary alternative corresponding to a zero physical growth rate would be a zero interest rate. The result in either case would be large-scale financial instability.

With such relationships in mind, . . . [the following questions can be posed (*TWP*)] regarding the future:

- What are the constraints and possibilities imposed by the matter-energy system?
- Can the human society be sustained at near optimum conditions?
- Will it be possible to so reform the monetary system that it can serve as a control system to achieve these results?
- If not, can an accounting and control system of a non-monetary nature be devised that would be appropriate for the management of an advanced industrial system?

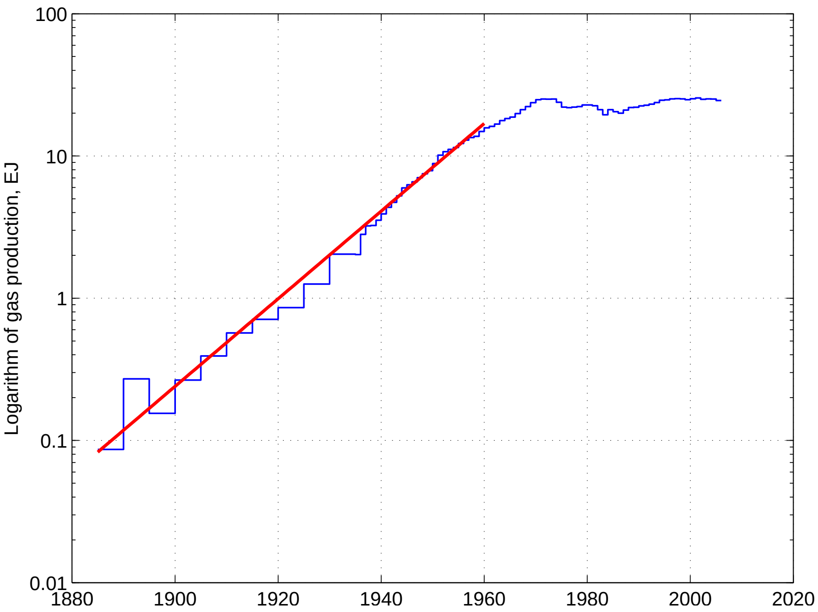


Figure 5.6: Between 1880 and 1960, the annual production rate of natural gas in the US was increasing 7.1% per year.

It appears that the stage is now set for a critical examination of this problem, and that out of such inquires, if a catastrophic solution can be avoided, a major scientific and intellectual revolution must take place.

5.6 Why Do Hubbert Cycles Exist?

As we will see soon, the HUBBERT cycles are related theoretically to the normal distribution and the error function. However, it is much easier to approximate them with the logistic S-shaped curve and its derivative. The logistic growth curve of human population was first proposed by the Belgian mathematician PIERRE FRANÇOIS VERHULST after he had read THOMAS MALTHUS' *Essay on the Principle of Population or, a View of its Past and Present Effects on Human Happiness; with an enquiry into our Prospects respecting the Future Removal or Mitigation of the Evils which it occasions* published in 1803.

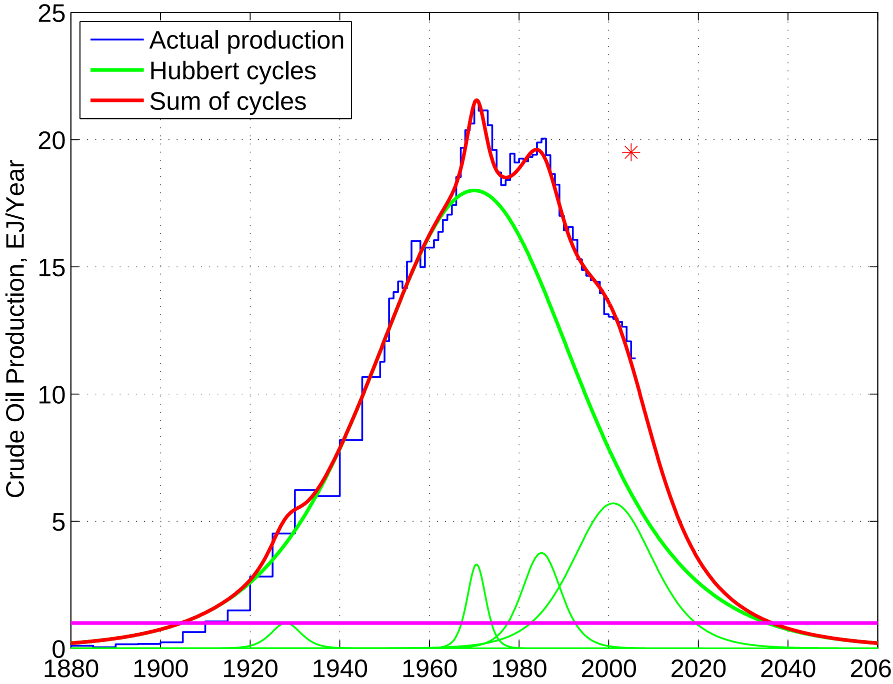


Figure 5.7: The HUBBERT cycle analysis of US crude oil/condensate endowment. The Main Cycle gives the original HUBBERT estimate of ultimate oil recovery of 200 billion bbl. The smaller cycles describe the new populations of oil reservoirs (Alaska, Gulf of Mexico, Austin Chalk, California Diatomites, etc.) and new recovery processes (waterflood, enhanced oil recovery, horizontal wells). Note that the total rate of production of all oil resources in the US goes through a peak, and *cannot* continue growing exponentially. In fact, in 2003, the total US oil production decreased all the way down to the 1950 level. The star shows the higher heating value of automotive gasoline burned in the US in 2004.

5.6.1 Logistic Growth

The cumulative mass production or yield in logistic growth depends on time as follows (Verhulst, 1838):

$$m(t) = \frac{m_{\max}}{1 + e^{-r(t-t^*)}} \tag{5.1}$$

where $m_{\max}$ is the ultimate production or carrying capacity, r is the fractional rate of growth; t is time, and t^* is the time of maximum production rate:

$$t^* = \frac{1}{r} \ln \left(\frac{m_{\max}}{m(0)} - 1 \right) \tag{5.2}$$

Remember that $m(0) > 0$!

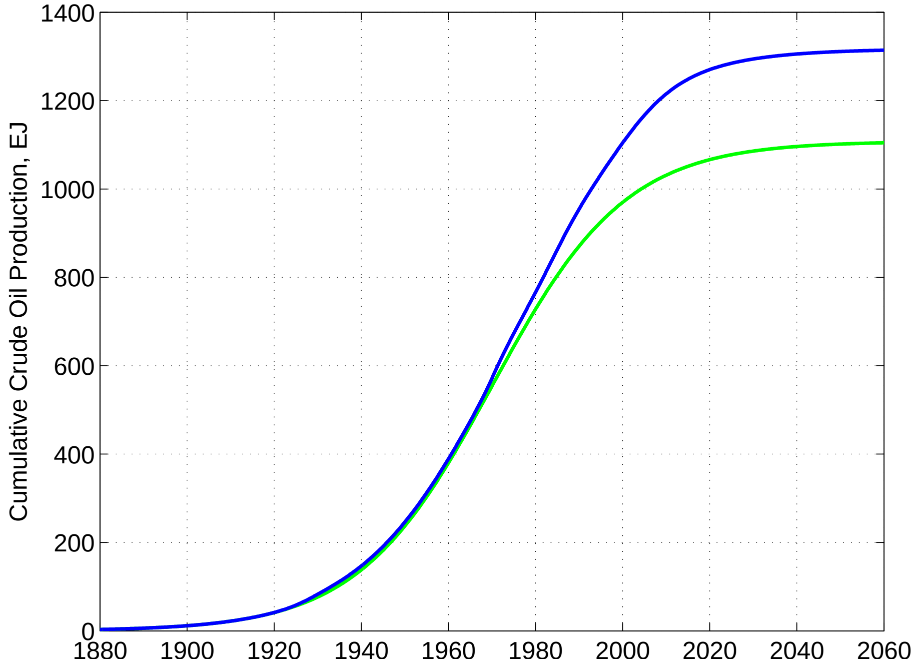


Figure 5.8: The cumulative oil production in the US cannot continue growing forever. The difference between the main HUBBERT cycle and the total recovery is equal to twice the total US energy consumption in 2003. This difference is the contribution of new technology and research in the oil industry. Coincidentally, this difference is equal to 650 years of ethanol production at 5 billion gallons per year.

The production rate can be obtained by differentiation of the cumulative production $m(t)$:

$$\dot{m} = \frac{dm}{dt} = \frac{2\dot{m}^*}{1 + \cosh[r(t - t^*)]} \tag{5.3}$$

where $\dot{m}^*$ is the peak production rate.

It may be easily shown that

$$m_{\max} = 4\dot{m}^*/r \tag{5.4}$$

5.6.2 Logistic vs. Gaussian Distribution

The logistic equation (5.1) and its derivative, Eq. (5.2), are close (*but not identical*) to the Gaussian distribution centered at t^*, and having the standard

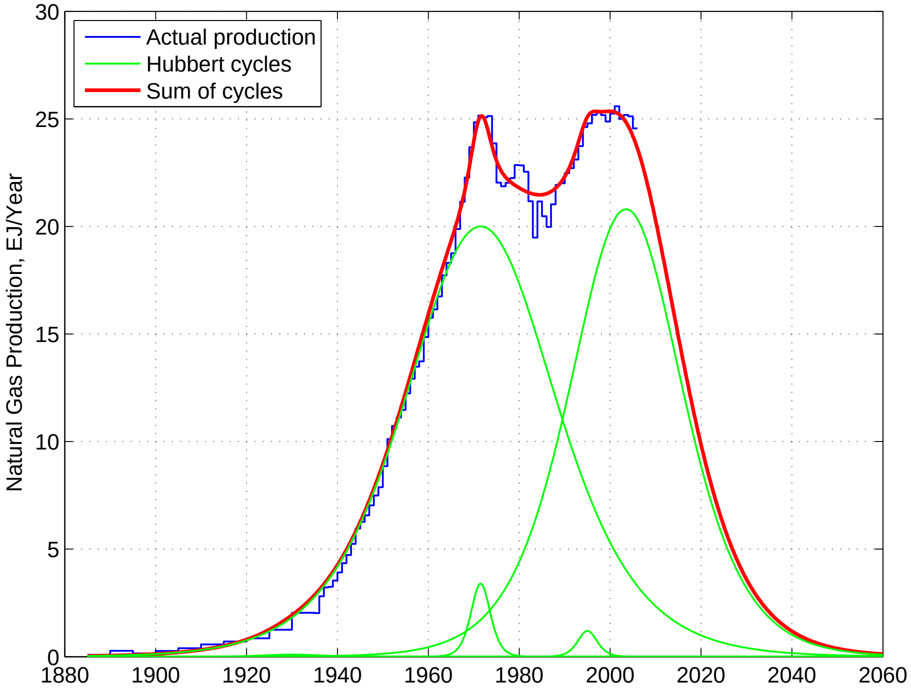


Figure 5.9: The HUBBERT cycle analysis of US natural gas endowment. There are two main cycles. The original HUBBERT cycle for conventional natural gas peaked in 1973. The second comparable cycle, mostly from the Gulf of Mexico gas fields and unconventional gas fields, saw the peak drilling activity in 1981. Note that the domestic production rate of natural gas will be declining soon at 15-20% per year. The gas produced from the second main HUBBERT cycle will be exhausted in the next 20 years.

deviation, σ, related to r as follows:

$$\sigma \approx \frac{1.76275}{r\sqrt{2\ln 2}} \qquad \text{Matched half-widths} \tag{5.5}$$

or, better,

$$\sigma \approx \frac{4}{r\sqrt{2\pi}} \qquad \text{Matched peaks} \tag{5.6}$$

See **Section 5.8** for the derivations.

The cumulative logistic growth and its rate are then given by the following equations:

$$m(t) \approx \frac{m_{\max}}{2}\left[1 + \mathrm{erf}\left((t - t^*)/\sqrt{2}\sigma\right)\right] \tag{5.7}$$

where $\text{erf}(x) = 2/\sqrt{\pi} \int_0^x e^{-t^2} dt$ is the error function

$$\dot{m} = m_{\max} \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(t-t^*)^2}{2\sigma^2}\right] \tag{5.8}$$

The two coefficients in red rescale the normal distribution to the actual production history.

An argument advanced against HUBBERT has been that the depletion histories of oil reservoirs are distinctly skewed towards longer times. However, the Central Limit Theorem of statistics states (Davis, 1986) that if sets of random samples are taken from any population, the sample means will tend to be normally distributed. The tendency to normality becomes more pronounced for samples of larger size.

Alternatively, a HUBBERT cycle may represent a normal process, e.g, (Ott, 1995). Many variables found in nature result from the summing of numerous unrelated components. When the individual components are sufficiently unrelated and complex, then the resulting sum tend towards normality as the number of components comprising the sum becomes increasingly large. Two important conditions for a normal process are: (1) summation of many continuous random variables, and (2) independence of these random variables. A normal process is also called a random-sum process ($\mathcal{R}-\mathcal{S}$-process).

- We may think of all the oil reservoirs as of a very large *statistical population* characterized by the time-dependent, asymmetric distributions of every conceivable property.
- Throughout each year, we take a sample of the population by measuring the annual production q_i from every reservoir in the population.
- We then sum up all the annual outputs of the reservoirs.

$$S_j = \sum_{i=1}^{N} q_i(t_j)$$

- This sum is proportional to the sample average for a given year

$$< q_j >= \frac{1}{N} \sum_{i=1}^{N} q_i(t_j)$$

- The number of reservoirs in the sample should not change. As the reservoirs in the sample are exhausted their production rates are set to zero.
- As we repeat this process over time, each year we get a set of $< q(t_j) >$, $j = 1, 2, \ldots, N_T$.
- In effect, we sample different (time-dependent) distributions of properties of the underlying population and the distribution of the sample averages becomes *approximately normal.*

- We can repeat this procedure for each distinctly new population of reservoirs (multi-cycle analysis). For example, in the US, the giant Proudhoe Bay field, or the Austin Chalk fields, or the offshore Gulf of Mexico fields, should form separate populations.
- By virtue of the future, unaccounted for reservoir populations, the Hubbert cycles of the current populations will underestimate the ultimate world recovery.

We may also think about the U.S. annual oil production as of a random-sum process. The annual production of each reservoir can be considered a random continuous variable. When we sum up the annual outputs of many reservoirs, we obtain a sum of the independent continuous random variables. This sum is normally distributed when we repeat the summation over many years.

In the U.S., there have been over 25 000 active oil fields, so the number of random variables is very large. From one year to another, though, the underlying independent variables should not become related because of artificial constraints, such as production curtailment caused by proration by the Texas Railroad Commission.

New oilfield discoveries and improved oil recovery methods introduce new random variables, which should be summed separately. This is the essence of "multi-Hubbert" cycle modeling.

In his fascinating paper (Laherrere, 1999), Jean H. Laherrere explains that many natural processes may be modeled with multiple Hubbert cycles, each having a different peak and centered at a different time. In the context of the oil industry, this corresponds to creating new sub-populations through new field discoveries or new oil recovery techniques. Laherrere calls this approach the "multi-Hubbert" modeling.

5.7 Problems

1. Suppose that you wanted to put all corn grain produced in the U.S. in 2003, the 257 million metric tonnes of it, on a chessboard. The chessboard has 64 squares, and you start by putting 1 corn grain on the first square, 2 on the second, 4 on the third, etc. How many chessboard squares will this grain occupy? Assume that 1000 corn kernels weigh 0.333 kg. The corn grain crop in the U.S. is the largest on the earth, and it constitutes 40% of all corn produced worldwide each year. How many more chessboard squares will be covered with the world production of corn? If we were to cover all 64 squares of the chessboard with corn grain, how many times more grain than the world annual production of corn would there be on the last square?
2. 156 million square kilometers of the earth surface is land. If you started from a single Model T Ford automobile, then doubled the production to 2 Fords, then doubled it again, and again, how many production doublings

would it take to cover the entire land area on the earth with cars that touch each other? Assume that one average car is 5 meters long and 2 meters wide.

3. Find on the Web the global production of crude oil going back from 2006 or 2004 as far back as you can get. Convert the barrels to exajoules using 44.8 $\mathsf{MJ\ kg}^{-1}$ of oil equivalent and 134 kg of oil equivalent per barrel. Calculate the initial exponential rate of growth of world oil production.

   Hint: My answer is in **Figure 5.10**.

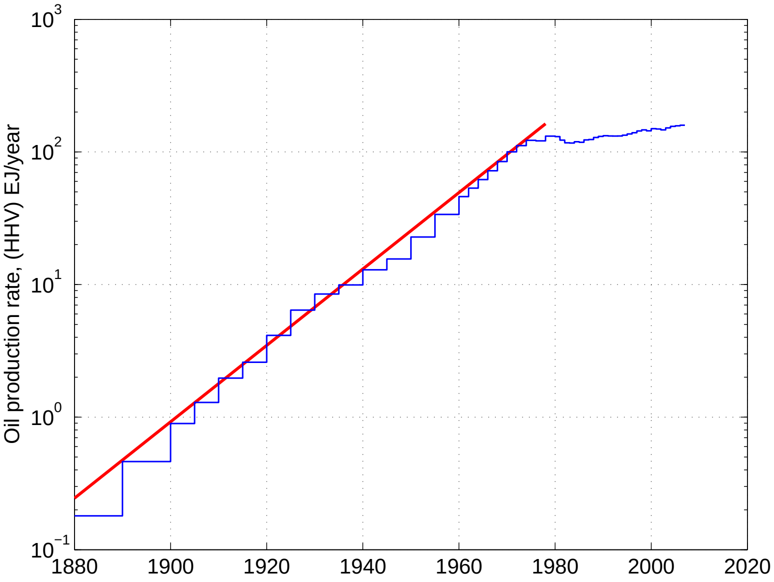


Figure 5.10: Exponential growth of world crude oil production between 1880 and 1970. Source: lib.stat.cmu.edu/DASL/Datafiles/Oilproduction.html.

4. Taking ethanol production statistics from the Renewable Fuel Association (RFA), www.ethanolrfa.org/industry/statistics, at face value[2], calculate the following:

   (a) The initial exponential rate of ethanol production. Comment on your estimated rate of exponential growth, and how it compares with other known exponential rates of resource production. Use an estimated production of 4700 million gallons of denatured ethanol in 2006. Try to use the HHV of ethanol, and multiply the RFA-reported volumes by 0.95 to eliminate the #14 gasoline denaturant and convert them to HHV using Table 3.2.

---

[2] The DOE and then RFA data were of poor quality up until 1995, or so, because of the sloppy reporting by the nascent industry, and ethanol production and import/export manipulations by ADM.

Hint: My answer is in **Figure 5.11**.

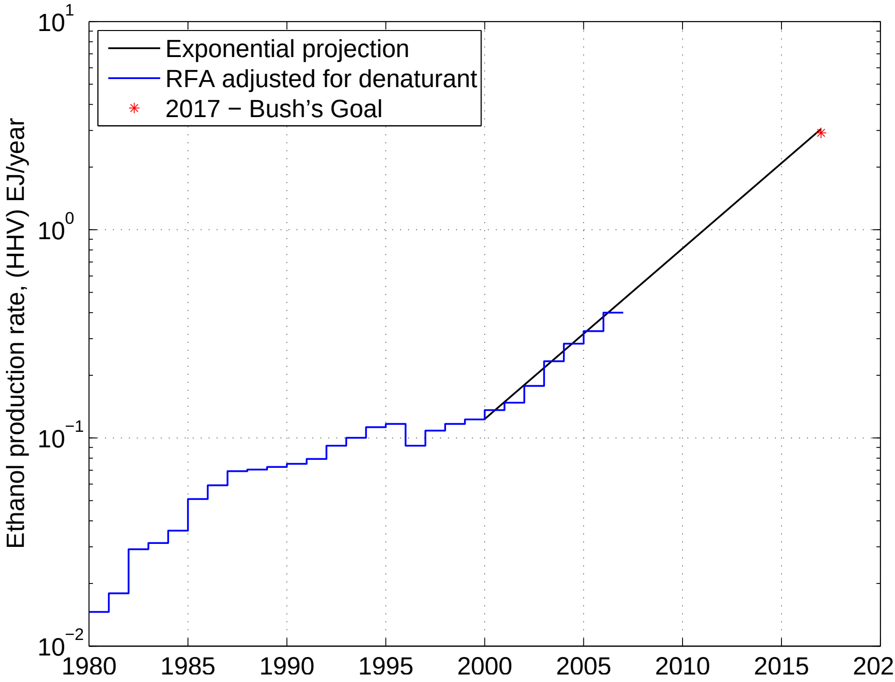


Figure 5.11: Exponential growth of ethanol production in the US between 2000 and 2017 required to implement President Bush's "vision."

(b) (**Difficult Bonus**) Try to fit a logistic S-curve to the data between the year 2000 and 2006. The early years are contaminated by the complete domination of US ethanol production by Archer Daniels Midland company and its production level manipulations. Note that ethanol production actually declined in 1996.

Hint: My answer is in **Figure 5.12**.

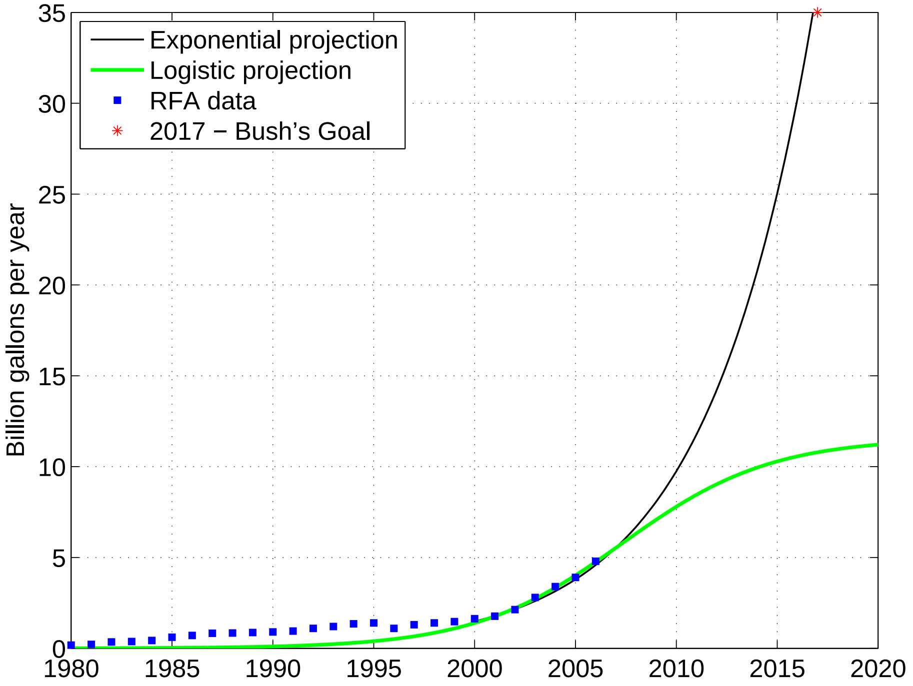


Figure 5.12: Exponential and logistic growth of ethanol production in the US between 2000 and 2017. Note that the logistic rate curve fits perfectly the RFA data between 2000 and 2006. The predicted plateau of sustained maximum ethanol production from US corn is 11 billion gallons per year.

(c) Now suppose that the US population grows according to the predictions by the Census Bureau. Let the US transportation fuel consumption grow with the population (no conservation measures). Assume that in the year 2006, 34 EJ in liquid transportation fuels were used by 300 000 000 people in the US, see **Figure 3.4**. Will the increase of ethanol production be able to keep pace with the increasing demand? Use your exponential projection and my logistic projection. What are your conclusions?

5. Suppose that the world oil production rate can be described as the sum of these two logistic curves: $\dot{m}_1^* = 160.0$ EJ year^{-1}, $t_1^* = 2008.5$, $r_1 = 0.059$; and $\dot{m}_2^* = 57$ EJ year^{-1}, $t_2^* = 1976.5$, and $r_2 = 0.27$. Suppose that the US per capita oil consumption is kept constant at the 2005 level and will grow only in proportion to the population growth. Calculate when the US oil consumption will be equal to the world oil production.

6. According to FAO (Global Forest Resources Assessment, 2005, www.fao.org/-forestry/site/fra2005/en/), the total area of forests in Indonesia has decreased from 116.6×10^6 ha in 1990 to 88.5×10^6 ha in 2005. In other words, an area equal to 28 million ha was logged, burned, and converted to agriculture and other uses. In comparison, corn in the US is grown on roughly 30 million ha, or one Arizona worth of fertile land area.

   (a) Assuming 145 tonnes ha^{-1} of dry above-ground biomass (Page et al., 2002; Patzek and Pimentel, 2006), calculate the total CO_2 emissions from this biomass in gigatonnes. Assume that the elemental composition of wood is C:O:H:N 44:45:5.8:1.2 by *mass*. Now assume that 1/2 of the removed forest grew on swampy peat, which was drained, dried, and also burned. This peat can be 20 meters thick in places. Assume that the burned peat stored 700 tonnes of carbon per hectare on the average (Page et al., 2002). Compare this release with the cumulative CO_2 emissions from the Unites States over the same time interval, see cdiac.ornl.gov/ftp/trends/emissions/usa.dat.

   Answer: $6.7 + 36 = 42.7$ gigatonnes of CO_2 were released from burning the forest and peat, respectively, without accounting for the nitrogen and sulfur oxides. Over the same time period, the US released about 87 gigatonnes of CO_2, or roughly twice as much.

   (b) The estimated historical area of palm oil plantations in Indonesia is listed in **Table 5.1**. Calculate the area's rate of exponential growth in percent per year. If the planation area continues to grow uninterrupted, by when 50% of the remaining forest in Indonesia will be cut?

   Hint: My answer is in **Figure 5.13**.

Table 5.1: Oil palm plantation area in Indonesia. Source: FAO

Year	Area[a]	Year	Area[a]
1962	0.070	1982	0.239
1963	0.079	1983	0.269
1964	0.089	1984	0.319
1965	0.090	1985	0.362
1966	0.081	1986	0.407
1967	0.080	1987	0.485
1968	0.080	1988	0.565
1969	0.084	1989	0.645
1970	0.101	1990	0.747
1971	0.099	1991	0.844
1972	0.093	1992	0.907
1973	0.101	1993	1.019
1974	0.111	1994	1.168
1975	0.135	1995	1.395
1976	0.123	1996	1.596
1977	0.144	1997	1.784
1978	0.177	1998	1.841
1979	0.191	1999	1.982
1980	0.207	2000	2.167
1981	0.231	2001	2.736

[a] Million hectares

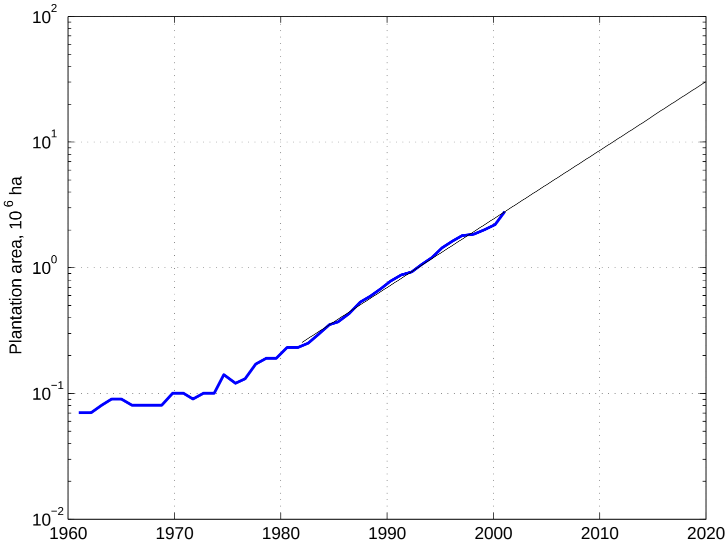


Figure 5.13: Projected exponential growth of oil palm plantation area in Indonesia.

7. (**Bonus**) Demonstrate validity of Eqs. (5.2) - (5.8). Plot the corresponding logistic and normal curves for production rates and cumulative production.

8. Show that the time derivative of

$$\begin{aligned} m(t) &\approx \frac{m_{\max}}{2}\left[1+\operatorname{erf}\left((t-t^*)/\sqrt{2}\sigma\right)\right] \\ \operatorname{erf}(x) &:= \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt \end{aligned} \tag{5.9}$$

is

$$f_1(t;\sigma,t^*,m_{\max}) = m_{\max}\frac{1}{\sqrt{2\pi}\sigma}\ \exp\left[-\frac{(t-t^*)^2}{2\sigma^2}\right] \tag{5.10}$$

5.8 Matching the Logistic and Normal Distributions

This section contains material not required in first reading.

To approximate the Gaussian distribution (rate) curve,

$$f_1(t;\sigma,t^*,m_{\max}) = m_{\max}\frac{1}{\sqrt{2\pi}\sigma}\ \exp\left[-\frac{(t-t^*)^2}{2\sigma^2}\right] \tag{5.11}$$

with the logistic curve,

$$f_2(t;r,t^*,m_{\max}) = \frac{m_{\max}r}{2}\ \frac{1}{1+\cosh[r(t-t^*)]} \tag{5.12}$$

we will first attempt to match their full widths at 1/2 heights.

For the Gaussian distribution

$$\begin{aligned} &f_1(t_0;\sigma,t^*,m_{\max}) = \frac{1}{2}f_1(t^*;\sigma,t^*,m_{\max}) \\ &\frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(t_0-t^*)^2}{2\sigma^2}\right] = \frac{1}{2}\ \frac{1}{\sqrt{2\pi}\sigma} \\ &\exp\left[-\frac{(t_0-t^*)^2}{2\sigma^2}\right] = \frac{1}{2} \end{aligned} \tag{5.13}$$

and

$$\begin{aligned} \frac{(t_0-t^*)^2}{2\sigma^2} &= \ln 2 \\ t_0 &= \pm\sigma\sqrt{2\ln 2}+t^* \end{aligned} \tag{5.14}$$

The full width at half maximum is therefore

$$2\sigma\sqrt{2\ln 2}$$

for the Gaussian distribution.

For the logistic distribution

$$\begin{aligned} &f_2(t_0;r,t^*,m_{\max}) = \frac{1}{2}f_2(t^*;r,t^*,m_{\max}) \\ &\frac{m_{\max}r}{2}\ \frac{1}{1+\cosh[r(t_0-t^*)]} = \frac{m_{\max}r}{8} \\ &\frac{1}{1+\cosh[r(t_0-t^*)]} = \frac{1}{4} \\ &\cosh[r(t_0-t^*)] = 3 \end{aligned} \tag{5.15}$$

An approximate solution to this transcendental equation is $r(t_0-t^*) \approx 1.76275$. The full width at half maximum is therefore

$$\frac{3.5255}{r}$$

for the logistic distribution.

To match the respective full widths, we require that

$$\begin{aligned} 2\sigma\sqrt{2\ln 2} &= \frac{3.5255}{r} \\ \sigma &= \frac{1.76275}{r\sqrt{2\ln 2}} \end{aligned} \tag{5.16}$$

To match the peaks, we require that

$$\begin{aligned} \frac{m_{max}}{\sqrt{2\pi}\sigma} &= \frac{rm_{max}}{4} \\ \sigma &= \frac{4}{r\sqrt{2\pi}} \end{aligned} \tag{5.17}$$

Since heights of the two distributions are somewhat different for equal half-widths (the t_0 in Eq. $(5.15)_4$ is in fact different than that in Eq. $(5.13)_3$), the half-width match is approximate, see **Figure 5.14**. The peak matching is also approximate, see **Figure 5.15**, but seems to be better.

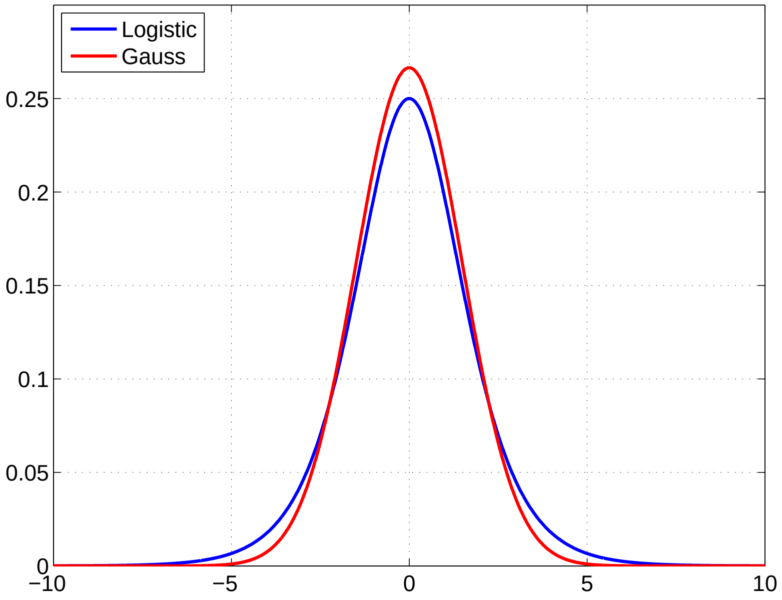


Figure 5.14: Logistic vs. normal distribution with matched half-widths, for $r = 1$, $t^* = 0$, $\dot{m}^* = 1/4$.

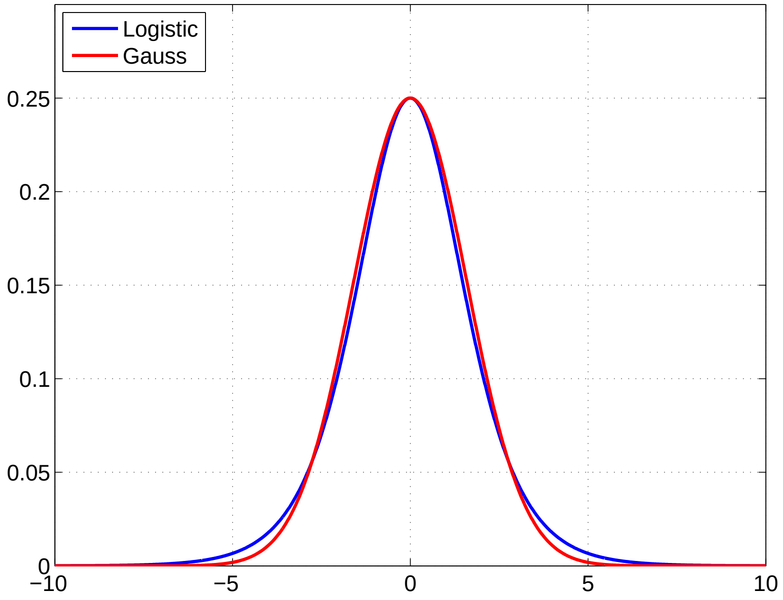


Figure 5.15: Logistic vs. normal distribution with matched half-peaks, for $r = 1$, $t^* = 0$, $\dot{m}^* = 1/4$.

Chapter 6

Geologic Time Scale on the Earth

> *All flesh is grass, and all the glory of man is the*
> *flower of grass. The grass withers, the flower fades...*
>
> — Prophet Isaiah (c.760-690 B.C.)
> *Isaiah 40.6-8*, (Septuagint)

6.1 What Are you Going to Learn?

Topsoil is a thin membrane that separates the Earth interior from the atmosphere in most places on land, protects it from pollutants, and supports life. You will learn how this membrane was made over the last 400-500 million years.

6.2 Why Is It Important?

Topsoil mineral material has been created by weathering rock minerals, washing them down slope by water, and scraping them off bed rock by ice sheets. Water flow on the Earth is determined by the Sun's radiation, the Earth's rotation, its atmosphere, and the physical and chemical properties of Earth's surface and the uppermost layers of her crust. Local flow of water is often determined at much larger scales. Top soil organic material has been created and reworked mostly by plants, bacteria, fungi, earth worms, and other critters. Complex connections among soil, water, and life, at different spatial and temporal scales are usually ill understood, and you should know about them.

6.3 Geologic Time Scales

Conservatively, one may estimate that 440 millions years ago land was firmly colonized by plants. Before, it took perhaps another 100 million years for the plants and animals to spread and diversify.

Inspired by WES JACKSON'S great book (Jackson, 1980), let me shrink time since the beginning of the Silurian period to 1 year, see **Figure 6.1**. On this new time scale, the living Earth has had *over 1 year* to make topsoil, sediments, aquifers, natural gas, crude oil, and coal. The oldest samples of crude oil from red algae are almost 4 years old, see **Figure 6.2**. In early January, the leafless vascular plants, *psilophytes*, were plentiful. Club mosses, horsetails, forest trees (*Cordaites*), and ferns developed by early April, and ferns and conifers in late May. They all flourished in late June, as well as cycads and ginkgoes, and later became so much coal. In August, the cycads and cycadeoides dominated, and conifers and ginkgoes became widespread. In early October, early flowering plants (*angiosperms*) and modern trees appeared on the Earth. In the first days of November, dinosaurs died and by mid-November mammals spread to all continents. In early December, the Earth cooled, grasslands expanded, and forest regions diminished. By late December, grasslands replaced forests over large areas on several continents. Just after midnight of December 28, the hominids *Australopithecines* lived in Africa.

If we now zoom on December of our geological year as in **Figure 6.3**, we see the following: On St. Nick's Day, early primates became visible on the Earth. On the First Day of Christmas the Antarctic ice sheet approached its present-day size and thickness. At noon of December 30, the Great Ice Age began making more soil than perhaps at any other month of this memorable

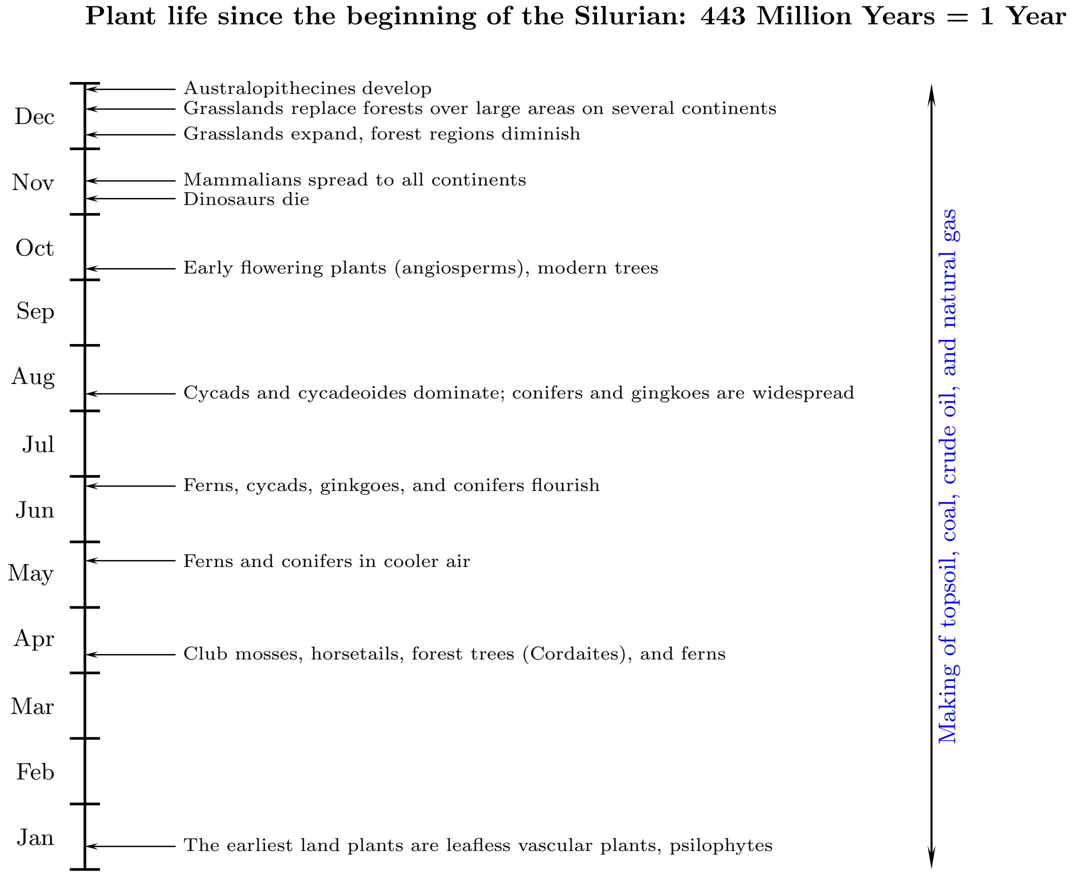


Figure 6.1: Life evolution since the beginning of the Silurian period 443 million years ago is mapped onto one calendar year. Note that I shaved more than 100 million years from the onset of the Cambrian Explosion of animal and plant life. On January 1 of this imaginary year, land was firmly colonized by plants. On this time scale, the oldest shale with crude oil from the Proterozoic red algae is almost 4 years old.

year. The oldest human species, *Homo habilis* were first seen in the early hours of New Year's Eve.

Let's now focus on the last day of December, see **Figure 6.4**. Just before noon, the common ancestor of modern humans and Neanderthals was seen. Just before 6 pm, a primitive human, *Homo heidelbergensis*, left footprints in powdery volcanic ash. By 9 pm, the earliest *Homo Sapiens* was spotted near the Omo River in Ethiopia. Our genetic Eve lived at 10 pm, and by 11 pm modern Homo Sapiens appeared in Africa. Just before midnight glaciers retreated after the last Ice Age, and agriculture-based civilizations developed and changed everything on the Earth.

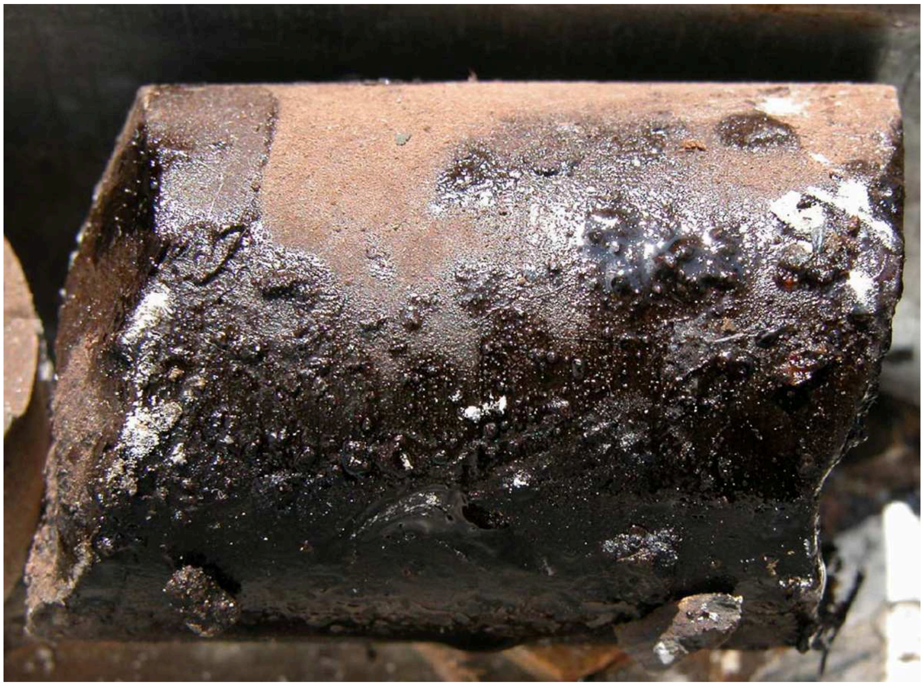


Figure 6.2: The oldest known live oil seeping out of a dolomitic mudstone of the 1.64 Ga Barney Creek Formation, Australia (drill core McA20; 375 meters depth). The oil source were red algae. Photo: Jochen J. Brocks, 4 August 2003.

Let us now look at the last hour-and-a-half of the last day of December, **Figure 6.5**. One hour and 10 minutes before midnight our ancestral Adam was spotted. One hour before midnight, humans migrated from Asia to Australia and Europe. Twenty five minutes later they arrived in North America. Just about 30 minutes before midnight the Neanderthals became extinct, and 20 minutes later humans reached across South America, thus colonizing all continents except Antarctica. About 9 minutes before the New Year's champagne and wishes, the earliest evidence of human culture was detected in Mesopotamia. Three minutes later the Egyptian civilization started, and in another three minutes the Greek civilization was gone.

Finally we zoom on the last 20 seconds of this extraordinary year in Earth's history, **Figure 6.6**. This last blink of geologic time belongs to humans. Seventeen seconds ago, the North American colonists declared their independence. In the 13th second the world population reached 1 billion. In the 11th second the US prairies were plowed, and half a second later oil was discovered in Pennsylvania. Mass oil and automobile production began in the US with 8 seconds before midnight. The Haber-Bosch process of producing ammonia became commercial 2 seconds later, and in another half a second the world population exceeded

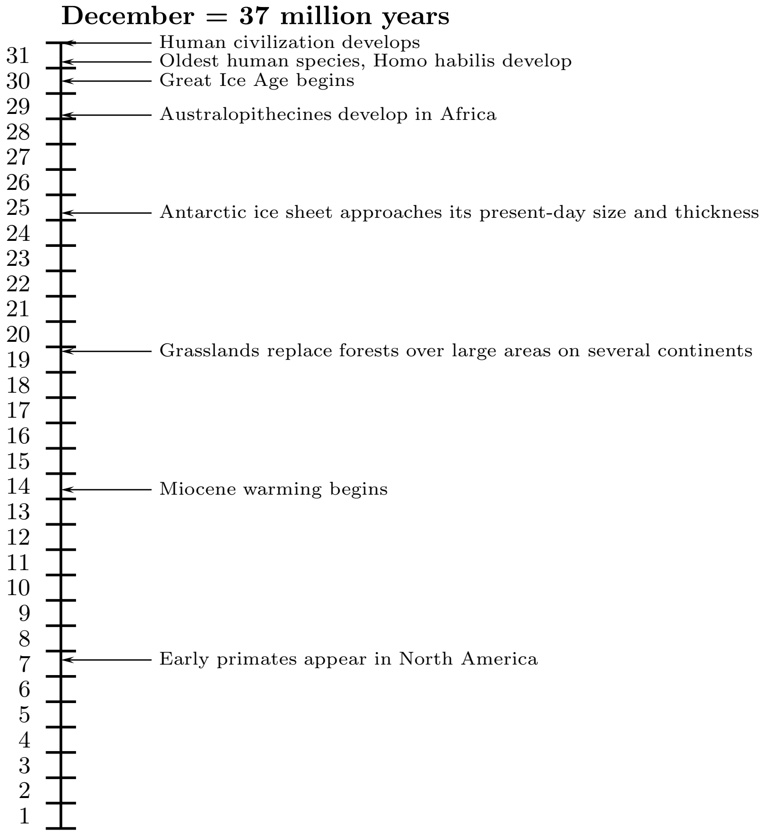


Figure 6.3: A history of the recent 37 million years mapped onto December of the imaginary calendar year of life evolution.

2 billion people. Can you hear the crowds shouting "Five!, Four!,..."? Just before "Four!" it was not a cork popping, but an atom bomb was dropped on Hiroshima. Between "Two!" and "Three!" 1/2 of US oil endowment was produced, and more that 1/3 of agricultural topsoil went to the sea. After "One!" was heard, the world population exceeded 6 billion people. Happy New Year everyone!

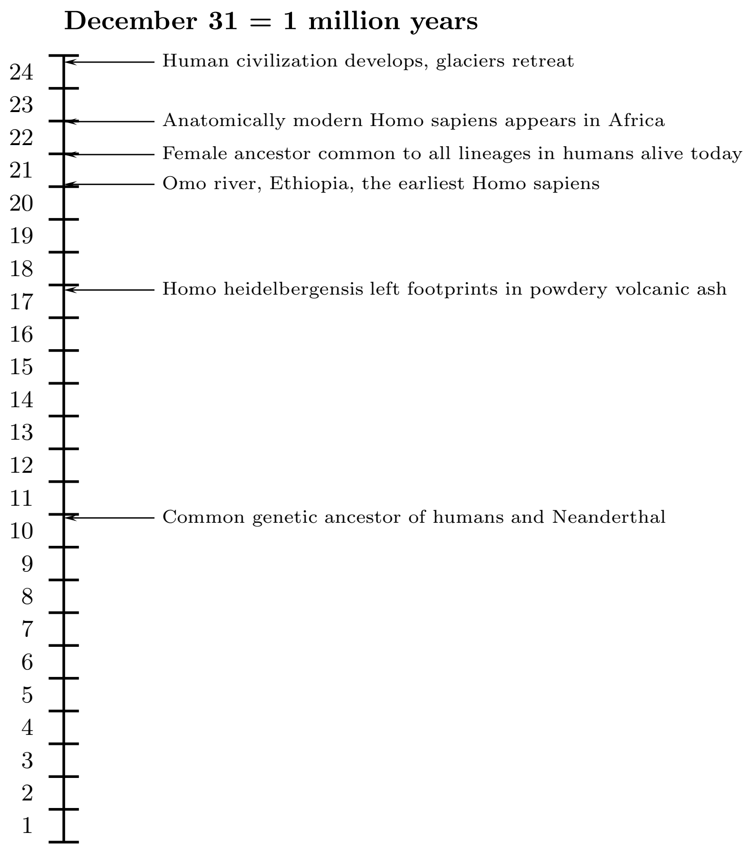


Figure 6.4: A history of the recent 1 million years mapped onto December 31 of the imaginary calendar year of life evolution. The mitochondrial Eve in Africa was born about 2 hours before midnight, or 150,000 years ago. She is the earliest female ancestor common to all mitochondrial lineages in humans alive today.

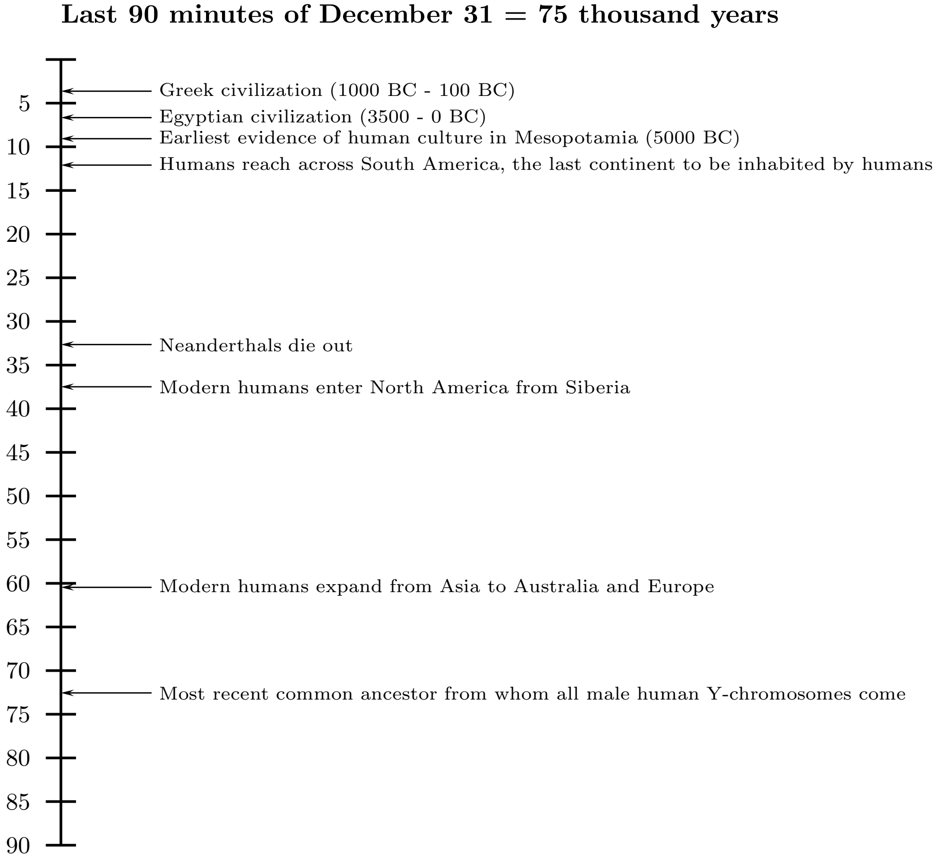


Figure 6.5: A history of the recent 75,000 years mapped onto the last 90 minutes of December 31 of the imaginary calendar year of life evolution. The Greek civilization started 4 minutes before midnight. The Y-chromosomal Adam was born in Africa (most likely Ethiopia or Sudan) 72 minutes before midnight or 60 thousand years ago. He is the most recent common ancestor from whom all male human Y chromosomes are descended.

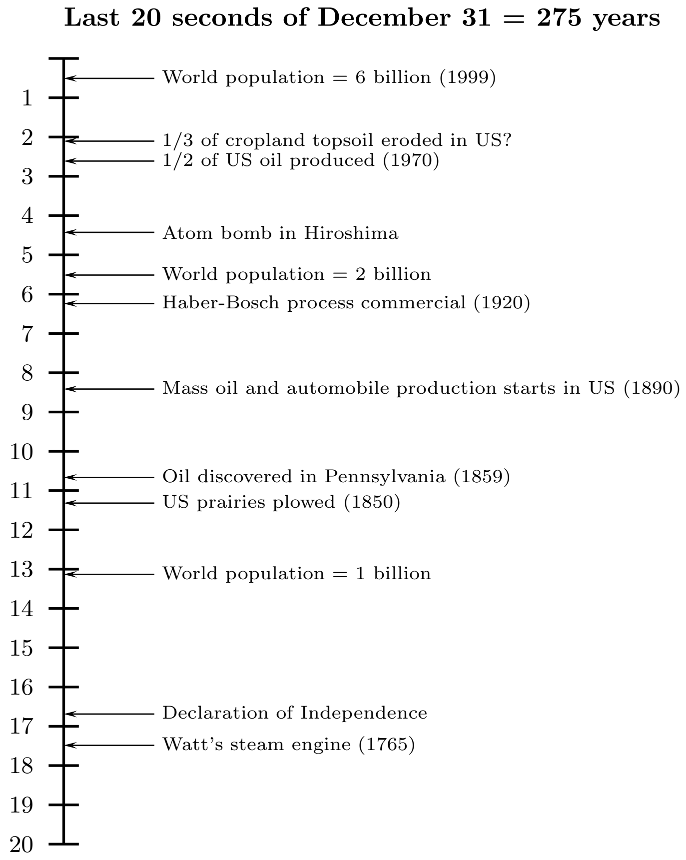


Figure 6.6: A history of the recent 275 years mapped onto the last 20 seconds of December 31 of the imaginary calendar year of life evolution. The prairies were plowed and oil discovered about 11 seconds before midnight. By 2 seconds before midnight, 1/3 of agricultural topsoil and 1/2 of crude oil were gone in the US. Note that all of this oil and soil were produced in mere 6 seconds!

Chapter 7

Basic Thermodynamics

> *We are not such optimists as were our teachers and parents. We do not have to equate "progress" with every $\delta f(t)$, if $\delta t > 0$, t being the time. . . . No-one will be surprised, consequently, by my use of a delta to define progress, since thermodynamics is the kingdom of deltas.*
>
> — Clifford Truesdell
> *The Tragicomical History of Thermodynamics 1822 – 1854* (1980)

7.1 What Are you Going to Learn?

You are going to learn the minimal set of definitions necessary to understand basic thermodynamics.

7.2 Why Is It Important?

Before you learn about the First and Second Law of thermodynamics and their consequences for ecosystems, you need to learn how to define and describe a thermodynamic system.

7.3 Introduction

When I was pondering "why write anything about thermodynamics?" I recalled that a man was once asked if he would go to a concert to hear a new brilliant performance of Beethoven's Fifth Symphony. He answered "No way, I've already heard it!" Reading another text on thermodynamics may lead to pretty much the same reaction. Little new has been said in classical thermodynamics after JOSIAH WILLARD GIBBS, **Figure 7.1**, the best American-born scientist of all times. So here I can only give you my insights and interpretation of thermodynamics, and make it easier for you to cope with this wonderful, general, and confusing science. In this role, I am just another conductor of the same Great Symphony of the Universe, also known as Thermodynamics.

In my lectures I will be relying heavily on the work of three master conductors *and* composers of thermodynamics: Professor JOSEPH H. KEENAN, Mr. GEORGE N. HATSOPOULOS, both from MIT, and Professor JOSEPH KESTIN of Brown University[1]. The other three great virtuosi of thermodynamics who taught at my Alma Mater, The Silesian Technical University in Poland, were Professors STANISŁAW OCHĘDUSZKO, TADEUSZ HOBLER and, most of all, JAN SZARGUT, who studied with both my parents, aunt and uncle, and has remained a friend of my family. I have learned a great deal from all of them, and will try to do justice to their excellent and quite lengthy monographs (Hatsopoulos and Keenan, 1965; Kestin, 1979a; Kestin, 1979b; Szargut et al., 1988).

7.4 Body, Primitive Property, and State

Definition 3 A **body** is whatever is enclosed by a well-defined surface which may be either material or imaginary, and through which matter does not pass.□

A body may assume different conditions at different times. The conditions a body assumes are described by its primitive properties.

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[1] Professor Kestin (1913 – 1993) was born in Warsaw and graduated from Technical University there in 1937. He fled the occupied Poland, reached England during World War II and earned his doctorate at the Imperial College in London.

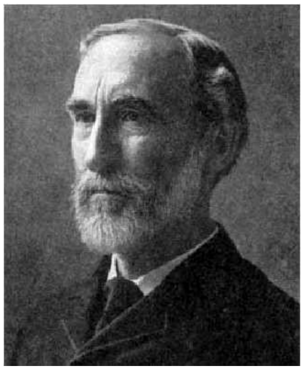

Figure 7.1: Josiah Willard Gibbs (1839 – 1903) was a modest shy man, who spent his whole professional life at Yale. He was known to just a few of the world's scientists – partly because his writings were extremely compact, abstract and difficult. As one of Gibbs' European colleagues wrote, "Having once condensed a truth into a concise and very general formula, he would not think of churning out the endless succession of specific cases that were implied by the general proposition; his intelligence, like his character, was of a retiring disposition."

Definition 4 A **primitive property** of a body is specified by describing an operation or a test to which the body is subjected. The value of this property at certain time is the result of the operation performed at that time. □

Definition 5 **State** is the condition of the body which is identified by means of all its primitive properties. A change of state of a body occurs when at least one of its primitive properties changes value. □

7.5 The System

In thermodynamics we divide reality into two slices: one representing the *system* determined by our interest, and the second, its *environment*, see **Figure 7.2**. These two parts are separated by an *analytic*[2] *boundary.* The boundary has two attributes. The first separates the system from the environment at any time (we can call this attribute the *interface*, or the *frontier*), and the second defines the *duration* of the system[3]. The terms *system* and *environment* are used interchangeably with *process* and *surroundings.*

> We may not describe a system by what happens inside or outside of it, but only by what crosses its boundary.

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[2] The word *analytic* means well-defined mathematically in space and/or time.

[3] The system is not defined outside its time interval.

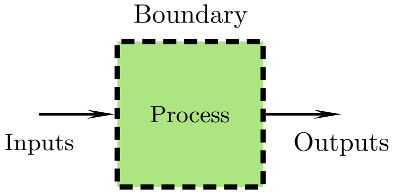

Figure 7.2: The *boundary* separates the process from the environment at any time (it is the *interface*), and it defines the *duration* of the process. We *may not* describe a process by what happens inside or outside of it, but only by what crosses its boundary.

Anything of interest crossing the boundary from the environment into the system is an *input*, and anything crossing the boundary in the opposite direction is an *output*. Solar energy is a typical example of only an input for any terrestrial system. Synthetic chemicals not present in nature are examples of only outputs. Because of the properties of its boundary, a system may or may not be able to exchange mass, work, heat, and/or energy with the surroundings. In other words, a system may be *closed* or *open* with respect to any or all of these exchanges.

7.5.1 A Simple System

A simple system is any system that is not influenced by capillarity, shape (shear) distortion of the solid phase, external force fields (gravitational, electric or magnetic), or internal adiabatic[4] walls.

7.5.2 Path

Path is the complete series of states a system assumes during a change of state. A path is usually identified only for slow changes of state. Rapid changes may result in states that cannot be described by classical thermodynamics or are too short-lived to measure their properties.

7.5.3 Thermodynamic Process

Now we can say that a process causing a change of state of a system is described by the initial and final state of the system, the path of the system, and the phenomena occurring at/across the boundary of the system.

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[4] The term *adiabatic* is from Greek *adiabatos* impassable (to heat).

Figure 7.3: **Left:** MIKHAIL VASILYEVICH LOMONOSOV (1711 – 1765) rejected the phlogiston theory of matter (Greek flammable *phlogistos*; a substance without color, odor, taste, or weight that is liberated in burning) commonly accepted at the time, and anticipated the kinetic theory of gases. He regarded heat as a form of motion, suggested the wave theory of light, and stated the idea of conservation of matter. **Right:** ANTOINE-LAURENT de LAVOISIER (1744 – 1794), whose careful weighings showed that mass is conserved in chemical reactions and that combustion involves a new element he named *oxygen*.

Real Processes

An infinitely slow process of rasing a weight in the gravitational field with no friction is *reversible*. If it is reversed, both the state of the system, and the state of its surroundings are restored.

Real processes are *irreversible* and can be characterized as follows:

1. An irreversible process occurs at a finite rate.
2. It proceeds in a definite direction.
3. It is started from an equilibrium state as a consequence of removing a *constraint*, and ends by the system assuming another equilibrium state.
4. The system is *not* in equilibrium during the process.
5. The process cannot be reversed without introducing *changes* in the immediate surroundings and in the constraints of the system.

If an *irreversible* process $1 \rightarrow 2$ has taken place between two equilibrium states, this does not mean that the initial equilibrium state 1 can *never* be restored from equilibrium state 2. In fact this is always possible by a suitable interaction with the surroundings.

7.5.4 Cycle

A cycle is a process whose end states are identical. Many processes in nature are cycles. Many industrial processes of importance, e.g., the mining of minerals, burning of fossil fuels, agriculture, deforestation, etc., are *not* cycles on the human time scale (or at any time scale).

7.6 General Definition of a Property

Any quantity whose value depends only on the state of a system is a **property**. The following are three corollaries of this definition

Corollary 1 *The change in the value of a property is fixed by the end states of a system undergoing a change of state and is independent of the process.* □

Corollary 2 *Any quantity which is fixed by the end states of a process is a change in the value of a property, provided that the sum of such quantities for a sequence of process steps equals the quantity evaluated for the overall process. (For example a change of volume* ΔV *and a change of the square of volume* ΔV^2 *are both fixed by the end points of a process, but only* ΔV *is the change of property.* □

Corollary 3 *The change in the value of any property in a cycle is zero.* □

Corollary 4 *Any quantity whose change in a cycle is always zero is a property of the system, provided that the sum of such quantities for a sequence of processes equals the quantity evaluated for the entire process (the quantity is additive, see the equivalent Corollary 2).* □

The change of a property in any process (*reversible* or *not*) that connects two states is equal to the change of this property in any reversible process. This is how we calculate property changes in thermodynamics. See Chapter 10 for more information on reversible and irreversible processes.

7.6.1 Independent Properties

Not all properties of a system may be varied independently of each other; that is we may not be able to vary a given property while keeping a prescribed set of properties fixed. If one can vary one property by a finite amount without changing another one, these two properties are *independent*.

The set of all properties of a system necessary and sufficient to determine the state of the system is called a *complete set of independent properties*.

7.7 The Law of Mass Conservation

The fundamental axiom of *mass conservation* that dates back[5] to ANTOINE-LAURENT de LAVOISIER (1789), **Figure 7.3**, can only be put to use relative to the *system boundary*:

- The mass of a closed system of matter remains constant, regardless of the processes acting inside the system.
- Matter changes form, but cannot be created nor destroyed. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products.
- In chemistry, so long as no nuclear reactions take place, a special form the conservation of mass also holds in regard to the conservation of the mass (and number of atoms) of each chemical element. In chemical reactions alone, atoms of no element may be created or destroyed.

In addition, mass cannot jump from between remote places (Hatsopoulos and Keenan, 1965):

Definition 6 Law of Mass Continuity: Mass cannot change from one position to another without passing through the intervening space. □

The unit of mass is 1 kg. One mole of carbon C^{12} isotope, or 6.0225×10^{23} carbon atoms, has the mass of 12 grams exactly.

7.8 Allowed States of a System

Definition 7 Allowed states of a system are all the states that the system can assume without violating (1) the laws of mass conservation and mass continuity, (2) passive resistances, and (3) constraints. □

7.8.1 Passive Resistances

Passive resistances allow us to ignore certain modes of behavior of the system for which the time required is much longer than that required for other modes which are of immediate interest to us.

For example, hydrogen and oxygen molecules at normal pressure and room temperature will not combine appreciably into water in one hour, even if we change the temperature and pressure a little. If we wait for one year, however, we cannot be so sure. We can say that the chemical reaction between H_2 and O_2 is prevented by a passive resistance for one hour. A *catalyst* is a destroyer of such passive resistances. An *anticatalyst* creates them.

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[5] The famous Russian scientist, polymath and writer MIKHAIL VASILYEVICH LOMONOSOV (1748) had previously expressed similar ideas and proved them in experiments.

Definition 8 A passive resistance prevents certain modes of behavior of the system regardless of what the state the system may assume or to what influences it may be subjected. □

The states a system with passive resistances may attain during a process may be radically different from those attained by the same system without these resistances.

7.8.2 Constraints

Constraints limit the states a system can assume. They do not isolate the system from interactions with the parts (bodies) of the environment except insofar as they prohibit certain states of the system (Hatsopoulos and Keenan, 1965).

Definition 9 **Constraints** are restrictions imposed *by the environment* on the states a system may assume. □

Some of the more important constraints in nature are:

1. No constraint. The system is not limited in volume and is not subjected to conservative force fields established by the environment.
2. An upper limit to volume. This constraint is imposed by a rigid impermeable vessel.
3. A conservative force field (e.g., gravity) established by bodies in the environment. For example, no state in which a part of fluid column in the gravitational field of the Earth is free of gravity is allowed.
4. An electrically insulating wall surrounding the system.

Example 1 **The Earth System, Passive Resistance, Constraint.**
Atmospheric gases scatter blue photons more than other photons, giving the Earth's visible edge a blue halo. Gradually, the atmospheric halo fades into the blackness of space, see **Figure 7.4**.

There is no clear dividing surface between the Earth's atmosphere and space, but for studying the balance of incoming and outgoing radiation on the Earth, it is conceptually useful to think of the altitude at about 100 km above[6] the Earth surface as the "top of the atmosphere." It is an imaginary spherical surface across which solar light enters the Earth, about 30% of the incoming light is reflected back into space, and thermal radiation from the warm Earth exits. The balance between incoming and outgoing radiation at the top of the atmosphere determines the Earth's average temperature. Greenhouses gases reduce the rate of flow of thermal radiation out and warm up the Earth over and above its black body temperature, see **Chapters 16** and **15**.

The first step therefore is to visualize the Earth as *the system*. From the point of view of this book, a useful Earth system would be encapsulated between

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[6] That is inside the *thermosphere* that extends $50 - 400$ km above the Earth's surface.

Figure 7.4: The top of the atmosphere can be visualized as a spherical surface about 100 km above the Earth surface. Image source: The photograph was captured on July 20, 2006, by a NASA astronaut, and is provided by the ISS Crew Earth Observations experiment and the Image Science & Analysis Laboratory, Johnson Space Center, earthobservatory.nasa.gov/Newsroom/-NewImages/Images/ISS013-E-54329_lrg.jpg.

two concentric surfaces. The inner surface follows the Earth surface. The outer sphere can be have different radii. First, we can place it at the mean Earth radius + 100 km, at the "top of the atmosphere." In this case the out surface of the Earth system is a partial a mirror that reflects 30% of the incoming solar radiation on the average. Second, we might place the outer sphere at the mean Earth radius + 400 km. No there is no reflection at the outer surface of the Earth system. The "top of the atmosphere" spherical surface no becomes a passive resistance that does not let 30% of the incoming radiation through. Third, we could place the outer surface at the average Earth radius + 99 km, or so. In this case, the "top of the atmosphere" surface surrounds the system and is a partially insulating wall that constrains the system from receiving all solar radiation.

7.8.3 Isolated Systems

Definition 10 A system is **isolated** for any period of time during which all changes in the system are independent of all changes in the environment. □

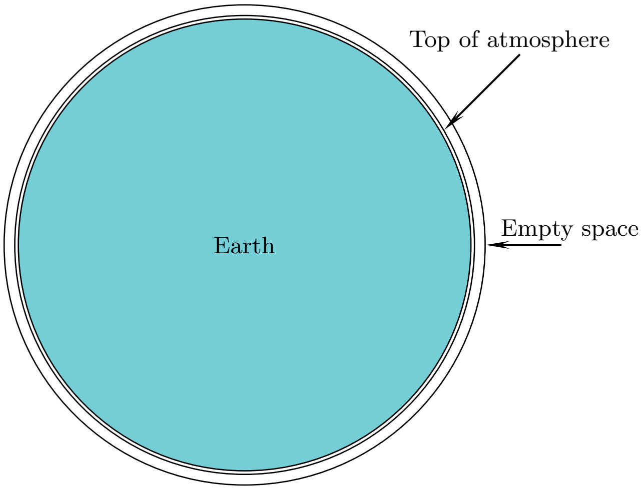

Figure 7.5: A system defined by the mean Earth surface at R_{earth} and the top of the atmosphere at $R_{\text{earth}} + 100$ km, or outer space at $R_{\text{earth}} + 400$ km. All radii are drawn to scale.

7.9 Temperature

There is no clean way of introducing the *thermodynamic temperature* so early on. So here is the best I can do: When a chunk of uniform matter is enclosed in a vessel with rigid, heat-conducting walls[7] and is allowed to interact with the surroundings, such as the Earth atmosphere or oceanic water, it is found that the independent properties that characterize the system change with time. After a sufficiently long time the independent properties of the system always assume fixed values. The system is then said to have reached a *state of thermal equilibrium* with the surroundings.

When two closed systems, A and B in **Figure 7.6**, whose primitive properties are $x_A, y_A, \ldots$ and $x_B, y_B, \ldots$, are allowed to interact through a diathermal[8] wall, their properties will change until they reach thermal equilibrium with each other. These two systems are coupled; any change in the state of one system will cause in general a change in the state of the other system. Clearly it is tempting to say that two systems coupled across a diathermal wall have a common primitive property after they have attained thermal equilibrium. This property is called the common *temperature* of the two systems and it is rigorously

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[7] Thus forming a closed, uniform thermodynamic system with diathermal rigid walls.

[8] *Diathermal* [Greek thoroughly warm; *dia′* through + *thermal* warm, hot. (Webster, 1993)] Freely permeable to radiant or conductive heat.

introduced in, e.g., (Kestin, 1979a).

The Zeroth Law of Thermodynamics

This law was formulated in 1931 by Richard F. Fowler, see e.g., (Fowler and Guggenheim, 1949):

- Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other (have equal temperatures).

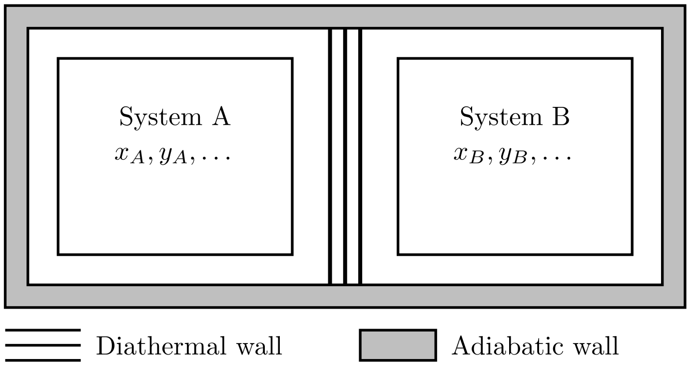

Figure 7.6: Two systems interacting through a diathermal wall. A diathermal wall is made of an excellent heat conductor (copper or silver), so that temperature drop through it is negligible. The rigid vessel walls are adiabatic (do not conduct heat).

The thermodynamic or absolute temperature unit is 1 Kelvin (K), equal to 1^0 Celsius (C). The *triple point* of water[9] corresponds to the temperature of 273.16 K.

1 mol of any gas at the *normal* temperature of water ice-point[10], 273.15 K, and the normal pressure of 1 atm occupies the volume of 22.4207 ± 0.0006 L.

7.10 Equation of State

The equation of state (EOS) is a relationship between one of the properties in the complete set of properties and the remaining properties. This relationship is single-valued and continuous, but the derivatives need not be continuous.

For example, the *ideal gas* EOS:

$$pV = nRT \tag{7.1}$$

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[9] The equilibrium temperature between pure water liquid, vapor, and ice.

[10] The equilibrium temperature between air-saturated water and ice, both at 1 atm.

allows to express any of the three gas properties, pressure p, volume V, and temperature T, through the two remaining ones. Here n is the number of moles of the gas and R is the universal gas constant.

More generally, we can say that any property y, regarded as dependent, is a single-valued function of the n independent properties, $x_1, \ldots, x_n$:

$$y = f(x_1, \ldots, x_n) \tag{7.2}$$

Usually the functional form of f is determined from measured data, but often it is possible to use first principles to either derive it or constrain empirical choices.

7.11 Problems

1. Give a few examples of passive resistances in mechanical and chemical systems, and of catalysts and anticatalysts.

2. Think about a natural process that moves along very different paths with and without a passive resistance of your choice, imposed on the system of your choice. Explain.

3. Give an example or two of constraints on a system.

4. Is planet Earth in space a closed system with respect to mass transfer? Explain.

Figure 7.7: Where would you draw the boundary of this agricultural land system?

5. Define the boundary (enveloping imaginary surface) of the agricultural land system in **Figure 7.7**. Carefully list your assumptions. Is your system closed or open? Closed or open to the flow of what? Does it matter if you include the farm buildings or not?

6. In Section 7.5.3, we have defined an irreversible process in a simple thermodynamic system without *memory*. Because we stipulated this lack of memory, we could always restore the initial state 1 from the final state 2 through some process. The living systems also perform irreversible processes. Can these processes be analyzed using the concepts you have learned thus far? Does, therefore, their irreversibility mean something different?

7. State briefly what happens in restoration of a contaminated aquifer. Does a thermodynamic process of restoring it conform to the description of a real process in Section 7.5.3?

8. (**From Greg Croft**) Saudi Arabia's Ghawar Field is the largest conventional oil field in the world. It accounts for more than 60% of both the current and the cumulative oil production of Saudi Arabia. In order to find the volume of oil, one must first find the volume of oil-filled (*oil-saturated*) rock. Oil saturation S_o is defined as the volumetric fraction of pore space filled with oil: $S_o = V_o/V_{\text{pore space}}$. The bulk rock volume is simply average *net* (subtract shales, etc.) reservoir rock (*pay*) thickness times productive area. Multiplying this result by the average rock porosity gives pore volume. Part of the pore volume is occupied by water, so the pore volume must be multiplied by one minus the water saturation to obtain the oil volume. The last correction is for the fact that oil loses volume as dissolved gas is liberated upon lowering the oil temperature and pressure from reservoir conditions to surface conditions. The ratio of volume of "live" oil in the reservoir rock to that of "dead oil" in a stock tank at atmospheric conditions is called the *formation volume factor*. If the reservoir oil volume is expressed in barrels (1 bbl = 42 US gallon = 5.615 ft^3), dividing by the formation volume factor gives stock tank barrels. Note that there are 7758 barrels in an acre-foot of pore volume.

$$\text{Oil in place} = \frac{\text{Area} \times \text{net pay} \times \text{porosity} \times \text{(1-water saturation)}}{\text{formation volume factor}} \qquad (7.3)$$

In order to convert oil-in-place volume (*resource*) to recoverable oil (*reserves*), a recovery factor must be estimated. These recovery factors can range from less than 5% to as much as 70%.

(a) Using the data available at www.gregcroft.com/ghawar.ivnu, calculate the oil in place in the Arab-D reservoir at Ghawar. Use average petrophysical values across the five areas since only a combined productive area is given.

(b) If the Ghawar Field has already produced 57 billion barrels of oil, how much of the original oil in place has been produced?

(c) Does this tell you anything about the recovery factor?

(d) Looking at the descriptions of each of the five areas, how do you think the recovery factor at Haradh will compare with that at Ain Dar?

Chapter 8

First Law of Thermodynamics

The historical development of thermodynamics has been . . . particularly susceptible to logical insecurity, . . . and there has been no adequate reexamination of the fundamentals.

— Percy Williams Bridgman (1882 – 1961)
The Nature of Thermodynamics (1961 edition, p. 226)

8.1 What Are you Going to Learn?

You will learn what work interaction in thermodynamics is and how it can be used to define the fundamental property of a thermodynamic system, its total *energy*. Energy change is then related to systems interacting with the surroundings only through *adiabatic* work.

8.2 Why Is It Important?

Without thorough understanding of the First Law of Thermodynamics you cannot do science.

8.3 Background

In 1824, Nicolas Léonard Sadi Carnot, **Figure 8.1**, introduced the concept of a cycle and showed that the reversible cyclic engine was the most efficient engine possible (Carnot, 1943). Not only did the young Carnot create *classical thermodynamics*, but he also stated the abstract Second Law.

Between 1840 and 1848, James Prescott Joule laid experimental foundation for the First Law (Joule, 1884). He made measurements to show that the amount of work required to bring about a given change of state was independent of the kind of work (whether mechanical, electric, or magnetic), the rate of doing the work, or the method of delivering the work.

Even much later, the various statements of the First Law of thermodynamics were truisms that relied on the concept of heat before stating the Second Law (Poincaré, 1908), were limited to simple systems (Carathéodory, 1909) or meaningless, because they were formulated as the law of *energy conservation*. Now we know that no general definition of the term *energy* is possible without the First Law.

8.4 Definition of Work Interactions

Thermodynamics must account for kinds of work other than that encountered in mechanics. To do this we realize that work is not associated with a particular state of the system. It is performed when the system changes position, such as in raising infinitely slowly a mass in the gravitational field.

After Joseph Kestin (Kestin, 1979a), we will adopt the following definition of the work performed by a thermodynamic system:

Definition 11 Work is performed *by* a system *on* its surroundings during a given process if the only effect external to the system **could** be the raising of the weight. Conversely, work is performed on a system by the surroundings during a given process if the only effect external to the surroundings **could** be the raising of the weight, see **Figure 8.2**. □

Figure 8.1: **Left:** Nicolas Léonard Sadi Carnot, 1796 – 1832, a brilliant French engineer who conceived modern thermodynamics. Classical thermodynamics was born in 1824 with his memoir, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, see the modern translation (Carnot, 1943). **Right:** James Prescott Joule, 1818 – 1889, established the equivalence between amounts of heat and mechanical work with his famous "paddle-wheel experiment."

8.4.1 Adiabatic Process

Any process involving only work interaction is called an adiabatic process.

8.5 The First Law of Thermodynamics

The first definition comes from (Hatsopoulos and Keenan, 1965):

> For any process involving no effects external to the system other than the change in elevation of a number of standard weights, this number of standard weights is fixed by the end states of the system and is independent of the details of the process.
>
> (This idea really belongs to Gibbs (Gibbs, 1994), who in 1873 suggested to get the magnitude of work done by the system on the surroundings by answering the question: "How great a weight does the [process] enable us to raise a given distance, no other permanent changes being produced in external bodies?")

The second definition comes from (Kestin, 1979a):

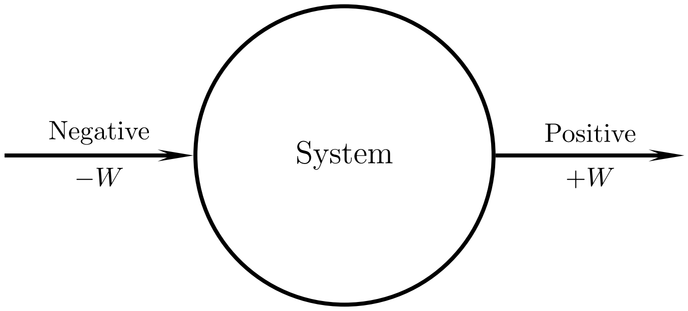

Figure 8.2: Sign convention for work. This historical convention originated from the study of heat engines performing work *on* the surroundings.

Given two arbitrary states of equilibrium 1 and 2 of *any* closed system, it is either possible to reach state 2 from state 1 or state 1 from state 2, but not both, by a pure work interaction (adiabatic process, reversible or not). The work performed is independent of the details of the process.

8.5.1 Energy

In view of **Corollary 1** of the definition of a thermodynamic property, it is the consequence of the First Law that the work involved in an adiabatic process can be used to define a change of the value of a very special property. We shall call this property (total) energy E of a system and shall define its change between two states 1 and 2 ($1 \rightarrow 2$) of a system by the relation:

$$\Delta E := E_2 - E_1 = -W_{12}^a \tag{8.1}$$

where W_{12}^a is the work done by the system in *any* adiabatic process from state 1 to state 2.

The term *energy* is derived from the late Latin *energia*, and from Greek *energeia* activity, from *energos* active, from *en* in + *ergon* work. In denotes the *ability to do work.*

Work is *not* the only interaction that may change the energy of a system. As we will see soon, interactions occurring during nonadiabatic processes, or *heat interactions*, may also result in energy changes.

8.5.2 Older Formulations

The First Law of Thermodynamics is sloppily called the *Energy Conservation Law* and is often expressed as:

- Energy can neither be created or destroyed;
- The energy of the universe remains constant; or
- You can't win.

The first two definitions are corollaries[1] to the First Law, and the third one is a joke.

8.6 More on Energy

The experimental evidence in support of the general formulation of the First Law of thermodynamics in Eq. (8.1) is meager. Furthermore, as observed by KESTIN (Kestin, 1979a), no systematic, precise experiments to verify this generalization directly have ever been conducted. On the other hand, no conclusions have ever been derived from the First Law that contradicted any experiment. Remember that NEWTON's laws of motion, MAXWELL's equations of electromagnetism, EINSTEIN's theory of relativity, etc., have all been accepted based on quite incomplete and circumstantial evidence.

Energy can be identified only for a set of states along an adiabatic path. If a state of a system should exist which did not belong to such a set, energy would not be identifiable for that state. Fortunately, such a state has never been found in Nature.

If the First Law is accepted as an axiom, it is obvious that in specific cases the adiabatic work done on the system can be seen as a generalization of *potential* and *kinetic energy* in mechanics. For example, if our system is a mass m lifted up (along the z-direction) in a uniform gravitational field, then the adiabatic work done on the system is

$$W_{12}^a = -mg\,dz \tag{8.2}$$

Here the negative sign denotes the external force $F = mg$ in the negative z-direction performing work on the system. Therefore,

$$dE = -W_{12}^a = mg\,dz \tag{8.3}$$

Similarly for a body accelerated by an external force $F = ma = m\,dv/dt$ over a distance $v\,dt$, the adiabatic work is

$$W_{12}^a = -m\frac{\mathrm{d}v}{\mathrm{d}t}\,vdt = -mv\,dv = -d\left(\frac{1}{2}mv^2\right) \tag{8.4}$$

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[1] Conclusions from the First Law that contain less information than the First Law, see Chapter 9.

Consequently, the change of system energy is

$$dE = -W_{12}^{a} = d\left(\frac{1}{2}mv^{2}\right) \tag{8.5}$$

Yet another change of energy can be brought about by changing the system pressure and/or temperature at constant volume. In this case the system will undergo a change in *internal energy*, denoted by the symbol U, used first by CLAUSIUS to denote energy:

$$E_2 - E_1 = U_2 - U_1 \tag{8.6}$$

More about internal energy will be said in the next chapter.

Because energy is a property of the system, from **Corollary 2** it follows that if different process steps involve pressuring a body (and later heating it), lifting it and accelerating, then the total change of system energy is:

$$E_2 - E_1 = (U_2 - U_1) + (mgz_2 - mgz_1) + \left(\frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2\right) \tag{8.7}$$

or

$$\Delta E = \Delta U + \Delta E_P + \Delta E_K \tag{8.8}$$

where E_P and E_K are the potential and kinetic energies of the body.

Equation (8.7) is stated as a fact in some books on thermodynamics, e.g., (Abbott and Van Ness, 1972).

8.7 Problems

1. Identify a suitable system and say whether positive, negative, or zero work occurs in the following situations (Problem 3.1 in (Hatsopoulos and Keenan, 1965)).
   (a) A tire pump is connected to a tire. The pump plunger is pushed down forcing air into the tire. Assume that the walls of tire, pump, and the connecting hose are adiabatic.
   (b) Liquid fills an adiabatic rigid container. The liquid comes to rest from its initial state of initial motion.
   (c) Hydrogen and oxygen in a combustible mixture are enclosed in a rigid cylinder. A spark (which may be considered of zero volume and otherwise negligible) caused the two gases to combine.
   (d) A rigid metallic vessel containing air is set on a stove. The pressure of the air in the container increases.
2. A box of unknown contents is well *insulated* from its surroundings except for the interaction resulting only in the *external* effects described below. State in each instance your opinion concerning the interaction.

Is it definitely work or not, or is the answer to the question indeterminate? State your arguments succinctly (Problem 3.2 in (Hatsopoulos and Keenan, 1965)).

(a) A weight is raised.
(b) A weight is lowered.
(c) A weight is lowered causing a moving block to rub on a stationary block which is in contact with the box; no warming of any part occurs.
(d) An electric bulb is caused to glow for a period of time.
(e) An electric capacitor is discharged.
(f) An electric motor is caused to rotate for a period of time and lift a weight.
(g) A stationary hot body is cooled to the temperature of melting ice.
(h) A stationary cold body is warmed to the temperature of melting ice.
(i) A flywheel is accelerated from rest.
(j) A flywheel is decelerated to rest.

Chapter 9

Second Law of Thermodynamics

Through me you enter the woeful city, through me you
enter eternal grief, through me you enter among the lost. . . .
Abandon every hope, you who enter.

— Dante Alighieri
Inferno - The Divine Comedy Canto III, p. 1, verse 1 (1321)

9.1 Background

CARNOT used no mathematical equations in (1943). Instead, he described his revolutionary theory of heat machines with words[1] and used the non-physical *caloric*[2] concept of heat.

KELVIN, **Figure 9.1**, pointed out (1911) the conflict between the caloric basis of CARNOT's arguments and the conclusions reached by JOULE (1884). He called for further experiments to resolve this dilemma.

With no further experimentation, CLAUSIUS (1850) reconciled the CARNOT principle with the work of JOULE. He did this by proposing that CARNOT's principle is another axiom of physics (Second Law), not requiring proof.

The modern statement of the Second Law of thermodynamics is due to PLANCK (1926):

> It is impossible to construct an engine which will work in a complete cycle, and produce no effects except the raising of a weight and the cooling of a heat reservoir.

This is the most widely used statement of the Second Law. It also proves to ba a tautology[3] (Hatsopoulos and Keenan, 1965).

9.2 Types of States

Once we have defined a system and observe it, we find that the system can be in a variety of states:

1. In an *unsteady state* the system changes with time because of removal of passive resistances and/or interactions with the environment. For example, a bath tub being filled with water and a flooding river are in unsteady states.

2. In a *steady state* the system does not change with time despite interactions with the environment. Examples of steady state systems include base-load power plants that operate at constant power output.

---

[1] Observes TRUESDELL: "Among all writers on natural philosophy only CARNOT equals the pre-Socratics in ability to provoke an infinite sequence of cyclic quandary, acute and painful ponderation, conjecture, gloss, controversy, and quandary again, which bears witness that the outcome is comprehensible to nobody." (Truesdell, 1980) p. 80.

[2] The caloric theory was introduced by ANTOINE LAVOISIER, see Chapter 8. LAVOISIER had discovered the explanation of combustion in terms of oxygen in the 1770s. In his book *Réflexions sur le phlogistique* (1783), LAVOISIER argued that phlogiston theory was inconsistent with his experimental results, and proposed a "subtle fluid" called *caloric* as the substance of heat. According to this theory, the quantity of this substance is constant throughout the universe, and it flows from warmer to colder bodies.

[3] An empty or vacuous statement composed of simpler statements in a fashion that makes it logically true whether the simpler statements are factually true or false; for example, the statement *Either it will rain tomorrow or it will not rain tomorrow.*

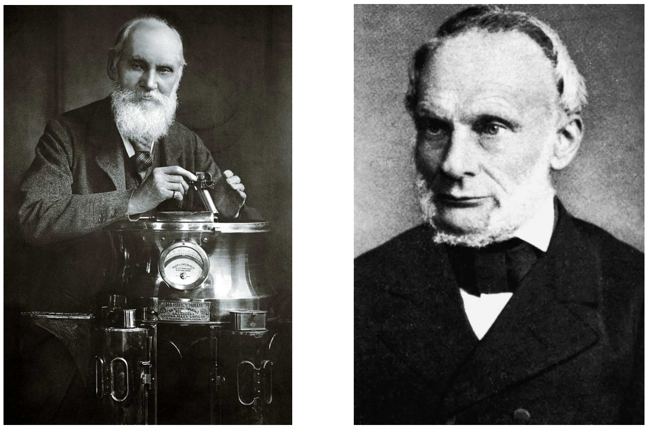

Figure 9.1: **Left:** Sir WILLIAM THOMSON (Lord KELVIN). **Right:** RUDOLF JULIUS EMMANUEL CLAUSIUS, 1822 − 1888, first stated in 1850 the basic idea of the second law of thermodynamics. He used it in showing that for a *Carnot cycle*, which transmits heat between two heat reservoirs at different temperatures and at the same time converts heat into work, the maximum work obtained from a given amount of heat depends solely upon the temperatures of the heat reservoirs and not upon the nature of the working substance.

3. In a *non-equilibrium state*, the system changes spontaneously as a function of time. This state evolves without interactions with the environment. For example, a calorimetric bomb is used to measure heats of combustion of flammable mixtures. Combustion initiated be a spark is spontaneous and non-equilibrium.
4. In an *equilibrium state* the system does not change with time while it is isolated from the environment.

9.3 Thermodynamic Equilibrium

Definition 12 A system is in a **state of equilibrium** if a change of the state cannot occur while the system is not subject of interactions. □

Equilibrium states may be *stable*, *neutral*, *unstable* and *metastable*.

9.3.1 Stable Equilibrium

A system is in *stable equilibrium* if a finite change of state of the system cannot occur without leaving a corresponding change in the state of the environment, or change the system primitive variables (e.g., component quantities) to an set of incompatible values.

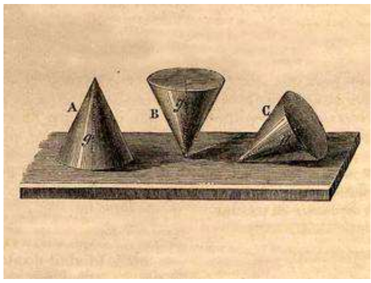

Figure 9.2: Types of mechanical equilibria: **A** Stable; **B** Unstable; **C** Neutral.

This is the most important kind of equilibrium, see **Figure 9.2**. A more complicated system would be a mixture of oxygen, hydrogen, and water vapor

$$H_2 + O_2 \rightleftarrows H_2O \tag{9.1}$$

In this system the molecules of oxygen and hydrogen combine to form water, or water disassociates. Under the influence of factors external to the system the two reactions will attain a stable equilibrium which can be shifted by changing these external factors.

Another example is a calorimetric bomb, see Chapter 3, filled with air and a hydrocarbon. After the hydrocarbon has been completely combusted, we cannot transfer energy from the bomb to a weight without either changing the bomb's volume or affecting the environment in ways other than lifting the weight.

9.3.2 Unstable and Neutral and Equilibria

Unstable equilibrium, see **Figure 9.2B**, is of least importance as it cannot exist in nature. An unstable equilibrium can be caused to proceed along a path to entirely different states by a small and short-lived interaction that has a negligible effect on the environment. For example, the upright cone in **Figure 9.2B** will fall down after a tiniest mechanical disturbance, e.g., a whiff of air generated by a butterfly's wing. Our calorimetric bomb charged with a combustible mixture is in an unstable equilibrium state because a small spark with no visible impact on the environment generates irreversibly a set of combustion products.

In a state of *neutral equilibrium*, at least one change of state can be caused by first lowering an external weight, which is then lifted up to its initial position when the system comes to rest at a new state.

9.3.3 Metastable Equilibrium

A *metastable equilibrium state* of a system can be altered without leaving net effects on the environment, and without changing the equilibrium values of the system's primitive variables to an incompatible set of values, but only through interactions that have a temporary finite effect on the environment. In a mechanical example in **Figure 9.3**, the mass can be lifted from point 1 to the the

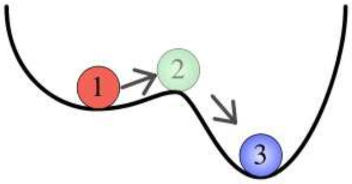

Figure 9.3: A metastable system with a weakly stable state (1), an unstable transition state (2) and a strongly stable state (3).

unstable point 2 by lowering a weight in the environment. By slowly translating down, the mass can lift the weight back to its initial position, thus restoring the environment, and then fall spontaneously to the lowest potential energy point 3.

A metastable equilibrium can often be made into a state of stable equilibrium by the introduction of a passive resistance which constitutes a change in the system description.

9.3.4 Mutual Equilibrium

If two equilibrium systems are brought into communication with each other in some manner, and this communication is (i) allowed and (ii) results in no change in either system, these systems are said to be in *mutual equilibrium*.

9.3.5 Thermodynamic Properties and States

The properties of a system in neutral equilibrium whose change can be achieved by temporary changes in the environment are called neutral properties. These properties cannot be expressed as functions of the remaining properties of the system.

A *thermodynamic property* is any property which is not neutral. Accordingly, the *thermodynamic state* of a system is identified by means of its thermodynamic properties.

9.4 Second Law of Thermodynamics

The definition here comes from (Hatsopoulos and Keenan, 1965):

> A system having specified allowed states and an upper bound in volume can reach from any given state a stable state and leave no net effect on the environment.

The term *an upper limit in volume* means that, if necessary, a rigid container is provided which the system may or may not fill, but beyond which it cannot extend. The rigid container may be a part of an isolating surface which prevents effects from passing from system to environment.

Corollary 5 *If a system is in a stable state, no change to an allowed state can have as sole effect external to the system the rise of a weight.* □

Please look back at PLANCK's formulation of the Second Law. The corollary is a consequence of the definition of a stable state. Its significance is that thermodynamic systems can assume stable states. The Second Law postulates the existence of such stable states. Thus the corollary, together with the definition of stable equilibrium, becomes applicable to systems under the Second Law. Furthermore, the Second Law allows us to recognize which of the possible states of a system are stable states by means of a process of elimination.

9.4.1 State Principle

The state principle postulates the following concerning the independent properties of the system (Hatsopoulos and Keenan, 1965):

> The stable state of a system bounded by a fixed surface and subjected to the fields prescribed by its environment is fully determined by the system energy.

The First Law, the Second Law, and the State Principle form the basis of classical thermodynamics.

9.5 Definition of Heat Interactions

In Figure 7.6, two isolated thermodynamic systems A and B at stable states were brought into communication[4] without altering their allowed states or causing any net effects on other systems. These two systems are now no longer isolated from each other. Their interaction cannot be work, because according to the Second Law neither system is capable of doing work starting from a stable state (for which no change could occur if the systems were isolated).

Since, according to the State Principle, energy is the sole independent property for stable states of an isolated system, the energies of the two systems may change. We shall call such interaction between systems in stables states *heat* (Hatsopoulos and Keenan, 1965):

> Heat is an interaction which may occur between two systems, initially isolated and at stable states, when they are brought into communication without altering their allowed states and without work done by the environment.

---

[4] You can imagine having initially a two-layer separator wall made of a perfect heat conductor and a perfect heat insulator. The perfect heat insulator is removed, and systems 1 and 2 come into communication. Thus we have replaced a thermodynamic “mirror” with a thermodynamic “transparency”.

In order to insure that the interaction is solely a heat communication, it is necessary that at each instant during the process the two systems would be in stable states if they were suddenly isolated. This requirement specifies slow interactions, which allows only slow states to change.

9.5.1 Definition of Heat Quantity

For an equilibrium system bounded by a prescribed surface (closed to transfer of mass), the system's energy determines its thermodynamic state. Thus, the change of energy of a system involved in a heat interaction between states 1 and 2 may serve as a measure of the heat. For system A interacting with system B, the quantity of heat exchanged is

$$Q_{AB} = E_{A2} - E_{A1} \tag{9.2}$$

Here the subscript 2 denotes the final state, after the interaction took place, and the subscript 1 denotes the initial state. If $Q_{AB} > 0$ then heat is said to flow from system B to A; $Q_{AB} < 0$, heat flows from A to B.

Corollary 6 *During a heat interaction involving systems A and B only, the heat interaction Q_{AB} of system A is equal and opposite in sign to the heat interaction Q_{BA} of system B.* □

When two systems undergo a heat interaction at a finite rate, they are said to have *different temperatures*. As they attain equilibrium and the interaction stops, they are said to have *equal temperatures*.

9.6 Energy Changes in Nonadiabatic Processes

It follows directly from the definitions of work and heat interactions that for any process involving both the change of energy of a closed system is

$$E_2 - E_1 = Q - W \tag{9.3}$$

Equation 9.3 holds whether Q, W, and $(E_2 - E_1)$ are large or small. Consequently, we may want to write these variables in the limit as states 1 and 2 become very close to each other $(2 \to 1)$, $E_2 - E_1$ approaches zero, and replace the increment of E with its linear part, the differential dE. But Q and W are *not* differences of a state property, do *not* become differentials, but just *small* quantities of heat, δQ, and work, δW:

$$dE = \delta Q - \delta W \tag{9.4}$$

I should emphasize that both Eqs. (9.3) and (9.4) are consequences of the First Law; none in itself is a statement of the First Law.

9.6.1 Law of Conservation of Energy

As a corollary of the First Law, one can prove easily that the energy of an isolated system remains unchanged regardless of the changes in the system. The statement can be deduced from the First Law, but it contains less information and is therefore a corollary. In most books on thermodynamics the Law of Energy Conservation is treated as the general First Law.

9.6.2 Importance of Boundaries

Heat and work have been defined as interactions between systems (or a system and its environment) which are closed to the transfer of matter. It then follows that the magnitudes of heat and work in the course of any event depend where you place the system boundaries. For example if a system consists of a plant irradiated with light from an external halogen lamp, then a heat interaction between the plant and lamp will occur. If both are in a greenhouse, then the same event will not involve heat. Similarly, if the system consists of a weight which is raised to a higher level by a fall of an external weight, then a work interaction occurs. If both weights are within the boundary of the same system, there is no work interaction.

9.7 Older Formulations of Second Law

Here are some popular formulations, but remember they are confusing and incomplete, and you do not know yet what *entropy* is:

- The entropy of the universe tends to a maximum.
- Without the compensating changes elsewhere, heat can flow only from a hotter to a colder body; or
- With passing chronological time, the entropy of the universe tends towards a maximum; or
- You can't break even.

The first formulation comes from the very source of the notion and word "entropy", CLAUSIUS' Ninth Memoir[5]: *On Several Convenient Forms of the Fundamental Equations of the Mechanical Theory of Heat*, 1865, p. 365.

9.8 An alternative Modern Formulation of Second Law

This formulation is due to ELIAS P. GYFTOPOULOS and GIAN PAOLO BERETTA (2005):

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[5] Clausius may be excused for his rather expansive formulation of the Second Law. He was thinking about it just after the death of his wife.

> Among all the states of a system that have a given (finite) value of the energy[6] and are compatible with a given set of values of the amounts of constituents and other parameters[7], there exists one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrarily specified amounts of constituents and parameters by means of a reversible weight process.

9.9 Problems

1. Explain in words the definition of neutral equilibrium, using the rolling cone in Figure 9.2.
2. What is the difference between unstable and metastable equilibrium states?
3. Devise examples of different states of equilibrium in biological systems.
4. Select a neutral property of one of the systems in Figure 9.2.
5. By applying the definition of stable equilibrium of the heat reservoir to PLANCK's formulation of the Second Law, show that it is a tautology, i.e., it is a conclusion (corollary) that follows from this definition.
6. Apply the concept of metastable equilibrium to a mangrove forest, see **Figure 9.4**. Learn first about the what the mangrove forest is and why is it so important. Prescribe then a passive resistance that would change its state to a stable equilibrium.
7. Explain whether the following processes violate the Second Law (Hatsopoulos and Keenan, 1965):
   (a) A cyclic device interacts with a system in a stable state and produces no external effect, except the rise of a weight.
   Answer: Yes, but why?
   (b) A cyclic device interacts with a system in a stable state and produces no external effect, except the fall of a weight.
   (c) A cyclic device interacts with a system in a stable state and produces no external effect, except a voltage drop across a capacitor.
   (d) A black box produces no external effect, except the rise of a weight.
   (e) A black box produces no external effect, except the fall of a weight.

---

[6] The State principle was incorporated here, and the system must have a finite volume.

[7] The complete set of primitive variables in our nomenclature.

Figure 9.4: A mangrove swamp, Tonle Sap, Cambodia. Source: toddadams.net/images/wallpaper/.

Chapter 10

Reversibility, Irreversibility, Etc.

Sir ARTHUR STANLEY EDDINGTON, *The Nature of the Physical World*, 1953, p. 74:

> The law that entropy increases – the Second Law of Thermodynamics – holds, I think, the supreme position among laws of nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations – then so much the worse for Maxwell's equations. If it is contradicted by observation – well, these experimentalists do bungle things sometimes. But if your theory is found against the Second Law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

10.1 What Are We Going to Learn?

Before we can discuss entropy, we must learn a little about heat machines, reversible and irreversible processes, heat reservoirs, perpetuum machines, and the like. This is hard work and a lot of memorizing of the rules of the game.

10.2 Why Is It Important?

If you want to say the word "sustainability" and actually understand what just have said, you must learn the material in this and next chapter. So please bear with me; the rewards will be rich!

10.3 Efficiency of a Heat Machine

A *heat machine* is a system that operates in a cycle while only heat and work cross its boundaries. Any heat machine operating between two heat reservoirs, see **Figure 10.1**, has thermodynamic efficiency

$$\eta := \frac{W}{Q_1} = \frac{|Q_1| - |Q_2|}{|Q_1|} \tag{10.1}$$

where $|Q_1| \geq 0$ is the absolute value of the heat quantity Q_1 transferred from the heat source T_1 to the machine, and Q_2 is the quantity of heat transferred from the machine to the heat sink T_2.

10.4 Reversibility

Building on the discussion in Section 7.5.3, a reversible process can be defined as follows (Hatsopoulos and Keenan, 1965):

Definition 13 A (infinitely slow) process in *any* system is *reversible* if the process could be performed in at least one way such that the system and all elements of its environment can be restored to their respective states, except for the differences of smaller order than the maximum changes that occur during the process in question. □

More discussion will follow in **Section 10.9**.

10.5 Thermodynamic Temperature

The thermodynamic scale of temperature can be defined with the help of a reversible heat machine in Figure 10.1 as

$$T_1 := -T_2 \frac{Q_1}{Q_2} = T_2 \frac{|Q_1|}{|Q_2|} \tag{10.2}$$

For convenience, T_2 may be assigned a special reference value T_R corresponding to a heat reservoir that consists of ice, liquid and vapor water coexisting in equilibrium. The algebraic *number* assigned to T_R by an important committee is 273.16 exactly, and the temperature scale in Eq. (10.2) is called the *absolute* or *thermodynamic* temperature scale. The temperature unit is called 1 Kelvin.

10.6 Perpetual Motion Machine of the Second Kind

A *perpetual motion machine of the second kind* (PMM2) is any heat engine that exchanges heat with a single thermodynamic system in a stable state ($Q_2 = 0$) and delivers net work. According to the First Law, Eq. (10.1), the heat received by a PMM2 is equal to the work it produces and its efficiency is one.

10.7 Heat Reservoir

A *heat reservoir* is a system in stable equilibrium state such that when subjected to finite heat interactions, its temperature remains constant. In practice a heat reservoir can be a very large system when compared with the systems of interest (an ocean or the atmosphere), have infinite heat conductivity, or we provide compensating interactions that maintain the reservoir in a fixed state (such as chemically pure liquid water and ice).

10.8 Irreversibility

If we fail to show that a process is reversible, we do not really know if this process is indeed irreversible or not. A better criterion of *irreversibility* may be stated as follows (Hatsopoulos and Keenan, 1965):

Definition 14 A process is irreversible if as a result of assuming it to be reversible, either (1) a system in a stable state could be made to change to another allowed state with the sole external effect of raising a weight, or (2) a PMM2 could be devised. □

10.8.1 Proving Irreversibility

The proof that a process A is irreversible can be accomplished as follows (Hatsopoulos and Keenan, 1965):

1. List the internal and external effects of A.
2. Assume that a process B exists by means of which the effects of A can be undone.

3. Observe that either B constitutes a violation of the Second Law (Chapter 9), or B in combination with a real process C will constitute either a violation of the Second Law or a cycle BC which is a PMM2.

A word of caution may be in order: First, it is neither necessary nor possible to describe the means or devices by which the inverse process B of an irreversible process A can be realized. Second, a cycle BC which is not a PMM2 neither proves nor disproves that A is irreversible, and is useless for the purpose of the proof.

10.8.2 Example of an Irreversible Process

We shall show that heat transfer between two heat reservoirs of unequal temperatures is an irreversible process.

Consider a heat interaction (direct transfer of a quantity of heat Q) between two heat reservoirs defined in Section 10.7 that are at two different temperatures, $T_1 > T_2$. Such an interaction results in a decrease by a finite result of the energy of the hot reservoir ($E_1 \to E_1 - Q$) and an increase of the energy of the cold reservoir ($E_2 \to E_2 + Q$), see Section 9.5.

Let us assume that the heat transfer process A of *directly* transferring heat Q into the cold reservoir T_2 was reversible. From Item 2 in Section 10.8.1, this assumption is equivalent to assuming that a process B can be found which would decrease of the energy of the cold reservoir by Q and increase of the energy of the hot reservoir by an equal amount. No other effects would occur.

After the transfer of heat the two heat reservoirs are separated. Thus far no changes have occurred in the environment. A heat engine B could be made to remove the heat quantity Q from the cold reservoir and lift a weight. Thus after the assumed process, the energy of the cold reservoir would be restored its initial value, and the net effect would be the lifting of a weight. The energy of the hot reservoir would still be decreased. Therefore, there is a net effect on the environment after A is reversed, and heat transfer between two reservoirs of unequal temperature is irreversible.

10.9 Internal and External Irreversibility

We have just seen that transfer of heat between two heat reservoirs of unequal temperature is an irreversible process, see Figure 10.1. Suppose, however that we focus our attention on the cold reservoir T_2. For example, we may connect the hot reservoir T_1 with the cold one T_2 through a reversible heat machine. Then heat will be delivered to T_2 by engine R, while heat is taken from T_1, and a weight is raised by R in the environment. Since, R is reversible, the effects of this process could be completely reversed: heat could be taken from T_2, weight lowered by R, and heat delivered to T_1, each effect being of the same magnitude but opposite in sign to that of the original process.

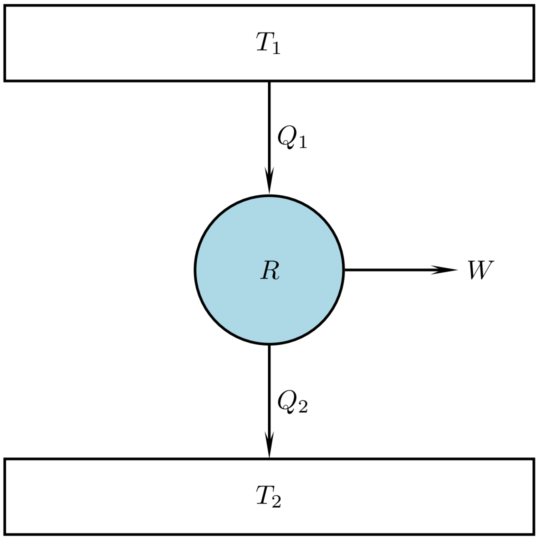

Figure 10.1: A reversible machine between two heat reservoirs of unequal temperatures $T_1 > T_2$.

Thus the same process in T_2 may be irreversible if it is caused by a direct heat interaction with T_1, or reversible if we may choose the interacting environment of T_2 at will.

We see, therefore, that the irreversibility of the original process was *external* to T_2, because it had to do with the kind of environment with which T_2 was interacting. On the other hand if a gradient of T_2 were established during the heating process, the irreversibility would be *internal* to T_2.

The distinction between *reversibility* in general and *internal reversibility* corresponds to the distinctions between **Definitions 13** and **14**.

A process is reversible if everything can be restored to its initial state. A process in a system is *internally reversible* if it can be performed in at least one way such that the system and all elements of its environment can be restored to their respective initial states.

The concept of *external reversibility* is merely an application of internal reversibility to the environment as a system. Thus if a process involves internal reversibility alone or external reversibility alone, it will be an irreversible process as regards an isolated system (our system + its environment). If on the other hand, a process involves both internal and external reversibility, then it will be a reversible process in an isolated composite system.

10.10 Problems

1. Using Definition 13 and the results of Section 10.9 formulate your necessary and sufficient condition of sustainability. Say in words what you think the term *sustainability* means if it is to be consistent with the Second Law of thermodynamics, and not with a well-meaning blog.

2. Using Definition 14 show that electricity generation from coal is irreversible.

3. Using Definition 14 show that the Green Revolution industrial agriculture is irreversible.

Chapter 11

Entropy

Question: Who governs the governors? Answer: Entropy
— Frank Herbert (1920 – 1986)

11.1 What Are We Going to Learn?

You are going to learn about entropy. An informal Google search on January 11, 2007, finds 14,000,000 entries devoted to entropy. So entropy is rather important to many people.

11.2 Why Is It Important?

Our ignorance of what entropy is only exceeded by our fascination with it and fantasies about it. Now you have a chance to test how much you want to know...

11.3 Background

The term *entropy* was introduced by CLAUSIUS (Clausius, 1865a):

$$\int \frac{\delta Q}{T} = S - S_0 \tag{11.1}$$

> We might call S the *transformation content of the body*, just as we termed the magnitude U its *thermal* and *ergonal* [energy] content. But as I hold it to be better terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the entropy of the body, from the Greek word $\tau\rho\pi\epsilon$, transformation. I have intentionally formed the word entropy so as to be as similar as possible to the word energy; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

The concept of entropy was introduced even earlier (Clausius, 1865b).

11.4 Existence of Entropy

Here I will follow (Hatsopoulos and Keenan, 1965):

Theorem 1 *The quantity $\delta Q/T$ in any reversible process of a system represents the change of a value of a property of the system.* □

Proof: Consider system A in **Figure 11.1**. This system executes a reversible cyclic process while receiving per each cycle a small heat quantity δQ at Kelvin temperature T. The heat quantities δQ are supplied to A by a reversible heat engine X, which for each cycle of A receives the small heat quantity δQ_{RX} from reservoir R at finite temperature T_R. At the end of a cycle of A the combined system AX has also executed a reversible cycle and has exchanged heat with a

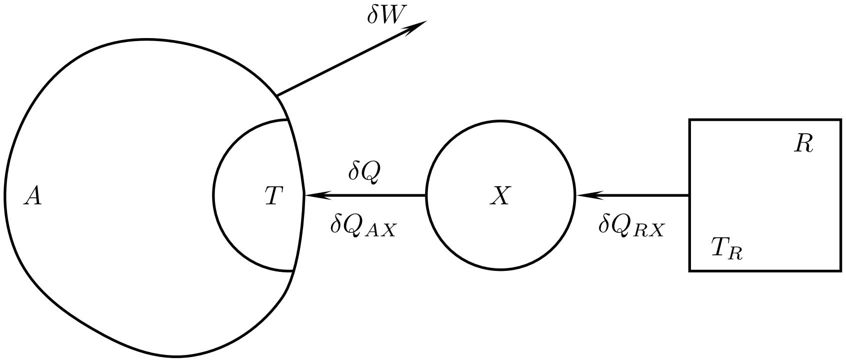

Figure 11.1: Proof of existence of entropy.

single reservoir. According to the definition of a reversible cycle (Definition 13), the heat reservoir must have returned to its initial state and

$$\oint_{\text{rev}} \delta Q_{RX} = 0 \tag{11.2}$$

From the definition of the Kelvin scale in Section 10.5 we must also have that

$$\frac{\delta Q_{RX}}{T_R} = -\frac{\delta Q_{AX}}{T} \tag{11.3}$$

By definition

$$\delta Q = -\delta Q_{AX} \tag{11.4}$$

By combining Eq. (11.4) into (11.3) and combining the result with Eq. (11.2), we get

$$T_R \oint_{\text{rev}} \frac{\delta Q}{T} = 0 \tag{11.5}$$

or, since T_R is finite

$$\oint_{\text{rev}} \frac{\delta Q}{T} = 0 \tag{11.6}$$

From Corollary 4 to the definition of a property, Eq. (11.6) proves the existence of a property S, such that

$$dS := \left(\frac{\delta Q}{T}\right)_{\text{rev}} \tag{11.7}$$

After Clausius, we shall call this property *the entropy of the system.*

11.4.1 Entropy Changes in Internally Reversible Systems

Although Eq. (11.6) was derived for a reversible process, it is stated only in terms of the temperature T of that part of system A that receives heat. Therefore, it will hold for any internally reversible process, regardless of the external irreversibilities that will only change the heat quantities δQ_{RX}. Therefore, the expression for entropy differential (the linear part of a small change), given by Eq. (11.7) holds for any internally reversible process, regardless of any external irreversibility.

11.4.2 Entropy Changes in Irreversible Systems

The analogue of Eq. (11.6) for irreversible systems was derived by Clausius and is called the *inequality of Clausius*:

> For an internally irreversible process, the integral of the ratio of the heat quantities δQ received by a system to the temperature T at which these quantities were received, Eq. (11.6), is always less than zero.

Proof: Assume that a reversible heat engine X that receives heat δQ_{RX} from a heat reservoir R at temperature T_R, delivers heat δQ to system A per each irreversible cycle of that system. The combined system AX also executes an irreversible cycle. The net work of the combined system, according to the First Law is $\oint \delta Q_{RX}$. This work cannot be positive according to the Second Law, because otherwise we would be able to get work from a cyclic machine that operates with a single heat reservoir. On the other hand, if $\oint \delta Q_{RX} = 0$, then at the end of the cycle, system A and all elements of its environment return to their original states, and the process must be reversible, contrary to our assumption. In the end, we are left with the only alternative:

$$\oint_{\text{rev}} \delta Q_{RX} < 0 \tag{11.8}$$

From Eqs. (11.3) and (11.4) it then follows that

$$T_R \oint_{\text{irr}} \frac{\delta Q}{T} = \oint_{\text{irr}} \delta Q_{RX} < 0 \tag{11.9}$$

Since $T_R > 0$, it also follows that for an irreversible cyclic process

$$\boxed{\oint_{\text{irr}} \frac{\delta Q}{T} < 0} \tag{11.10}$$

11.4.3 Entropy and Heat in Irreversible Processes

The (finite) change of entropy $\int dS$ in an irreversible process is greater than the integral of the heat divided by the absolute temperature:

$$\int_{\text{irr}} dS > \int_{\text{irr}} \frac{\delta Q}{T} \tag{11.11}$$

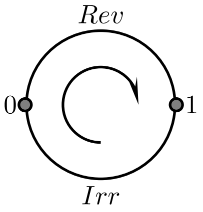

Figure 11.2: A cycle begins at state 0, follows a reversible process *Rev* to state 1, and returns to 0 along an irreversible process *Irr*.

Proof: Consider a cycle shown in **Figure 11.2**. Since entropy is a property its total change is zero for a cycle:

$$\oint dS > \int_{0,\text{rev}}^{1} dS + \int_{1,\text{irr}}^{0} dS = 0 \tag{11.12}$$

From Eqs. (11.7)– (11.11) we get

$$\oint \frac{\delta Q}{T} = \int_{0,\text{rev}}^{1} \frac{\delta Q}{T} + \int_{1,\text{irr}}^{0} \frac{\delta Q}{T} < 0 \tag{11.13}$$

and

$$\int_{0,\text{rev}}^{1} dS = \int_{0,\text{rev}}^{1} \frac{\delta Q}{T} \tag{11.14}$$

After some manipulation we obtain

$$\int_{\text{irr}} dS > \int_{\text{irr}} \frac{\delta Q}{T} \tag{11.15}$$

For small changes of state we may write

$$dS_{\text{irr}} > \left(\frac{\delta Q}{T}\right)_{\text{irr}} \tag{11.16}$$

Combining the small change of entropy for a reversible cycle, Eq. (11.7), with that for the irreversible cycle we obtain the important general relationship

$$\boxed{dS \geq \frac{\delta Q}{T} \qquad (11.17)}$$

It now follows directly from the First Law that

$$\oint T\, dS = \oint_{\text{rev}} \delta Q = \oint_{\text{rev}} \delta W \tag{11.18}$$

11.4.4 Isentropic Process

Entropy is constant in an *isentropic process*. According to the definition of entropy Eq. (11.7) the change of entropy in a reversible and adiabatic process ($\delta Q_{\mathrm{rev}} = 0$) is zero. Thus, the term *reversible-adiabatic* implies the term *isentropic*. The reverse, however is no true, isentropic does *not* imply reversible-adiabatic. For an isentropic process we always have

$$dS = 0 \tag{11.19}$$

But $0 = dS \geq \delta Q/T$, and

$$\frac{\delta Q}{T} \leq 0 \tag{11.20}$$

Therefore, for an isentropic process either $\delta Q = 0$ or $\delta Q < 0$.

11.4.5 Principle of the Increase of Entropy

From Eq. (11.17)

$$dS \geq \frac{\delta Q}{T}$$

For an isolated system, see Section 7.8.3, $\delta Q \equiv 0$ and, therefore

$$dS_{\mathrm{isol}} \geq 0 \tag{11.21}$$

This is the famous principle of the increase of entropy (*Entropy Law*).

Remember that any system can be enlarged to contain anything that it influences, and the new composite system is isolated. Where to stop the enlargement is a matter of judgement and estimating the relative magnitudes of the influences. Therefore, the principle of the increase of entropy is extremely general. Some say that it is the most important *law of nature* known to science (Eddington, 1953; Georgescu-Roegen, 1971).

The entropy increments are always determined in the direction of *Time*[1], from the *earlier* to the *later* moment in Time. So, if chronological Time τ_2 is later than another Time τ_1, then the entropy of the universe (or another closed system) is

$$S(\tau_2) > S(\tau_1) \tag{11.22}$$

The *Entropy Law* is the simplest (and thus far the only) law known to science, by which the existence of true *happening* in nature is recognized. The

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[1] Time is a notion of extraordinary complexity (Georgescu-Roegen, 1971). Here I use the historical or chronological *Time*, as opposed to the mechanical clock *time*.

Entropy Law defines the boundaries of what *cannot* happen, but does not prescribe entirely what *can*. This loophole resulted in life. All life[2] feeds on an environment of low-to-moderate entropy (highly organized ecosystems[3], such as shallow sea water, a river or lake, a jungle, etc.), and is extinguished when the entropy of the environment becomes too high (the degraded environment of sterile desert or chemically polluted water).

11.4.6 Entropy Change for a Simple System

From the definition of entropy, Eq. (11.7), and the First Law, Eq. (9.3), we get

$$dS_{\text{rev}} > \left(\frac{dE + \delta W}{T}\right)_{\text{rev}} \tag{11.23}$$

Work in a reversible process cannot involve viscous or frictional forces. For a simple system, the only kind of work permitted in a reversible process is work done by normal forces at slowly moving boundaries of the system. Therefore work quantity for a process connecting two equilibrium states of a simple system is

$$\delta W_{\text{rev}} = p\, dV \tag{11.24}$$

Moreover, with the restriction of no external fields, and no fast moving parts, the system's total energy is equal to its internal energy:

$$dS_{\text{rev}} > \left(\frac{dU + p\, dV}{T}\right)_{\text{rev}} \tag{11.25}$$

which is often written as

$$dU = T\, dS - p\, dV \tag{11.26}$$

Although Eq. (11.26) was derived for a reversible process, all quantities appearing in it depend only on the end-states of a sufficiently small change of state (on the linear first differential).

It follows then that Eq. (11.26) is valid for any process, *reversible* or *no*t, as long as this process connects two *equilibrium states* of a *simple system*. Only in a reversible process, however, $T\, dS$ and $p\, dV$ represent the small quantities of heat and work, respectively. In an irreversible process $T\, dS$ will exceed the heat and $p\, dV$ will exceed the work by equal amounts.

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[2] Not only biological life, but also social life. Consider the following comment made by JOSEPH SAMAHA in the daily *Al Safir* of Beirut about the desperately dissipative, high-entropy political situation in the Middle East: "Let us expel every mediator. Let us banish every international organization. Let the situation collapse. Let electricity and water be cut off. Let the pumping of oil stop. Let theft prevail. Let the universities and schools close down. Let businesses go bankrupt. Let civilian life break down." Source NYT, August 21, 2003, page A13.

[3] *eco* – From late Latin *oeco-* household, from Greek *oik-*, *oiko-*, from *oikos* house habitat or environment (Webster, 1993). *Eco*systems are the earth's households, and *ecology* is the study of these households.

Finally, between two close *non-equilibrium* states, it may be that

$$dU \neq T\,dS - p\,dV \tag{11.27}$$

and this combination of the First and Second Law does not hold.

11.5 Entropy, Order, and Probability

When we talk about black body radiation of the Sun and the Earth, we will have to deal with photons and their statistical mechanics description.

Statistical mechanics is an attempt to recast the laws of thermodynamics by using different explanations of thermodynamic equilibrium, while preserving the original meaning of these laws as they were first cast by CLAUSIUS and refined by HATSOPOULOS & KEENAN (Hatsopoulos and Keenan, 1965), and KESTIN (Kestin, 1979a; Kestin, 1979b). The latter three monographs have been summarized in the last four chapters.

Figure 11.3: After an explosion all pieces of this building, its furniture, and inhabitants came down at random. Mass and energy are conserved, but something is very different: Order is missing. This is the Second Law of thermodynamics in action. In order to make intelligent decisions about ecosystems, we must account for entropy. First Law energy analyses of natural systems are woefully insufficient and may lead to exactly wrong decisions.

As so nicely summarized by GEORGESCU-ROEGEN (1971), Chapter VI, the new approach is relatively simple: heat consists of the *irregular* motion of particles, and thermodynamic equilibrium results from a *shuffling process* of particles and their velocities which goes on by itself. The main stumbling block of statistical thermodynamics has been the description of the shuffling process. Different collections of particles (gas molecules, photons, or electrons) will undergo different shuffling processes. Analogies such as the shuffling of playing cards or the beating of an egg have been used to describe the meaning of the term shuffling. In a more striking analogy, the process has been likened (Schrödinger, 1957) to the plundering of a library by a mad mob[4], see **Figure 11.3**. Nothing is destroyed (mass and energy are conserved), but everything is scattered to the four winds. Now, please go back and look at the photograph of a beach on Oahu I took in December, 2006. It shows the creation of disorder by the various good people tossing little things overboard. Each one of these people could have easily prevented the disorder by recycling. Together, they have created an unbelievable mess that will cost a fortune to sort out. Again, the law of mass conservation has worked rather nicely, and my photo has visualized the real-life effects of Eq. (11.21).

According to statistical mechanics, the degradation of the Earth is even more extensive than that envisaged by Classical Thermodynamics: It encompasses not only energy but also material structures. In technosphere, there is a constant tendency for order to turn into disorder.

Since classical statistical mechanics is concerned only with mechanical properties of particles (their positions and momenta), all particles are like faceless individuals distinguished only by their names. The concept of *macrostate*, in which no particle names are used, reflects the fact that the physical properties of a large assembly of particles do not depend on which particular particle occupies a certain state, i.e., has a certain position and momentum. Each "personal" arrangement of particles in a given macrostate constitutes a *microstate*. The criterion according to which two such arrangements constitute two microstates is an additional convention which varies from one type of particles to another. Also the criteria of what constitutes an acceptable macrostate differ.

In BOLTZMANN's classical approach, two particle arrangements constitute two different microstates if and only if the names of the particles in some state or states are not the same. No restriction is imposed as to how many particles can occupy the same state.

If there are m states and N particles, the measure of the disorder of the macrostate $(N_1, N_2, \ldots, N_m)$, $\sum N_i = N$, is given by the familiar formula of combinatorics:

$$W = \frac{N!}{N_1! N_2! \ldots N_m!} \tag{11.28}$$

BOLTZMANN's epochal formula for entropy viewed as a measure of disorder is

$$S = k \ln W \tag{11.29}$$

where k is BOLTZMANN's constant. This formula was engraved on his tombstone, even though he never actually wrote it down.

In statistical mechanics, BOSE - EINSTEIN ($\mathsf{B-E}$) statistics determines the statistical distribution of identical *indistinguishable* particles, *bosons*, over the energy states in thermal equilibrium. $\mathsf{B-E}$ statistics was introduced for

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[4] Remember the looting of the Baghdad Museum after our invasion of Iraq?

photons in 1924 by Bose (1924) and generalized to atoms by Einstein in 1924 – 25 (1924). B – E statistics becomes Maxwell – Boltzmann statistics at high temperatures or low boson concentrations. We will use B – E statistics in Chapter 15.

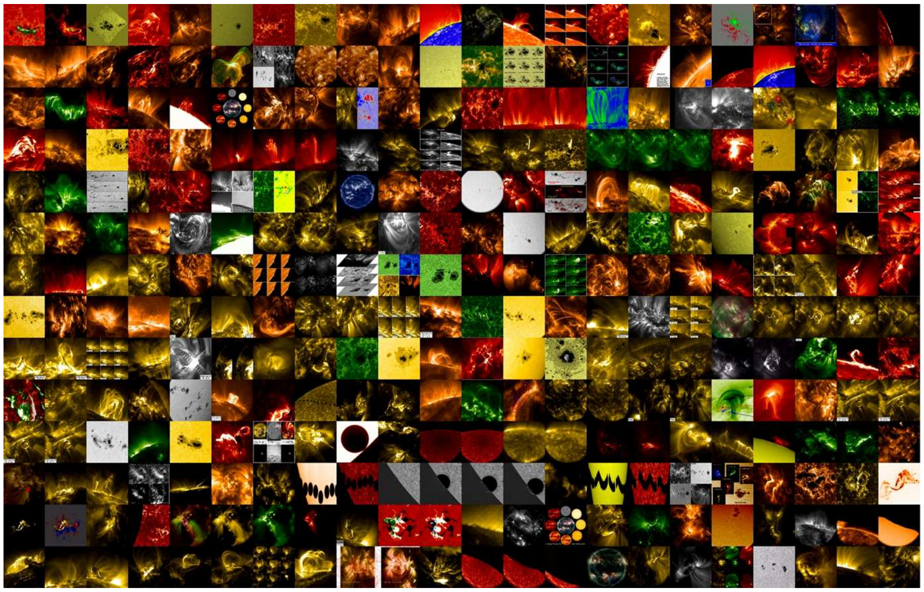
11.6 Problems

1. Prove Eq. (11.15).
2. Prove Eq. (11.18).
3. Finish this sentence: *Reversible-isentropic* implies _________, *isentropic-adiabatic* implies _________, and *irreversible-isentropic* implies heat flow (in/out) of the system.
4. This problem introduces you to solar radiation. The pressure of a photon gas is a function of temperature only and is related to energy and volume by $p(T) = \frac{1}{3}U(T)/V$. A system consisting of this gas is confined to a cylinder and a piston undergoes a Carnot cycle between two pressures p_1 and p_2
    (a) Find expressions for work and heat of reversible isothermal and adiabatic processes.
    (b) Plot the Carnot cycle on the $T - s$ and $p - V$ diagrams
    (c) Find the efficiency of the cycle in terms of pressures.
    (d) What is the functional relationship between pressure and temperature.
5. Let U, X, Y, Z be four particles and A, B, D, D, E the possible states. In Boltzmann's statistics the macrostate "two particles in A and two particles in B", generates six microstates. Put together a table listing these microstates.
6. Using Second Law (entropy) arguments, try to demonstrate the following:
    (a) The value of recycling goes beyond conserving mass and energy.
    (b) The "Green Revolution" that relies heavily on fossil fuels and field chemicals poisonous to all plants but the favored monoculture, is in the long run bad for the people and the planet. Why did I say "in the long run"? What causes the bad effects not to kick in immediately?
    (c) "Asymmetric warfare" (terrorism) is cheap and the fight with it is very expensive; give examples.
    (d) Bacteria, phages, viruses, etc. have been waging asymmetric warfare on other species, including humans. Try to formulate a Second Law opinion what is better: (i) Provide simple means of subsistence for the local population in a poor African country, so that it can live

close to a tropical forest, or (ii) log the forest and chop it for wood, and breed mosquitos in the pools of water standing on damaged soil? Is it better to spray the inhabitants with the cheap DDT, find an expensive vaccine, or prevent mosquitos from excessive breeding using natural means? What does entropy have to do with all this?

Chapter 12

Thermodynamic Functions and Their Differentials



No attempt is made at mathematical rigor, since in physics it is always illusory.

— Landau and Lifshitz
Statistical Thermodynamics (Oxford Univ. Press, London, 1938)

12.1 What Are You Going to Learn?

You will learn about the differential forms of fundamental equations of thermodynamics for closed and open simple systems that contain multiple phases and undergo reversible or irreversible processes. In particular, you will learn about the significance of chemical potential and LEGENDRE transformations that relate different thermodynamic functions, such as energy, enthalpy, and Helmholtz and Gibbs free energies. You will also learn about the GIBBS-DUHEM constraint and GIBBS phase rule for a multicomponent, multiphase system in equilibrium.

12.2 Why Is It Important?

You cannot do quantitative thermodynamics without knowing the contents of this Chapter.

12.3 General Definitions

Constancy is the condition of having the same form or value everywhere and at every time (always), as in *constant system pressure and temperature.*

Uniformity is the condition of having the same form everywhere; not varying in space, as in *uniform system pressure and temperature.* We allow uniform conditions to (slowly) change with time.

Homogeneity is the property of a parameter whose values are similar over a region of space, as in a *homogeneous fluid density, or homogeneous aquifer or soil.*

Heterogeneity (or inhomogeneity) is the property of a parameter whose values vary over a region of space, as in an *inhomogeneous fluid, or inhomogeneous layer of rock or soil.*

Phase is a region of space filled with a homogeneous substance (fluid or solid) and bounded by a *closed* surface that separates this region from all other phases. A surface of contact between two phases is called an interface. Interfaces may be predominantly flat (as in water filling a large beaker), or curved (as in water in a capillary separated from air by a hemispherical meniscus).

Intensive property is a thermodynamic property that does not depend on the extent or size of a phase. Examples are pressure, temperature, density, specific volume, compressibility, specific energy, etc.

Extensive property is a thermodynamic property that scales with the size of a phase or system. Examples are total (phase or system) energy, total volume, total entropy, etc.

12.4 Energy Balance for PVT Systems of Variable Composition

The derivations in this section follow closely the excellent and concise engineering thermodynamics book by ABBOTT and VAN NESS (Abbott and Van Ness, 1972).

Let us consider a homogeneous pressure-volume-temperature (PVT) system containing N_c chemical species present in mole numbers $n_1, n_2, \ldots, n_{N_c}$. The internal energy, entropy, and volume are extensive properties, so that the total system properties are $U = nu$, $S = ns$, and $V = nv$, where u, s, and v are the molar properties and $n = \sum n_i$ is the total number of moles of all chemical species. The species may be distributed among phases $1 \leq j \leq N_p$, but here we require that the surfaces separating all phases (interfaces) be *flat*. We will relax this requirement later and introduce the interface curvatures.

For a particular case of a reversible process in which all of the n_i are constant, we have

$$\begin{aligned} \delta Q_{\text{rev}} = Td(ns), \qquad \delta W_{\text{rev}} &= pd(nv) \\ d(nu) &= Td(ns) - pd(nv) \end{aligned} \tag{12.1}$$

where p is the external pressure, and the system pressure because of reversibility.

Equation $(12.1)_2$ is an exact differential and

$$\begin{aligned} \left(\frac{\partial(nu)}{\partial(ns)}\right)_{nv,n} &= T \\ \left(\frac{\partial(nu)}{\partial(nv)}\right)_{ns,n} &= -p \end{aligned} \tag{12.2}$$

The additional subscript n indicates that all the n_i are held constant.

For the general case, nu must also depend on the mole numbers n_i, $i = 1, 2, \ldots, m$, as wells as on ns and nv. We may write formally:

$$d(nu) = \left(\frac{\partial(nu)}{\partial(ns)}\right)_{nv,n} d(ns) + \left(\frac{\partial(nu)}{\partial(nv)}\right)_{ns,n} d(nv) + \sum_{i=1}^{N_c} \left(\frac{\partial(nu)}{\partial n_i}\right)_{ns,nv,n_k \neq n_i} dn_i \tag{12.3}$$

Combining Eqs. (12.1)-(12.2), and introducing formally the **chemical potential** of species i as

$$\mu_i := \left(\frac{\partial(nu)}{\partial n_i}\right)_{ns,nv,n_k \neq n_i} \tag{12.4}$$

we can write Eq. (12.3) as

$$\boxed{d(nu) = Td(ns) - pd(nv) + \sum_i \mu_i dn_i \qquad (12.5)}$$

Remark 1 Equation (12.5) is the *fundamental* property relation for a homogeneous PVT system of variable composition, and is the basis for *all* derived property relations for such systems. The system of interest may be **open** or **closed**, and composition changes may result either from *transport* of matter in and out of the system or *chemical reactions* or both.

Equation $(12.1)_2$ is a special case of (12.5) valid when all mole numbers are fixed. This equation has separate validity for all processes connecting equilibrium states for any closed PVT system, whether homogeneous or heterogeneous.

All the equations of this section could equally well be written in terms of unit-mass (specific) properties rather than molar properties. The symbol n would then represent mass rather than number of moles.

12.4.1 Legendre Transformations

In terms of molar quantities ($n = 1$), the combined First and Second Laws of thermodynamics for a reversible, closed system can be written as

$$\begin{aligned} du &= -pdv + sdT \\ dY &= C_1 dX_1 + C_2 dX_2 \\ Y &= u, \quad X_1 = v, \quad X_2 = T \\ C_1 &= \frac{\partial Y}{\partial X_1} = -p, \quad C_2 = \frac{\partial Y}{\partial X_2} = s \end{aligned} \tag{12.6}$$

We can formally introduce the following transformations

$$\begin{aligned} \mathfrak{T}_1 &= \mathfrak{T}_1(C_1, X_2) := Y - C_1 X_1 \\ \mathfrak{T}_2 &= \mathfrak{T}_2(X_1, C_2) := Y - C_2 X_2 \\ \mathfrak{T}_3 &= \mathfrak{T}_3(C_1, C_2) := Y - C_1 X_1 - C_2 X_2 \end{aligned} \tag{12.7}$$

The functions defined above are called the *Legendre transformations*.

$$\begin{aligned} h &\equiv \mathfrak{T}_1 = u + pv, \quad \text{molar enthalpy} \\ a &\equiv \mathfrak{T}_2 = u - Ts, \quad \text{molar Helmholtz free energy} \\ g &\equiv \mathfrak{T}_3 = u + pv - Ts, \quad \text{molar Gibbs free energy} \end{aligned} \tag{12.8}$$

We can write Eqs. (12.8) for $n \neq 1$ and after some rearrangement obtain the following relationships:

$$\begin{aligned}
d(nh) &= Td(ns) + (nv)dp + \sum_i \mu_i dn_i \\
d(na) &= -(ns)dT - pd(nv) + \sum_i \mu_i dn_i \\
d(ng) &= -(ns)dT + (nv)dp + \sum_i \mu_i dn_i
\end{aligned} \tag{12.9}$$

Therefore, in particular,

$$\begin{aligned}
\mu_i &= \left(\frac{\partial(nh)}{\partial n_i}\right)_{ns,p,n_k \neq n_i} \\
\mu_i &= \left(\frac{\partial(na)}{\partial n_i}\right)_{T,nv,n_k \neq n_i} \\
\mu_i &= \left(\frac{\partial(ng)}{\partial n_i}\right)_{T,p,n_k \neq n_i}
\end{aligned} \tag{12.10}$$

12.5 Equilibrium in Closed, Heterogeneous Systems

We will consider now a closed system in which temperature and pressure are uniform (but not necessarily constant). The system may consist of an arbitrary number of phases, the composition of each phase being uniform but not necessarily the same as the composition of any other phase. We further imagine that the system exchanges heat reversibly with the surroundings (both at the same temperature) and the system volume changes in such a way that work exchange is also reversible. The process considered results from a change in the system *from* a nonequilibrium state *toward* an equilibrium state. with respect to the distribution of species among the phases.

A total property of a closed system is still denoted by a capital letter. Thus U, S, and V are the energy, entropy and volume of the entire system. Total energy is the summation over all components distributed among all phases. Some authors use the superscript t, e.g., $U^{(t)}$, to stress that we are dealing now with a multiphase system.

For a reversible exchange of heat δQ the entropy change of the surroundings is

$$dS_{surr} = \frac{-\delta Q}{T} \tag{12.11}$$

where the minus sign arises because δQ is the quantity of heat transferred into the system from the surroundings, whereas dS_{surr} refers to the surroundings.

The temperature T is common to the system and the surroundings because the heat transfer is imagined as reversible.

The Second Law applied to the process requires

$$\begin{aligned} dS + dS_{surr} &\geq 0 \\ dS &\geq \frac{\delta Q}{T} \end{aligned} \tag{12.12}$$

The inequality sign reflects the irreversible transfer of mass among the system phases, since all heat and work transfers are assumed to be reversible. The First Law requires that

$$dU = \delta Q - pdV \tag{12.13}$$

or

$$\boxed{dU - TdS + pdV \leq 0 \tag{12.14}}$$

Remark 2 This relation involves properties only and must be satisfied for changes of state in **any closed PVT system whatsoever**, without restriction to the conditions of reversibility assumed for its derivation. This inequality is satisfied by any process that starts from an initial state of uniform T and P but otherwise not a state of internal equilibrium, and it dictates the direction of change that leads towards an equilibrium state. □

12.5.1 Special Forms of Equation (12.14)

Equation (12.14) is so general that its implications are difficult to visualize. It may be readily restricted to several simpler forms. For example, if a process occurs at constant system entropy and volume

$$(dU)_{S,V} \leq 0 \tag{12.15}$$

Similarly, for processes restricted to constant U and V

$$(dS)_{U,V} \geq 0 \tag{12.16}$$

From the definitions of the total enthalpy, Helmholtz free energy and Gibs free energy, it also follows immediately that

$$(dH)_{p,S} \leq 0, \qquad (dA)_{T,V} \leq 0 \tag{12.17}$$

and

$$(dG)_{T,p} \leq 0 \tag{12.18}$$

Therefore, at equilibrium, the total GIBBS free energy must attain a minimum with respect to all possible (small) variations of temperature and pressure.

An application of Eq. (12.18) to phase equilibrium requires the following expression:

$$dG = \sum_{j=1}^{N_p} d(n^{(j)} g^{(j)}) \tag{12.19}$$

where the summation occurs over all phases j. But from Eq. (12.10) it follows that at constant T and P

$$d(n^{(j)} g^{(j)}) = \sum_{i=1}^{N_c} (\mu_i^{(j)} dn_i^{(j)}) \tag{12.20}$$

and we obtain the important inequality

$$\sum_{j=1}^{N_p} \sum_{i=1}^{N_c} (\mu_i^{(j)} dn_i^{(j)}) \leq 0 \tag{12.21}$$

The inequalities (12.21) and (12.18) are equivalent, and both represent a criterion of equilibrium.

In equilibrium, equality holds, and since a decrease of moles of substance i in phase α is equal to the sum of increases of moles of i in the remaining phases, one can easily show that

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(N_p)}, \quad i = 1, 2, \ldots, N_c \tag{12.22}$$

With *flat* interfaces, the number of degrees of freedom[1] of our closed heterogeneous system is

$$\text{Number of degrees of freedom } = N_c - N_p + 2$$

The first two terms follow directly from Eq. (12.22), and the +2 comes from the requirement of uniform system pressure p (mechanical equilibrium) and temperature T (thermal equilibrium).

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[1] Independently adjustable parameters characterizing the system.

12.6 Gibbs-Duhem Equation

By following Eqs. (12.19) and (12.9) for a single-phase system with N_c components, we get

$$\begin{aligned} dG &= \sum_{i=1}^{N_c}(n_i d\mu_i + \mu_i dn_i) \\ dG &= -(ns)dT + (nv)dp + \sum_{i=1}^{N_c} \mu_i dn_i \end{aligned} \tag{12.23}$$

Equation $(12.23)_1$ is true because for any *molar intensive quantity* m, the total differential of the extensive quantity $M \equiv nm$ is by definition

$$\begin{aligned} dM = d(nm) &= \sum_{i=1}^{N_c}(n_i d\bar{M}_i + \bar{M}_i dn_i) \\ \bar{M}_i &:= \left(\frac{\partial(nm)}{\partial n_i}\right)_{T,p,n_k \neq n_i} \end{aligned} \tag{12.24}$$

Here the *partial molar property* $\bar{M}_i$ denotes the rate of change of the total molar property M with the number of moles of components i at constant temperature and pressure and moles of all other components. For example, if $m = g$, $\bar{M}_i \equiv \mu_i$, see Eq. $(12.10)_3$.

By combining the right hand sides of Eqs. $(12.23)_1$ and $(12.23)_2$, we get the **Gibbs-Duhem** equation for each phase j:

$$\boxed{\begin{aligned} (n^{(j)}s^{(j)})dT - (n^{(j)}v^{(j)})dp + \sum_{i=1}^{N_c} n_i^{(j)} d\mu_i^{(j)} &= 0 \\ j &= 1, 2, \ldots, N_p \end{aligned} \qquad (12.25)}$$

where $n^{(j)}$ is the total number of moles in phase j, $n_j = \sum_i n_i^{(j)}$.

12.7 Available Free Energy

Relative to a *datum environment* ($T_0 = 25^0$ C, $p_0 = 1$ atm), the quality of heat rejected by a process depends on temperature:

$$\begin{aligned} \text{1J of heat at } 500^0\text{C} &= 0.614 \text{ J of work} \\ \text{1J of heat at } 50^0\text{C} &= 0.077 \text{ J of work} \end{aligned} \tag{12.26}$$

Gibbs, Guoy, Stodola, and Keenan's available free energy, see **Appendix A**, is known in chemical and engineering thermodynamics as *exergy*,

Figure 12.1: Professor JAN SZARGUT has taught at the Chemical Engineering Department of my *Alma Mater*, the Silesian Technical University, Gliwice, Poland. Source: T. W. Patzek, March 21, 2007.

and is denoted with the symbol B. The concept of exergy and its cumulative consumption in an industrial process has been significantly advanced by the distinguished Polish thermodynamicist, JAN SZARGUT, see **Figure 12.1**. His monograph, published in English with DAVID R. MORRIS and FRANK R. STEWARD in 1988 (Szargut et al., 1988) was based on two decades of development and industrial applications of life-cycle analysis. Today, this monograph is still the most comprehensive source of exergy concepts, data, and examples.

12.7.1 Introduction to Exergy

An easy to understand definition of exergy was proposed by LUDWIG RIEKERT (1975).

Definition 15 Exergy, B, is equal to the shaft work or electrical energy necessary to produce a material in its specified state from materials common in the environment in a reversible way, heat being exchanged with the environment at constant temperature T_0. □

We distinguish the *potential* exergy, B_p, *kinetic* exergy, B_k, *physical* exergy B_{ph}, and *chemical* exergy, B_{ch}:

- **Physical exergy**, B_{ph} is the work obtainable by a reversible physical process from its initial state (T, P) to the environment state (T_0, p_0).

- **Chemical exergy**, B_{ch}, is the work obtained by taking a substance at the pressure and temperature of the environment to the state of thermodynamic equilibrium with the datum levels of components of the environment.

- **Thermal exergy**, B_{th}, is the sum of physical and chemical exergies:

$$B_{\mathrm{th}} = B_{\mathrm{ph}} + B_{\mathrm{ch}} \tag{12.27}$$

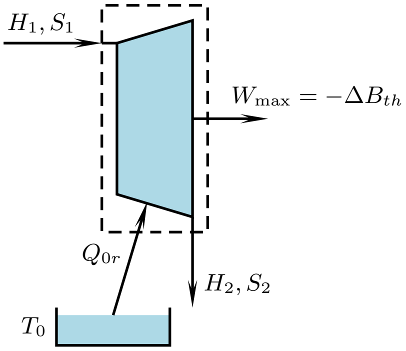

Figure 12.2: Exergy balance in an isothermal, ideal flow machine. The maximum possible shaft work from this machine is equal to the negative change of thermal exergy.

12.7.2 Change of B_{th} between Two States

Consider an ideal (reversible) flow machine, see **Figure 12.2**. An exergy carrier with enthalpy H_1, and entropy S_1 enters the machine. After physical and/or chemical changes, the effluent has enthalpy H_2, and entropy S_2. Heat is transferred between the environment and the working fluid at the ambient temperature T_0. The first and second law of thermodynamics are simply:

$$\begin{aligned}
&W_{\max} = B_{\mathrm{th}_1} - B_{\mathrm{th}_2} = H_1 - H_2 + Q_{0r} \quad \text{(I Law)}\\
&S_2 - S_1 - \frac{Q_{0r}}{T_0} = 0 \quad \text{(II Law)}\\
&B_{\mathrm{th}_1} - B_{\mathrm{th}_2} = -\Delta B_{\mathrm{th}} = H_1 - H_2 - T_0(S_1 - S_2) \quad \text{(I+II Law)}
\end{aligned} \tag{12.28}$$

Physical exergy can be calculated immediately from Eq. (12.28)

$$B_{\mathrm{ph}} = H - H_0 - T_0(S - S_0) = H_{\mathrm{ph}} - T_0 S_{\mathrm{ph}} \tag{12.29}$$

12.7.3 An Industrial Flow Process

Consider now an industrial steady-state flow process, which can occur in a heat engine, corn field, or ethanol plant, see **Figure 12.3**. The input to this

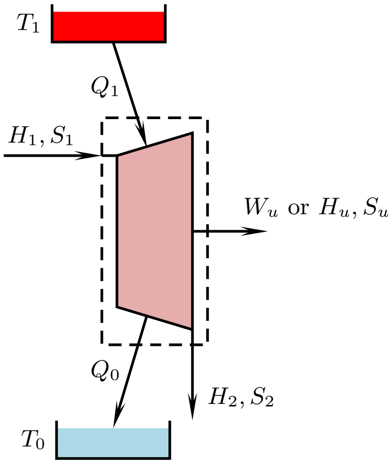

Figure 12.3: Exergy balance in ideal (reversible) and real (irreversible) non-isothermal industrial process.

irreversible process is an exergy carrier with the enthalpy H_1, and entropy S_1. The process is also supplied with the quantity of heat Q_1 from the source having temperature $T_1 > T_0$. The process effluent has enthalpy H_2, and entropy S_2. The rejected amount of heat Q_0 is transferred to the environment. The useful outcome of the process can be mechanical work W_u or a chemical product having parameters H_u and S_u. The effect of irreversibility is studied by comparing the industrial process with a reversible process with the same inflow and outflow parameters, and the same amount of driving heat. The only difference between these two processes is the amount of heat rejected to the environment. For the reversible process this heat is Q_{0r}, and for the irreversible one, it is Q_0.

The first and second law balances for the two processes are:

$$\begin{aligned} H_u &= H_1 - H_2 + Q_1 - Q_0 && \text{Real process} \\ H_{ur} &= H_1 - H_2 + Q_1 - Q_{0r} && \text{Reversible process} \\ H_{ur} - H_u &= Q_0 - Q_{0r} \end{aligned} \tag{12.30}$$

The increased useful effect of the reversible process causes the amount of rejected heat to be smaller than that in the industrial process, $Q_{0r} < Q_0$. The sum of all entropy increases in the industrial process is

$$\sum \Delta S = -\frac{Q_1}{T_1} + S_2 - S_1 + \frac{Q_0}{T_0} + S_u > 0 \tag{12.31}$$

while that in the reversible process is

$$\sum \Delta S_r = -\frac{Q_1}{T_1} + S_2 - S_1 + \frac{Q_{0r}}{T_0} + S_{ur} \equiv 0 \tag{12.32}$$

From Eqs. (12.31) and (12.32) it follows that

$$Q_0 - Q_{0r} = T_0 \left(\sum \Delta S + S_{ur} - S_u\right) \tag{12.33}$$

and we obtain

$$\underbrace{(H_{ur} - T_0 S_{ur})}_{B_{\mathrm{th,r}}} - \underbrace{(H_u - T_0 S_u)}_{B_{\mathrm{th}}} \equiv \delta B = T_0 \sum \Delta S \tag{12.34}$$

The left hand-side of Eq. (12.34) represents the difference of the useful thermal exergy in the reversible and industrial process, δB. It therefore represents the *exergy loss* due to the irreversibility of the industrial process under consideration. We have recovered, again, the famous GUOY-STODOLA law, also derived in **Appendix A**.

12.7.4 Cumulative Exergy Consumption (CExC)

All steps of a production process leading from natural resources taken from the environment to the final product result in *exergy losses* or exergy *consumption.*

Definition 16 (CExC) The cumulative exergy consumption (CExC) is the sum of the exergy of all natural resources in all the steps of a production process. □

The problem of cumulative *energy* consumption (CEnC) is better known, but calculation of CExC is more informative because it accounts for the exergy of non-energetic raw materials (soil, water, air, minerals) extracted from the environment.

Example 2 In contrast to the sun-driven tropical forest at steady state, the industrial biomass cycle relies on fossil energy, minerals, and chemicals. Therefore, a part W_R of the useful work W_u from the cycle, must be diverted to restore the non-renewable resources depleted by this cycle, see **Figure 12.4**. As long as the useful work exceeds the restoration work, $W_u > W_R$, the industrial biomass plantation may be beneficial, otherwise it is indefensible; for details, see (Patzek, 2004).

From Definition 16 it follows that the minimum restoration work is equal to the sum of the cumulative exergy consumption (CExC) by all the processes that convert natural resources into inputs of the industrial biomass cycle. The specific CExC for each such input has been listed in (Patzek, 2004), Table 23. The CExCs per kg of elemental P, K, and Ca can be converted from those listed in Table 23 per kg of P_2O_5, KCl, and CaO.

12.8 Problems

1. The relationship between entropy S and energy E for the stable equilibrium states of an electromagnetic field (a photon gas) confined to a cavity of volume V is $S = (4/3)a^{1/4}E^{3/4}V^{1/4}$, where $a := 8\pi^5 k^4/(15h^3c^3) = 7.569 \times 10^{-16}\ \mathrm{J\,m^{-3}K^{-4}}$, k is BOLTZMANN's constant, h is PLANCK's constant, and c is the speed of light in vacuum.

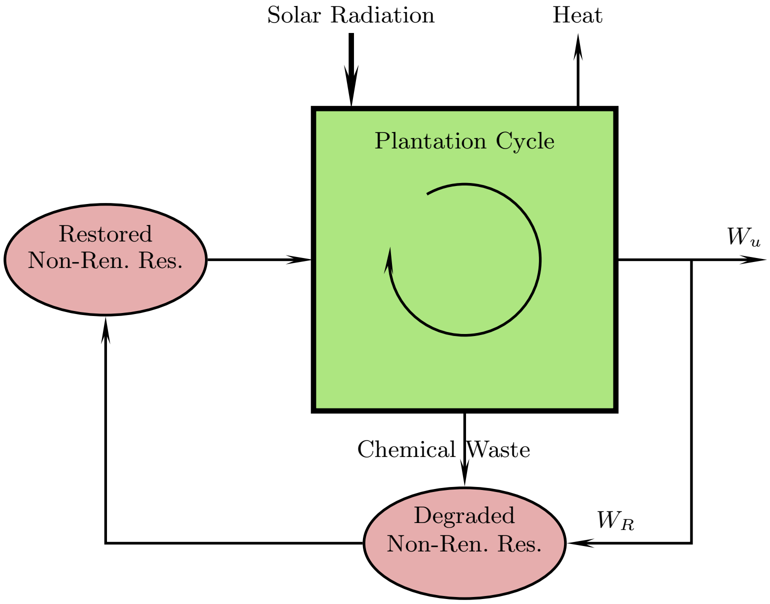

Figure 12.4: A part, W_R, of the useful work, W_u, from the industrial biomass cycle is diverted to "undo" mining of the environment by this cycle. If $W_u > W_R$, there is net benefit from the plantation, otherwise its use should be abandoned (Patzek, 2004).

(a) Prove the following relationships

$$\begin{aligned} S &= (4/3)aVT^3 \\ E &= aVT^4 \\ p &= (1/3)E/V \end{aligned} \tag{12.35}$$

(b) The pressure of the background radiation of the universe, modeled as a photon gas in a stable equilibrium state is 13.4×10^{-15} Pa. What is the temperature of the background radiation? Note: This temperature is the background of Earth's thermal radiation into the universe. Through this radiation, the Earth exports its thermal entropy, and there is life on her.

(c) What is the energy of the background radiation contained in 1 cubic light-year?

2. When two cavities (regions of space bounded by analytic surfaces) 1 and 2, each filled with radiation in a stable equilibrium state but at different temperatures T_1 and T_2, are placed in "contact" through an opening of

cross-sectional area $\mathcal{A}$, the electromagnetic field establishes a flow of energy and entropy from the cavity at higher temperature to the other one. The respective rates of flow are:

$$\begin{aligned} \dot{E}_{12} &= \mathcal{A}\,\frac{c}{4}\left[\left(\frac{E}{V}\right)_1 - \left(\frac{E}{V}\right)_2\right] \\ \dot{S}_{12} &= \mathcal{A}\,\frac{c}{4}\left[\left(\frac{S}{V}\right)_1 - \left(\frac{E}{V}\right)_2\right] \end{aligned} \tag{12.36}$$

where E/V and S/V are, respectively, the density of energy density and entropy of the radiation in each cavity, and c is the speed of light in vacuum.

(a) Using the results of Problem 1, show that the energy and entropy flow rates, in terms of the uniform temperatures T_1 and T_2 of the radiation in the two cavities, can be expressed as

$$\begin{aligned} \dot{E} &= \mathcal{A}\sigma(T_1^4 - T_2^4) \\ \dot{S} &= \mathcal{A}\,\frac{c}{4}\,\sigma(T_1^3 - T_2^3) \end{aligned} \tag{12.37}$$

where $\sigma = 5.6703 \times 10^{-8}$ $\mathsf{W\,m^{-2}K^{-4}}$.

(b) The rate at which energy flows from the hot center of the Earth is 3.25×10^7 MW (about 1/5000 of the rate of solar energy intercepted by the Earth). What would be the Earth's surface temperature without the sun?

(c) Assuming the Earth's surface temperature of 255 K and outer space temperature of 4 K, calculate the entropy flux j_S^E in $\mathsf{W\,m^{-2}\,K^{-1}}$ exported by the Earth.

Answer: $j_S^E \approx 1.2$ $\mathsf{W\,m^{-2}\,K^{-1}}$.

Chapter 13

Solar Energy Sequestered by Agriculture

Whenever, then, the usual and ordinary rate of the profits of agricultural stock, and all the outgoings belonging to the cultivation of land, are together equal to the value of the whole produce, there can be no rent.

— DAVID RICARDO
(*Principles of Political Economy and Taxation*, 1817)

13.1 What Are We Going to Learn?

You are going to learn about the main cereal foods of the world and major US agricultural crops.

13.2 Why Is It Important?

US agriculture is perhaps the most ruthlessly efficient machine that devours natural resources in exchange for huge quantities of agricultural commodities, formerly known as food. Yet, despite its deep reliance on fossil fuels and field chemicals, US agriculture in its best year ever, 2004, was able to sequester as seeds/grain a mere 0.37 $\mathsf{W\ m^{-2}}$ on annual basis, or not quite 0.2 percent of the average annual US insolation of 200 $\mathsf{W\ m^{-2}}$. All agricultural biomass (aboveground plants and their root systems) sequestered 0.67 $\mathsf{W\ m^{-2}}$ or 0.33 percent of average insolation.

It is important to understand the obvious limitations on the amount of biomass that can be produced on available land, as well as the long-term productivity of the land from which this biomass is removed. Over time, the net result will be soil depletion, water contamination, and gradual desertification.

13.3 Main Agricultural Crops

Table 13.1 lists annual production of major cereal grains in 2005. All but buckwheat (a pseudocereal) are true grasses. Maize, wheat and rice, between them, accounted for about 90% of all grain production worldwide, and roughly 50% of all food calories[1].

Below, brief summaries of the most important food and biofuels crops are provided. Unless stated otherwise, these summaries are based on FAOSTAT and Wikipedia.

13.3.1 Barley

Barley is a major animal feed crop, with smaller amounts used for malting and in health food. It is a member of the C_3 grass family *Poaceae*, see **Figure 13.1**. In 2005, barley ranked fourth largest grain crop in the world, see **Table 13.2**.

Two-row barley is the oldest form, wild barley having two rows as well. Two-row barley has a lower protein content than six-row barley and thus a lower enzyme content. High protein barley is best suited for animal feed or malt that will be used to make beers with a large adjunct content. Two-row barley is traditionally used in English ale style beers. Six-row barley is traditional in German and American lager style beers. Four-row is unsuitable for brewing.

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[1] Food and Agriculture Organization of the United Nations, Statistics Division (FAOSTAT). FAOSTAT provides access to over 3 million time-series and cross sectional data relating to food and agriculture, and contains data for 200 countries and more than 200 primary products and inputs.

Table 13.1: Main world cereals. Source: FAO^a

Grain	Mt^a	Description
Rice^b	700	The primary cereal of tropical regions
Maize	709	A staple food of peoples in the Americas, Africa, and of livestock worldwide
Wheat	623	The primary cereal of temperate regions
Barley	138	Grown for malting and livestock on land too poor or too cold for wheat
Sorghums	59.2	Important staple food in Asia and Africa and popular worldwide for livestock
Millets	30.2	A group *proso* cereals and important staple food in Asia and Africa
Oats	23.9	Formerly the staple food of Scotland and popular worldwide for livestock
Rye	15.2	Important in cold climates
Triticale	13.0	Hybrid of wheat and rye, grown similarly to rye
Buckwheat	2.1	Used in Europe and Asia for pancakes and groats
Fonio^c	0.3	Several varieties are grown as food crops in Africa

[a] Mega tonnes produced, FAOSTAT accessed March 31, 2007

[b] 628 Mt from rice paddies

[c] White fonio (*Digitaria exilis*) is the most important of a diverse group of wild and domesticated *Digitaria* species that are harvested in the savannas of west Africa. Fonio is the smallest of all species of millet

Half of the world's barley production is used as an animal feed. Most of the remainder used for malting and is a key ingredient in beer and whiskey production. A small amount is used in health foods.

Barley production has been declining worldwide due to the conversion of barley fields to corn. In fact, in 2007, the shortage of barley may be significant enough to affect prices of beer: Joe six-pack is on the way to becoming Joe three-pack, who drives a little on corn ethanol.

13.3.2 Maize (Corn)

Maize (*Zea mays* also known as corn) is a C_4 grass producing the most important grain worldwide, see **Table 13.3**. It was domesticated in Mesoamerica and then spread throughout the American continents and the rest of the world after European contact with the Americas in the late 15th century.

Maize stems superficially resemble bamboo canes and the joints (nodes) can reach $20-30$ cm apart. Maize has a very distinct growth form, the lower leaves being like broad flags, $50-100$ cm long and $5-10$ cm wide; the stems are erect, conventionally $2-3$ m in height, with many nodes, casting off flag-leaves at every node. Under these leaves and close to the stem grow the ears, see **Figure 13.4**. An ear contains from 200 to 400 grains, and is from $10-25$ cm in length. The ears are female inflorescences, tightly covered over by several

Figure 13.1: A six-row barley field. Barley can be divided by the number of kernel rows in the head. Three forms have been cultivated; two-row barley (traditionally known as *Hordeum distichum*), four-row (*Hordeum tetrastichum*) and six-row barley (*Hordeum vulgare*). In two-row barley only one spikelet is fertile, in the four-row and six-row forms, all three are fertile.

layers of leaves, and so closed-in by them to the stem that they do not show themselves easily until the emergence of the pale yellow silks from the leaf whorl at the end of the ear. The silks are elongated stigmas that look like tufts of hair, at first green, and later red or yellow. The apex of the stem ends in the tassel, an inflorescence of male flowers. Each silk may become pollinated to produce one kernel of corn.

Genetically modified Bt-maize (see Footnote 2) pollen is toxic to Monarch butterfly larvae (Losey et al., 1999), but it is not toxic to bees, at least not directly (Malone and Pham-Delègue, 2001).

The average mass composition of dry maize grain is listed in **Table 13.4**.

13.3.3 Cotton

Cotton is a soft fiber that grows around the seeds of the cotton plant (*Gossypium spp.*), a shrub native to tropical and subtropical regions around the world, see

Table 13.2: Top barley producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
Russia	16.7
Canada	12.1
Germany	11.7
France	10.4
Ukraine	9.3
Turkey	9.0
Australia	6.6
United Kingdom	5.5
United States	4.6
Spain	4.4
World	138

[a] Accessed March 29, 2007

Table 13.3: Top corn producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
United States	282
China	140
Brazil	35.1
Argentina	20.5
Mexico	18.0
Indonesia	12.0
France	13.8
India	14.7
South Africa	11.7
Italy	10.5
World	709

[a] Accessed March 29, 2007

Figure 13.3.

Currently, there are five prominent types of cotton being grown commercially around the world. They are *Egyptian*, *Sea Island*, *American Pima*, *Asiatic* and *Upland*. Because cotton plants need a long, sunny growing period with at least

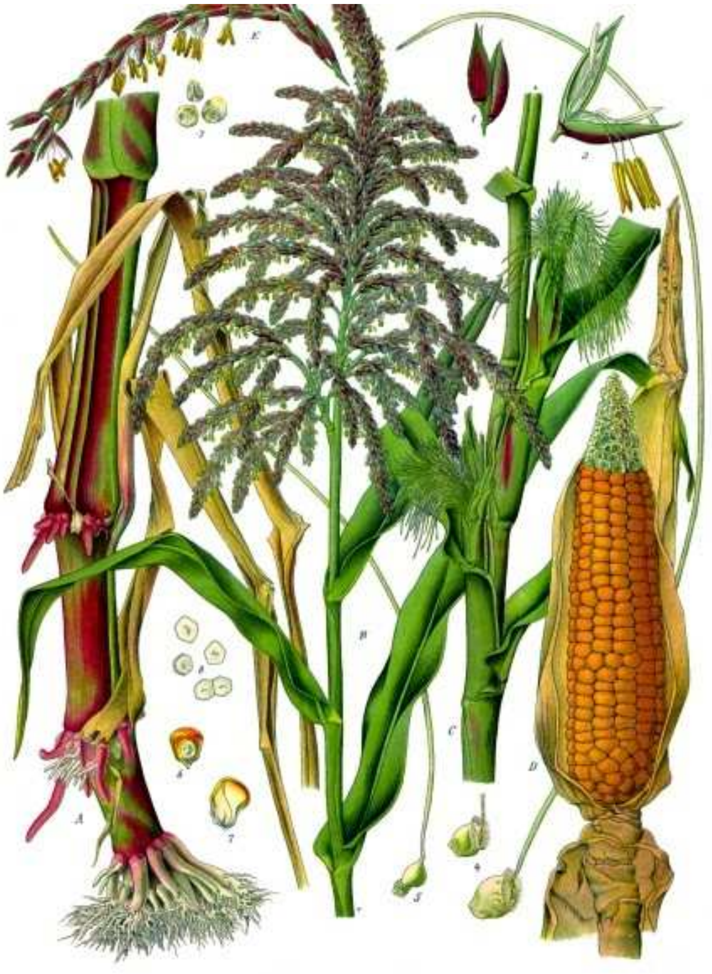

Figure 13.2: Maize, *Zea mays* also known as corn. Source: Wikipedia.

160 frost-free days, they are grown between latitudes 45 degrees north and 30 degrees south. The major producing countries within this region are China, the United States, India, Pakistan and Republic of Uzbekistan. Together with 45 million tonnes of cottonseed, 25 million tonnes of cotton were produced in 2005, see **Table 13.5**.

The fiber is most often spun into thread and used to make a soft, breathable textile, which is the most widely used natural-fibre cloth in clothing today. The English name derives from the Arabic word *al qutun*, meaning “cotton fiber.”

Cotton fiber, once it has been processed to remove seeds and traces of wax, protein, etc., consists of nearly pure cellulose, a natural polymer. Cotton production is very efficient, in the sense that ten percent or less of the weight is lost

Table 13.4: Average dry mass composition of maize grain (White and Johnson, 2003)

Component	% by mass
Starch	66
Oil	3.9
Gluten feed (21% protein)	24
Gluten meal (60% protein)	5.7
Losses	0.4

in subsequent processing to convert the raw cotton bolls (seed cases) into pure fiber. The cellulose is arranged in a way that gives cotton fibers a high degree of strength, durability, and absorbency. Each fiber is made up of twenty to thirty layers of cellulose coiled in a neat series of natural springs. When the cotton boll is opened, the fibers dry into flat, twisted, ribbon-like shapes and become kinked together and interlocked. This interlocked form is ideal for spinning into a fine yarn. Cotton is an important commodity worldwide.

The cotton industry relies heavily on fertilizers and insecticides, as well as on genetically-modified plants, the so-called Bt-cotton, with a *Bacillus thuringiensis* bacterium[2] gene which codes for a plant-produced protein that is toxic to a number of pests such as tobacco budworm, cotton bollworm and pink bollworm. BT-cotton is not toxic to bees, at least not directly (Malone and Pham-Delègue, 2001).

13.3.4 Potatoes

Potato (*Solanum tuberosum*) originated some 8000 years ago in high-altitude tropical areas of Peru, where a staggering 5500 cultivated varieties have been developed by generations of farmers. Taken by the Spanish to Europe in the 16th century, the tuber quickly adapted to northern growing conditions and soon became a staple food at a time of rapid population growth. From Europe it spread further across the globe: today potatoes are grown on an estimated 180,000 square km of farmland, ranging from China's Yunnan plateau and the subtropical lowlands of India, to Java's equatorial highlands and the steppes of the Ukraine. In terms of sheer quantity harvested, the humble potato tuber

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[2] *Bacillus thuringiensis* (Bt) is a soil-dwelling bacterium of the genus *Bacillus.* Bt is closely related to *B. cereus*, a soil bacterium, and *B. anthracis*, the cause of anthrax. Like other members of the genus, all three are aerobes capable of producing endospores. Upon sporulation, Bt forms crystals of proteinaceous insecticidal δ-endotoxins (Crystal (Cry) toxins) which are encoded by cry genes (de Maagd et al., 2001). Cry toxins act specifically against species of the orders *Lepidoptera* (Moths and Butterflies), *Diptera* (Flies and Mosquitoes) and *Coleoptera* (Beetles). Thus, Bt serves as an important reservoir of Cry toxins and cry genes for production of biological insecticides and insect-resistant genetically modified crops. Recently Bt-maize has been shown to cause liver damage in rats, which for the first time implicates Bt-plants as a possible human health risk (Séralini et al., 2007).

Figure 13.3: Cotton, *Gossypium spp.*. **Top:** A cotton plant showing the outlines of cotton bolls, segmented pods, each containing 32 immature seeds from which the cotton fibers will grow. A boll is considered a fruit because it contains seeds. **Bottom:** Mature cotton bolls. Source: Wikipedia.

is, in fact, the world's fourth food crop - after maize, rice, and wheat - with production in 2005 of more than 323 million tonnes, see **Table 13.6**.

While potatoes are considered relatively poor in nutrients, they are rich in carbohydrates, making them a good source of energy. They have the highest protein content (around 2.1 percent on a fresh weight basis) in the family of

Table 13.5: Top cottonseed producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
China	11.4
United States	7.7[b]
India	5.0
Pakistan	4.4
Uzbekistan	2.5
Brazil	1.8
Turkey	1.1
World	45

[a] Accessed March 29, 2007

[b] There is also a comparable mass of cotton fiber

root and tuber crops, and protein of a fairly high quality, with an amino-acid pattern that is well matched to human requirements. They are also very rich in vitamin C - a single medium-sized potato contains about half the recommended daily intake.

Under temperate and subtropical conditions, an irrigated crop of about 120 days can yield from 25 to 35 tonnes/ha of fresh tubers, while farmers in the tropics can harvest between 15 and 25 tonnes within 90 days of planting. These high yields require proportionally high fertilizer application rates, e.g., $200-300$ kg N per hectare and similar quantities of P and K, soil-damaging planting techniques, and large quantities of insecticides and nematocides. In the lowlands of Bangladesh and eastern India, potato has become a valuable winter cash crop, while in the Philippines and Indonesia, potato production helps to satisfy rapidly increasing demand from snack food industries. In sub-Saharan Africa, potatoes have become a preferred food in urban areas, and an important staple and cash crop in highland production zones of Cameroon, Kenya, Malawi, Nigeria, Rwanda and South Africa.

13.3.5 Rapeseed

Rapeseed is in the *Brassica* family and is related to broccoli, cabbage and cauliflower. Rapeseed plants grow $60-120$ cm tall, branching from the central stem. The bright yellow flowers have four petals and the pods, which are $2.5-4$ cm long and approximately 3 mm wide. The rapeseed fruit consists of a pod that is long and narrow, approximately $5-10$ cm in length. These pods may contain fifteen to forty small round seeds that are about $1-2.5$ mm long. The oil content of the seed ranges from 33.2 to 47.6% (8.5% moisture basis) (Salunkhe et al., 1992). The rest is protein and carbohydrates.

Rapeseed, see **Figure 13.5**, is widely cultivated throughout the world for the

Figure 13.4: Potato, *Solanum tuberosum* is the fourth largest world crop. **Top:** A potato field in Prince Edwards Island. Source: Government of Prince Edward Island, Canada. **Bottom:** Planting potatoes is an arduous and soil erosion enhancing activity. Source Wikipedia.

production of animal feed, vegetable oil for human consumption, and biodiesel. The leading producers are listed in **Table 13.7**. According to the United States Department of Agriculture, rapeseed was the third leading source of vegetable oil in the world in 2000, after soybean and oil palm, and also the world's second leading source of protein meal, although only one-fifth of the production of the leading soybean meal. Rapeseed oil is also used to make biodiesel.

Natural rapeseed oil contains erucic acid, which is mildly toxic to humans in large doses but is used as a food additive in smaller doses. Canola, originally a

Table 13.6: Top potato producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
China	73.0
Russia	37.3
India	25.0
Ukraine	19.5
United States	19.1
Germany	11.6
Poland	10.4
Belarus	8.2
Netherlands	6.8
France	6.7
Canada	4.4
World	323

[a] Accessed March 29, 2007

Table 13.7: Top rapeseed producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
China	13.0
Canada	8.0
India	6.8
Germany	5.0
France	4.5
United Kingdom	1.9
Poland	1.4
US	0.7
World	46.4

[a] Accessed March 29, 2007

syncopated form of the abbreviation “Can.O., L-A.” (Canadian Oilseed, Low-Acid) that was used by the Manitoba government to label the seed during its experimental stages, is now a tradename for low erucic acid rapeseed.

Figure 13.5: Rapeseed, *Brassica napus*. **Top:** flowers. **Bottom:** Seed pods. Source: arglist.com/photos/brassicales.html.

13.3.6 Rice

Rice is two species in the C_3 *Poaceae*[3] (true grass) family, *Oryza sativa* and *Oryza glaberrima*, see **Figure 13.6**. These plants are native to tropical and subtropical southern and southeastern Asia and in Africa. Rice provides more than one fifth of the calories consumed by humans in their global diets and is the second largest grain crop on the Earth, see **Table 13.8**. Recently, rice has been overtaken by corn used to produce ethanol fuel but not food.

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[3] Pronunciation of Latin plant names is explained nicely at www.swcoloradowildflowers.-com/plant%20names.htm.

Rice is a monocarpic[4] annual plant, growing to $1 - 1.8$ m tall, occasionally more depending on the variety and soil fertility. The grass has long, slender leaves $50 - 100$ cm long and $2 - 2.5$ cm wide. The small wind-pollinated flowers are produced in a branched arching to pendulous inflorescence 3050 cm long. The seed is a grain 512 mm long and $2 - 3$ mm thick.

Table 13.8: Top rice producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
China	182
India	137
Indonesia	54
Bangladesh	40
Vietnam	36
Thailand	27
Myanmar	25
Pakistan	18
Philippines	15
Brazil	13
Japan	11
US	10
World	700

[a] Accessed March 29, 2007

Rice is often grown in paddies. The shallow puddles take advantage of the rice plant's tolerance to water; the water in the paddies prevents weeds from outgrowing the crop. Once the rice has established dominance of the field, the water can be drained in preparation for harvest. Paddies increase productivity, although rice can also be grown on dry land (including on terraced hillsides) with the help of chemical weed controls.

13.3.7 Sorghum

Sorghum is a genus of about 30 species of C_4 grasses raised for grain, native to tropical and subtropical regions of Eastern Africa, with one species native to Mexico. The plant is cultivated in Southern Europe, South America, Central America, North America and Southern Asia. Grain sorghum seeds are very small - about 12 000 to 15 000 seeds equal one pound of grain sorghum. There are approximately 70 to 1250 seeds in one grain sorghum head or panicle, see **Figure 13.7**.

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[4] Plants that flower, set seeds, and then die.

Figure 13.6: American long-grain rice. The term “wild rice” can refer to wild species of *Oryza*, but conventionally refers to species of the related genus *Zizania*, both wild and domesticated. Source: Wikipedia.

Sorghum is well-adapted to growth in hot, arid or semi-arid areas. The many subspecies are divided into four groups: grain sorghums (such as milo), grass sorghums (for pasture and hay), sweet sorghums, and broom corn (for brooms and brushes). Sorghum is used for food, fodder, and the production of alcoholic beverages. It is drought-tolerant and heat-tolerant and is especially important in arid regions. Sorghum is an important food crop in Africa, Central America, and South Asia, and is the fifth most important cereal crop grown in the world. Sorghum straw (stem fibres) can be made into excellent wall board for house building, as well as biodegradable packaging. Sorghum grain is also used to produce ethanol.

Figure 13.7: In contrast to corn, both the male and female flowers of sorghum plants are in a panicle at the end of the culm. Source: soilcrop.tamu.edu/-photogallery/cornsorghum.

13.3.8 Soybean

Today's soybean plants are $60 - 100$ cm in height, bearing typically $20 - 90$ pods with $2 - 3$ seeds each. The seeds range in mass from 8 to 50 grams per 100 seeds. Prior to the 20th century, soybeans bearing non-yellow seeds were very common worldwide: black, green, brown, yellowish green, or mottled; today's seeds are largely straw yellow, see **Figure 13.8**.

Soybean (*soya*) is an important source of high quality, inexpensive protein and oil. With an average protein content of 40% and oil content of ∼20%, soybean has the highest protein content of all food crops, and is second only to groundnut in terms of oil content among food legumes.

Cultivation is successful in climates with hot summers, with optimum growing conditions in mean temperatures of 20^0C to 30^0C; temperatures of below 20^0C and over 40^0C retard growth significantly. Soybean plants can grow in a wide range of soils, with optimum growth in moist alluvial soils with a good organic content. Soybeans, like most legumes perform nitrogen fixation by establishing a symbiotic relationship with the bacterium *Bradyrhizobium japonicum*.

Table 13.9: Top sorghum producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
United States	10.0
Nigeria	9.2
India	7.5
Mexico	5.5
Sudan	4.3
Argentina	2.9
China	2.6
Ethiopia	2.2
Australia	2.0
Brazil	1.5
World	59.2

[a] Accessed March 29, 2007

However, for best results an inoculum of the correct strain of bacteria should be mixed with the soybean (or any legume) seed before planting. Modern crop cultivars generally reach a height of around 1 m (3 ft), and take between 80-120 days from sowing to harvesting. About 370,000 soybean plants per hectare is usually associated with high yields.

According to the FAOSTAT database, in 2005, over 210 million tonnes of soybean was produced worldwide[5] on 91 million hectares. The leading producer was the USA which accounted for 39% of soybean; Brazil produced 24%, Asia 12%, and Africa 0.5%, see **Table 13.10**. The average yield in 2005 was 2300 kg/ha, ranging from about 3500 kg/ha in Western Europe, 2870 kg/ha in the USA and 2190 kg/ha in Brazil, to 985 kg/ha in Africa.

Soybeans provide majority of the edible consumption of fats and oils in the United States. Soya beans, which possess high quantities of protein, and soybean products are used in a wide range of food and industrial products. Soya products have three major divisions: soy oil products, whole bean products, and soy protein products. Food products include baby food, cereal, diet foods, imitation meats, processed meats, soy sauce, tofu and miso, salad dressings and margarine, cooking oil, candy, and baked goods. Soybeans are used in pet foods and as the leading source of protein meal for US livestock. Industrial uses for soybeans include wallboard and plywood, medicines, soaps and disinfectants, pesticides, fertilizers, candles, linoleum, varnish, fire extinguisher fluid, and paint. Soybean oil is also used to make biodiesel.

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[5] In comparison, the USA alone produced 300 million tonnes of corn grain in 2004.

Figure 13.8: A soybean field (left) and soybean varieties (right). Source: Wikipedia.

Table 13.10: Top soybean producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
United States	83.4
Brazil	51.2
Argentina	38.3
China	16.8
India	6.3
Paraguay	3.5
Canada	3.0
Bolivia	1.7
Italy	0.5
World	214.3

[a] Accessed March 29, 2007

13.3.9 Sugarbeets

Sugar beet (*Beta vulgaris L.*), a member of the *Chenopodiaceae* subfamily and the *Amaranthaceae* family, is a plant whose large (12 kg) storage root contains

Table 13.11: Soybean mass composition and heating values

Soybean Component	LHV[a] MJ/kg	HHV[a] MJ/kg	Mass[b] %	HHV %	Heating Value Data Source
Oil	37.0	39.6	18.4	40.3	(Domalski et al., 1987), p. 237
Dirt	0.0	0.0	0.8	0.0	
Hulls[c]	17.1	18.2	7.4	7.5	Estimated, (Domalski et al., 1987), p. 9-29
Water	0.0	0.0	16.0	0.0	
Meal[d]	15.4	16.5	57.4	52.3	http://www.gnb.ca/0170/01700003-e.asp
Total	16.9	18.1	100.0	100.0	

[a] LHV = Low (Net) Heating Value, HHV = High (Gross) heating Value
[b] (Sheehan et al., 1998), Table 82, p. 136
[c] Estimated from heating values of various nut hulls
[d] The high heating value is assumed to be 1.07×LHV

a high concentration of sucrose (13 – 22%), see **Figure 13.9**.

The European Union, the United States, and Russia are the world's three largest sugar beet producers, see **Table 13.12**, although only Europe and Ukraine are significant exporters of sugar from beet. Beet sugar accounts for 30% of the world's sugar production.

Sugarbeet is a biennial plant which was developed in Europe in the 18th century from white fodder beets. Sugar reserves are stored in the sugarbeet root during the first growing season for an energy source during overwintering. The roots are harvested for sugar at the end of the first growing season but plants which overwinter in a mild climate will produce flowering stems and seed during the following summer and fall. Sugarbeet roots do not survive the winter in North Dakota, Minnesota, and Wisconsin. Sugarbeet is a summertime crop in the northern United States and a winter or summer crop in more southern, semi-arid regions. Sugarbeet seed for the United States is produced in Oregon where the climate is cool enough for vernalization[6] but warm enough for the roots to live through the winter.

Sucrose from sugarbeets is the principal use for sugarbeets in the United States. Sugarbeet pulp and molasses are processing by-products widely used as feed supplements for livestock. These products provide required fiber in rations and increase the palatability of feeds. Sugarbeet tops also can be used for livestock feed. Sheep and cattle ranchers allow grazing of beet fields in the fall to utilize tops. Cattle and sheep also will eat small beets left in the field after harvest but producers grazing livestock in harvested fields should be aware of the risk of livestock choking on small beets.

Beet tops (leaves and petioles) also can be used as silage. Sugarbeets that produce 20 tons/acre of roots also produce a total of about 5 tons acre^{-1} of total digestible nutrients. Tops are an excellent source of protein, vitamin A,

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[6] Acquisition of the competence to flower in the spring by exposure to the prolonged cold of winter.

Figure 13.9: A sugarbeet field in Colorado. Source: USDA ARS Fort Collins, Co.

and carbohydrates.

Sugarbeets are unique in their nitrogen requirements. Too little nitrogen results in poor leaf canopies, premature yellowing and reduced yields, while too much nitrogen leads to a reduced sucrose content, increased impurities and lowered sucrose extraction. Sugarbeets require about 130, $50-80$, and $100-200$ $\mathsf{kg\ ha}^{-1}$ of N, P and K, respectively (Vos and van der Putten, 2000).

Table 13.12: Top sugarbeet producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
France	31.2
Germany	25.3
United States	25.1
Russia	21.4
Ukraine	15.5
Italy	14.2
Poland	11.7
Belgium	6.0
Netherlands	5.9
Iran	5.3
Czech Republic	3.5
World	250.9

[a] Accessed April 3, 2007

13.3.10 Sugarcane

Sugarcane (*Saccharum officinarum*) is a genus of 6 to 37 species (depending on taxonomic interpretation) of tall grasses (family *Poaceae*, tribe *Andropogoneae*), native to warm temperate to tropical regions of the Old World. The stout fibrous sugarcane stalks are rich in sugar and measure 2 to 6 m in height and 2.5 to 7.5 cm in diameter. Graceful, sword-shaped leaves, similar to those of the corn plant, fold in a sheath around the stem, see **Figure 13.10**. The plant grows in clumps of solid stalks with regularly spaced nodes or joints, each with a bud that can be planted for commercial asexual propagation. Otherwise, sugarcane propagates by wind-blown seed.

Sugarcane is a tropical C_4 plant that cannot survive freezing temperatures. It thrives in abundant sunlight and warm temperatures (25-30^{0}C), and with plentiful water (75-150 cm yr^{-1}) (Srivastava, 2004).

All of the sugarcane species interbreed, and the major commercial cultivars are complex hybrids. Brazil is by far the largest sugarcane producer, followed by India and China, see Table 13.13. The 2005 world sugarcane crop was 1.27 billion tonnes, making it by far the largest single agricultural harvest. However, the high water content in sugarcane stems puts its harvest dry mass behind the three top cereal crops (Patzek and Pimentel, 2006). Sugarcane harvest in the US is almost identical to sugarbeet harvest, see Tables 13.13 and 13.12, and Problem 1.

Figure 13.10: Sugarcane plant *Saccharum officinarum*. The cut, juice-rich stalk is the foreground (left). From the brown stems grow green tops (right). Some dying brown leaves are also shown. Sources: Wikipedia (left), T. W. Patzek, The Dole Plantation Garden, Oahu, Hawaii (right).

13.3.11 Wheat

Globally, wheat is the most important human food grain and ranks third in total production as a cereal crop behind rice; the second being maize. Wheat grain is a staple food used to make flour for leavened, flat and steamed breads; cookies, cakes, pasta, noodles and couscous; and for fermentation to make beer, alcohol, vodka or biofuel.

Wheat and barley were the first cereals known to have been domesticated. Wheat originated in southwest Asia in the area known as the Fertile Crescent, see **Figure 13.11**. The earliest archaeological evidence for wheat cultivation comes from the Levant and Turkey. Around 10,000 years ago, wild einkorn and emmer wheat were domesticated, see Figure **13.12**, as part of the origins of agriculture in the Fertile Crescent. Cultivation and repeated harvesting and sowing of the grains of wild grasses led to the selection of mutant forms with tough ears which remained attached to the stem during the harvest process, and larger grains. Selection for these traits is an important part of crop domestication. Because of the loss of seed dispersal mechanisms, domesticated wheats

Table 13.13: Top sugarcane producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
Brazil	423
India	232
China	87.8
Pakistan	47.2
Mexico	45.2
Thailand	43.7
Colombia	39.8
Australia	37.8
Indonesia	29.5
United States	25.3
South Africa	21.3
Philippines	20.8
Argentina	19.3
Guatemala	18.5
World	1267

[a] Accessed April 3, 2007

cannot propagate in the wild. In fact, out of some 25 species of wheat, only two are widely cultivated worldwide: Common Wheat or Bread wheat, *Triticum aestivum*, and Durum, *T. durum*.

The cultivation of wheat began to spread beyond the Fertile Crescent during the Neolithic period. By 5,000 years ago, wheat had reached Ethiopia, India, Ireland and Spain. A millennium later it reached China. Agricultural cultivation using horse collar leveraged plows (3000 years ago) increased cereal grain productivity yields, as did the use of seed drills which replaced broadcasting sowing of seed in the 18th century. Yields of wheat continued to increase, as new land came under cultivation and with improved agricultural husbandry involving the use of fertilizers, threshing machines and reaping machines (the combine harvester), tractor-draw cultivators and planters, and better varieties. Wheat production is expensive and has started to decline worldwide. Nevertheless, wheat remains one of the most important cereals worldwide, see **Table 13.14**.

Figure 13.11: The Fertile Crescent is a crescent-shape region in the Middle East incorporating the Levant, Mesopotamia and Ancient Egypt. Watered by the Nile, Jordan, Euphrates and Tigris rivers and covering some 400-500,000 square kilometers, the region extends east and south from the eastern shore of the Mediterranean. The Levant, “the country where the sun rises,” encompasses land SE of Anatolia, including Israel, the Palestinian territories, Jordan, Lebanon and Syria.

13.4 Solar Energy Sequestered by US Agriculture

13.4.1 Land Use in the US

Based on the 2002 Census of Agriculture US Department of Agriculture (Ann M. Veneman et al., 2004), Table 8, fertile land in the US was used as follows:

1. Prime agricultural land comprised 176 million hectares. Out of this pool, 123 million hectares were used as harvested cropland, 24.5 million hectares were used as pastures, 7 million hectares were idle, and 15 million hectares were used by failed crops.

2. There were 160 million hectares of pastureland and rangeland.

3. Interdispersed between the first two categories of land were 31 million hectares of woodland.

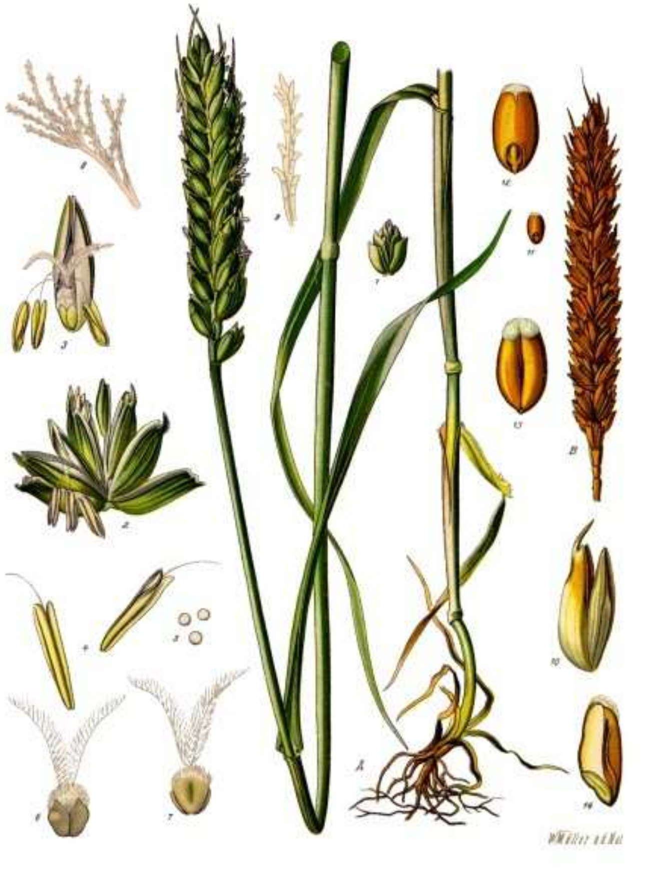

Figure 13.12: Morphology of wheat plants. Source: Wikipedia.

The area of prime agricultural land continues to decline at the rate of ∼1200 ha day^{-1} due to urban "development" and other land use conversions (Markham and Steinzor, 2006).

Finally, there are almost 300 million hectares of forest and timberland (Smith et al., 2001). While total forest area has been relatively stable for the last 100 years, there have been significant regional shifts in the area and composition of the nation's forests. Eastern forests cover about 155 million hectares and are predominantly broadleaf (74%), with the exception of extensive coniferous forests and plantations in the southern coastal region. These are largely in private ownership (83%). By contrast, about 145 million hectares of western forests are predominantly coniferous (78%) and in public ownership (57%).

The fertile land distribution in the US is shown in **Figure 13.13**.

Table 13.14: Top wheat producers - 2005 (million metric ton). Source: FAO[a]

Country	Production
China	97.4
India	72.0
United States	57.3
Russia	47.7
France	36.8
Canada	26.8
Australia	25.1
Germany	23.7
Pakistan	21.6
Turkey	21.0
World	623

[a] Accessed March 29, 2007

13.4.2 Calorific Values of Whole Plants

Our goal is to calculate the Higher Heating Value (HHV), see Chapter 3, of most of the biomass photosynthesized each year by US agriculture. We want to account not only for the measured crop yields, but also for the mass of stems, leaves, and roots. Luckily, plants are self-similar (Mandelbrot, 1977), and different parts of plants have almost constant proportions independent of plant size.

The quantities commonly used to characterize above-ground biomass and plant roots on water-free basis, and convert this mass to HHV are:

1. The harvest index

$$\text{HI} = \frac{\text{kg harvested seeds dmb}}{\text{kg biomass above ground dmb}} \tag{13.1}$$

   where `dmb` denotes dry-matter basis. The harvest index is defined as the ratio of seed yield to aboveground biological yield, or the total dry matter the plant produces above ground. It was originally conceived by Donald (1962) as an aid in selecting efficient genotypes for plant breeding, but it has also been used to estimate aboveground biomass production from published agricultural yield statistics (Donald and Hamblin, 1976). Prihar & Stewart (1990) found that, except under extreme stress conditions, HI of sorghum, corn, and wheat varied little for each crop.

2. The root-to-shoot ratio

$$\text{RtS} = \frac{\text{kg roots at harvest dmb}}{\text{kg biomass above ground dmb}} \tag{13.2}$$

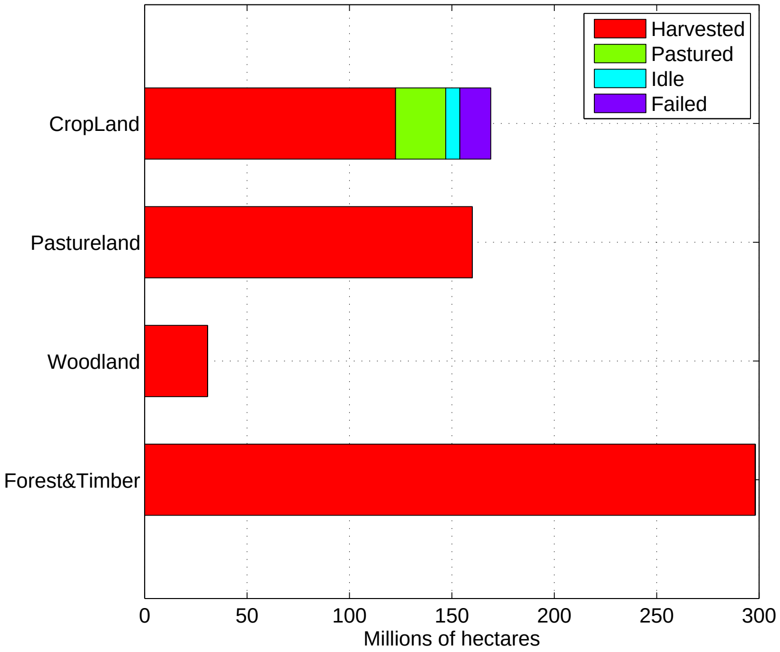

Figure 13.13: Use of fertile land over the entire land mass of US. The bars comprise 72% of land area of the contiguous 49 states, Alaska, and Hawaii. Sources: The 2002 USDA Census of Agriculture (Ann M. Veneman et al., 2004) and US Forest Service (Smith et al., 2001).

Estimation of total plant mass from measurements of aboveground production requires knowledge of the partitioning of photosynthetic products between above- and below-ground plant parts (Snyder and Carlson, 1984). For annual crops, the root-to-shoot biomass ratio, measured at or near harvest maturity, may be an adequate estimator from which total production may be obtained. Errors are likely to arise when significant production is lost to senescence and detachment, above or below ground, before harvest.

3. Moisture contents of crops, above-ground biomass, and roots. To allow meaningful calculations using HI and RtS, the wet harvest must be reduced to water-free dry matter.

4. High heating values of plant parts in MJ/kg dry biomass. As we already know from Chapter 3, different plants and their parts have different calorific values, which must be measured separately using the calorimetric bomb, see e.g., (Domalski et al., 1987).

Table 13.15: Characterization of top US crops in 2004

Crop	Yield[a]	Area	Water[b]	HI[c]	RtS[d]	HHV[e]
	kg/ha	10^6 ha	–	–	–	MJ/kg
Soybean	2411	29.931	0.15	0.42	0.18	18.1
Corn	8565	29.798	0.15	0.53	0.18	18.8
Hay	2002	25.078	0.10	1.00	0.87	18.4
Wheat	2596	20.235	0.11	0.39	0.20	18.1
Cottonseed	1268	5.284	0.10	0.55	0.14	19.4
Cotton fiber	863	5.284	0.10	1.00	0.00	19.4
Sorghum	3058	2.637	0.30	0.51	0.09	18.0
Corn Silage	10346	2.469	0.74	1.00	0.18	17.7
Barley	3389	1.627	0.10	0.50	0.50	17.1
Rice	6663	1.346	0.15	0.50	0.63	17.4
Oats	2140	0.723	0.08	0.52	0.40	19.1
Sugarbeets	10321	0.529	0.80	0.70	0.00	17.7
Beans	1391	0.493	0.15	0.55	0.26	16.3
Potatoes	13490	0.472	0.73	0.66	0.08	11.9
Canola	1271	0.335	0.30	0.15	0.24	23.8
Rye	1346	0.121	0.22	0.35	0.24	17.1
Rapeseed	1392	0.003	0.11	0.17	0.31	23.8

[a]All yields on dry-mass basis, [b]Mass fraction [c]Harvest Index, Eq. (13.1), [d]Root-to-Shoot ratio, Eq. (13.2), [e] Higher Heating Value, Chapter 3

13.4.3 Main US Crops

The procedure of calculating solar energy sequestered as biomass by US agriculture is as follows:

1. The main US crops in **Table 13.15** are sorted by the harvested areas obtained from the US Department of Agriculture, National Agricultural Statistics Service (NASS, www.nass.usda.gov/Publications/index.asp). The total harvested area of these crops is 121.1 million hectares, see Figure 13.14, or 98% of the harvested cropland in 2002.
2. For the calculations of solar energy sequestered by these crops, I picked the year 2004 because of the all-time yield records set by the US agriculture that year.
3. The average dry mass yields listed in Table 13.15 have been obtained

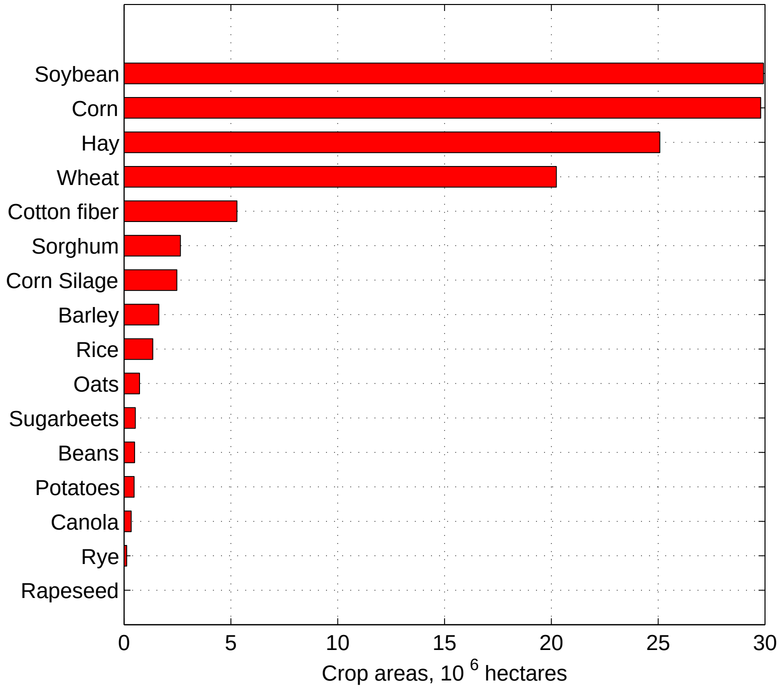

Figure 13.14: Harvested areas of the largest US agricultural crops. Source: USDA NASS. Total area of the crops is 121.1 million hectares.

from NASS and multiplied by 1 minus the average water mass fractions of harvested biomass in Column 4 of Table 13.15. These yields have been converted into kg ha^{-1} from the various customary units used in the USDA database. The conversions have been done according to the guidelines in (Anonymous, 1992).

4. For simplicity, I have assumed that the other parts of harvested plants (stems, leaves, root systems, etc.) have the same average water content. If anything, these parts contain more water than grain and solar energy sequestered by them will be less than calculated here. Therefore my calculation is somewhat optimistic.

5. For each crop, the above-ground dry biomass of all plant parts other than seed is calculated as

$$\text{AG remaining biomass} = \frac{\text{Seed/grain yield dmb} \times (1 - \text{HI})}{\text{HI}} \qquad \text{kg ha}^{-1} \tag{13.3}$$

6. Dry biomass of root systems is calculated as

$$\text{Root biomass} = \text{Seed/grain yield dmb} \times \text{RtS} \qquad \text{kg ha}^{-1} \tag{13.4}$$

7. Total plant dry biomass is then

$$\begin{aligned}\text{Total Biomass} &= \text{Seed/grain yield} + \text{AG remaining biomass} + \\ &+ \text{Root biomass} \qquad \mathsf{kg\ ha^{-1}}\end{aligned} \tag{13.5}$$

8. Total energy of that biomass is

$$\text{Total Energy} = \text{Total Biomass} \times \text{HHV} \qquad \mathsf{MJ\ ha^{-1}} \tag{13.6}$$

   Note that if anything the HHV's of other plant parts are lower than that of seed/grain. Therefore my calculation is somewhat optimistic.

9. All other quantities are calculated by the multiplication by harvested crop areas and the division by the number of seconds in one year.

10. To estimate solar energy sequestered by US rangeland and pastureland, I have used the above-ground precultivation productivity of the productive Great Plains biome, estimated in (Bradford et al., 2005) to be 164 g C $\mathsf{m^{-2}\ yr^{-1}}$. The result is 7.43 EJ $\mathsf{yr^{-1}}$.

The calculation results are summarized in Figures **13.15** – **13.20**.

13.5 Conclusions

The main conclusions of this chapter are:

1. The entire humanity depends for its food on a couple of species of the following three cereal crops: rice, maize, and wheat. All other crops are tiny compared with these three.

2. In the US, the 16 largest (by harvested area) commodity crops are maize (corn), soybeans, hay, wheat, cotton, sorghum, corn silage, barley, rice, oats, sugarbeets, beans, potatoes, canola, rye, and rapeseed. I have not included sugarcane, leaving it as a homework exercise.

3. By harvested grain mass, US agriculture is completely dominated by corn, all other major crops together yield less grain/seed than corn.

4. The total HHV of 16 largest US crops is 18.95 EJ $\mathsf{yr^{-1}}$ as above-ground biomass and 3.64 EJ $\mathsf{yr^{-1}}$ as roots, or about 22.7 EJ $\mathsf{yr^{-1}}$ total. This amount of sequestered solar energy balances almost exactly the 20 EJ $\mathsf{yr^{-1}}$ of fossil energy spent on US food system, see Chapter 3.

5. In terms of continuous thermal power that can be obtained by burning the crops and condensing water vapor, US agriculture develops 0.37 W $\mathsf{m^{-2}}$ as seed/grain and 0.67 W $\mathsf{m^{-2}}$ as entire plants, including their root systems.

6. In comparison, a statistical American uses almost 12000 W continuously[7], see Chapter 3. Our lifestyles could be supported by burning crops on 10 million square kilometers or whole plants and their excavated roots on 6 million square kilometers. Because the US land area is 9.2 million square kilometers[8] and we need energy for more than one year, both ideas are rather insane.
7. My calculations have been optimistic for two reasons: (a) I have picked the best year ever for US agriculture, and (b) I have somewhat overestimated energy contributions of plant stems, leaves and root systems. Their HHV's are lower from the seed HHV's by about 10%.
8. The accessible HHV of US pastureland and rangeland is estimated quite optimistically to be 7.43 $\mathsf{EJ\ yr}^{-1}$. The total productivity, including grass roots is 5.53 $\mathsf{EJ\ yr}^{-1}$ higher.
9. By efficiently burning the entire above-ground biomass grown annually by US agriculture, pastureland and cropland one can generate $18.95 + 7.43 = 26.4$ $\mathsf{EJ\ yr}^{-1}$ of thermal energy or 8.7 $\mathsf{EJ\ yr}^{-1}$ of electricity.
10. If one were to convert this biomass to liquid transportation fuels with today's efficiency of corn-ethanol plants (Patzek, 2006c), one would obtain $26.4 \times 0.26 = 6.9$ $\mathsf{EJ\ yr}^{-1}$ or 34% of current gasoline use. Of course one would spend $7 - 14$ $\mathsf{EJ\ yr}^{-1}$ of fossil energy supporting agriculture and producing ethanol. No technology exists that is capable of transforming cellulosic biomass to ethanol at this scale and efficiency. Therefore the whole argument is not only insane but moot.

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[7] $110 \times 10^{18}\text{J yr}^{-1}/300 \times 10^{6}$ people/$(365 \times 24 \times 3600 \text{ s yr}^{-1}) = 11600$ $\mathsf{W\ person}^{-1}$

[8] US area: 9826630 km^2 total; 9161923 km^2 land; and 664707 km^2 water. This estimate includes only the 50 states and District of Columbia. Source: CIA.

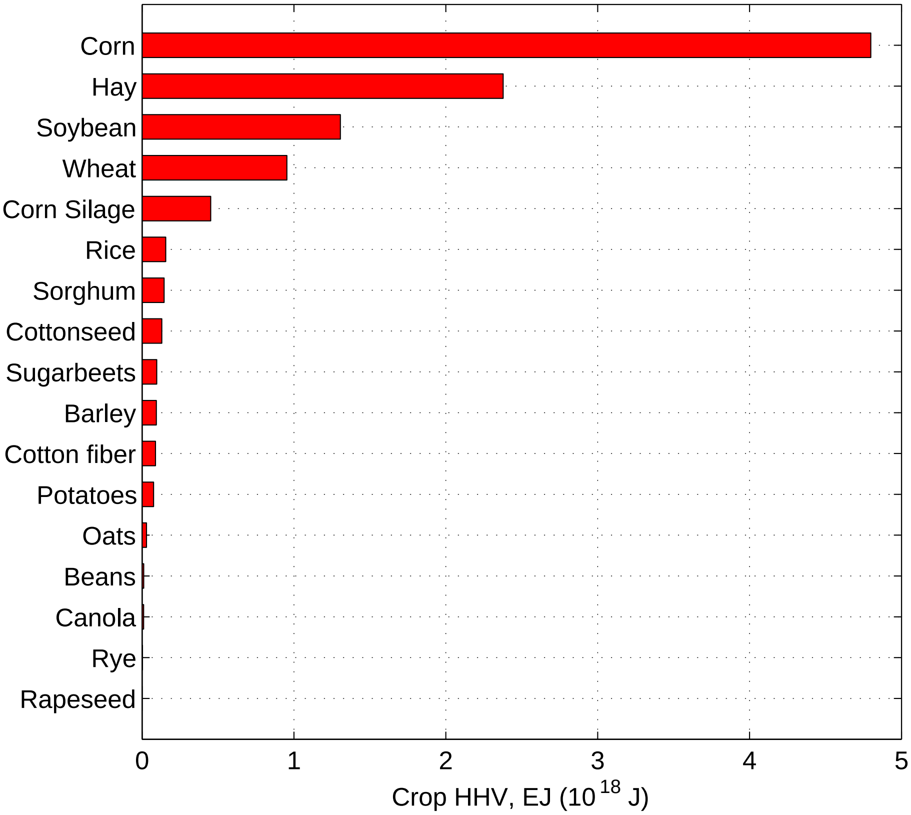

Figure 13.15: The HHVs of the largest US agricultural crops. The total HHV of the crops is 10.72 EJ. Sources: USDA NASS, Table 13.15.

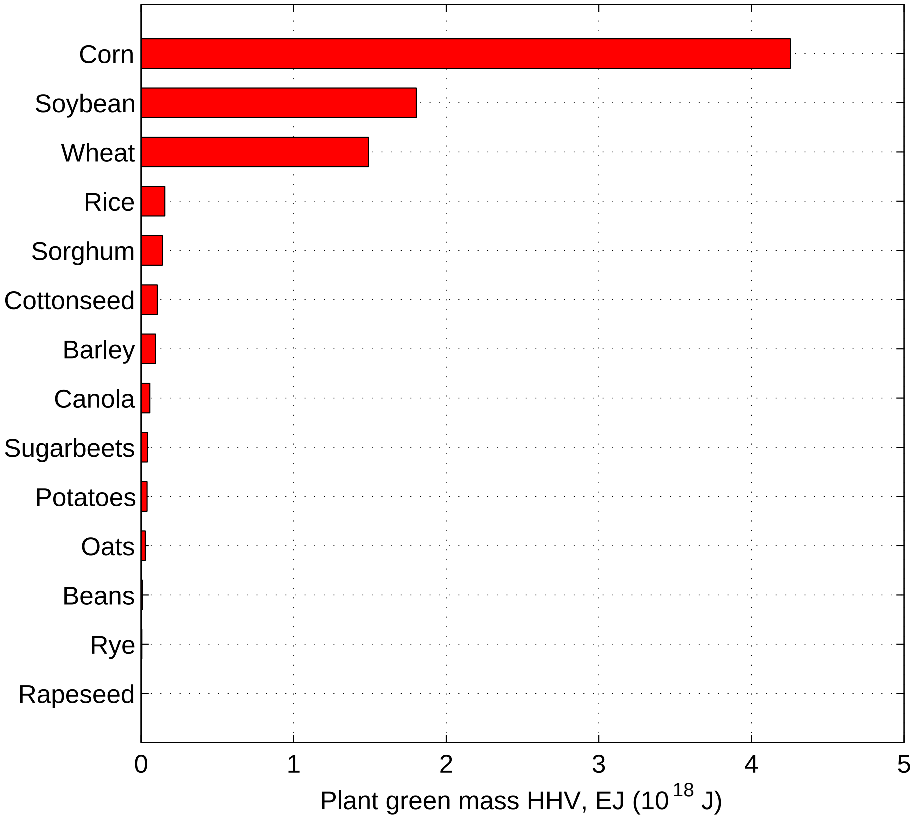

Figure 13.16: The HHVs of the remainder of above-ground plants (stems, leaves, etc.) for the largest US agricultural crops. The total HHV of remaining above-ground plant biomass = 8.23 EJ. Sources: USDA NASS, Table 13.15.

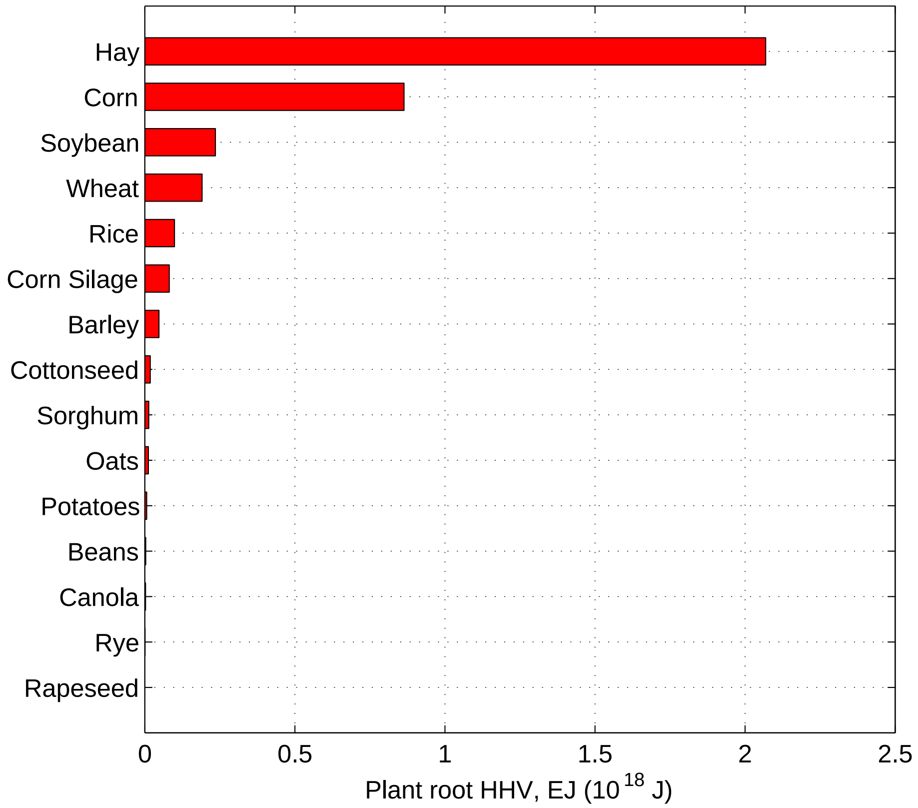

Figure 13.17: The HHVs of root systems for the largest US agricultural crops. The total HHV of root biomass = 3.64 EJ. Sources: USDA NASS, Table 13.15.

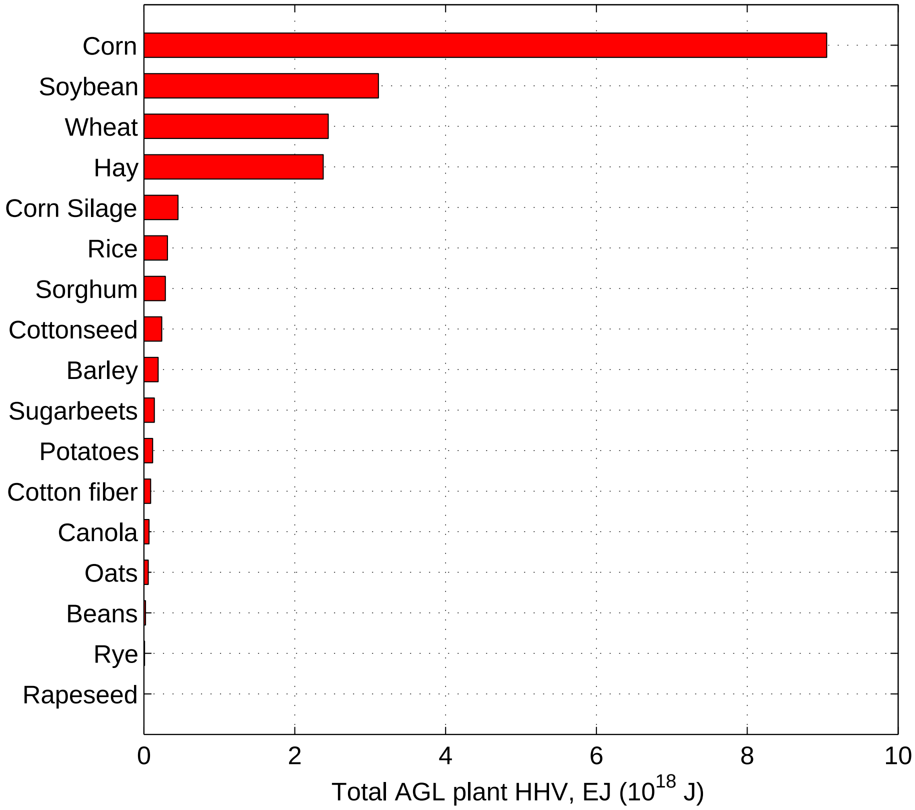

Figure 13.18: The HHVs of above-ground biomass for the largest US agricultural crops. Total above-ground biomass HHV of the crops is 18.95 EJ. Sources: USDA NASS, Table 13.15.

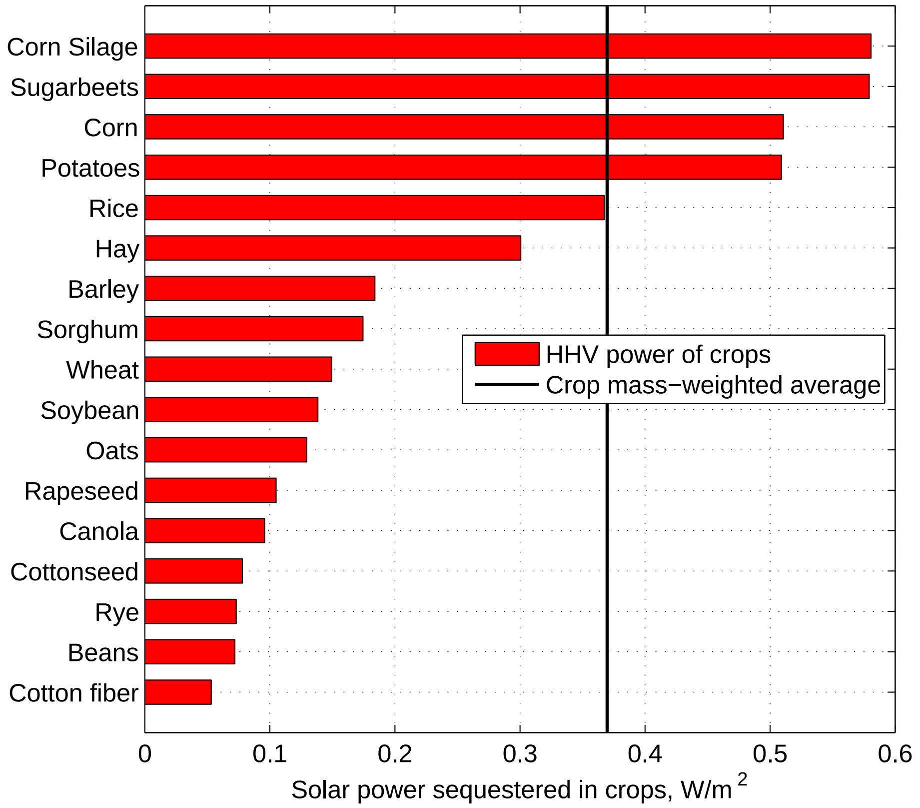

Figure 13.19: Continuous thermal power that could be drawn from the largest US crops. The mass-averaged power is 0.37 W m^{-2}. Sources: USDA NASS, Table 13.15.

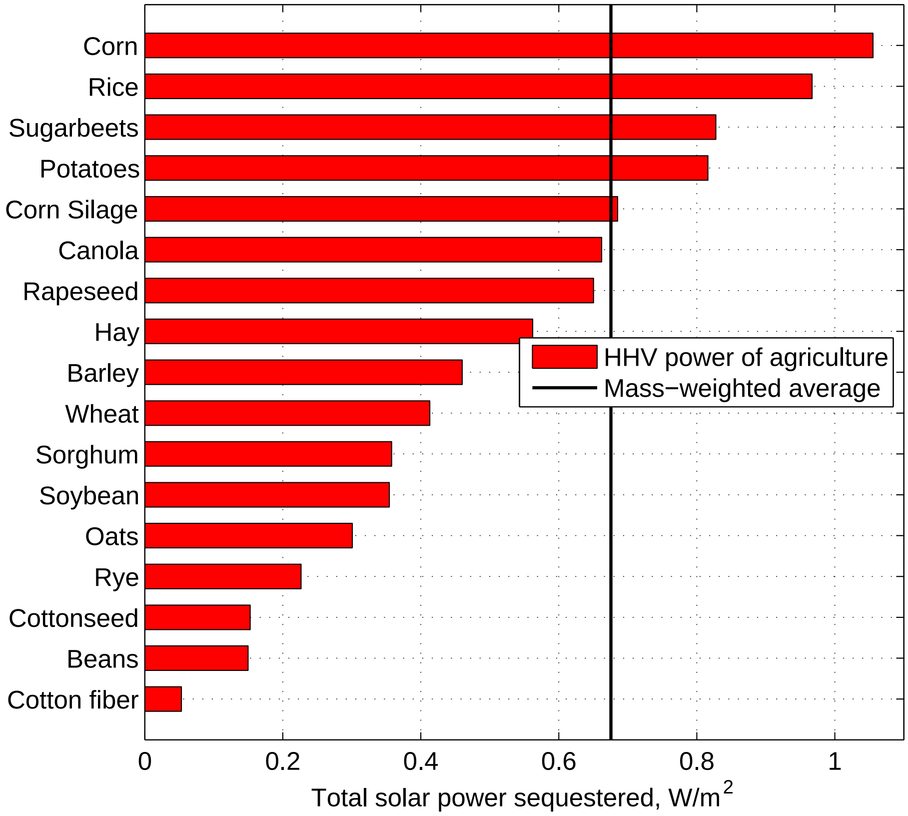

Figure 13.20: Continuous thermal power sequestered as plants and their root systems for the largest US crops. The plant mass-averaged power is 0.67 W m^{-2}. Sources: USDA NASS, Table 13.15.

13.6 Problems

1. **Solar energy sequestration by sugarcane**. Go to the USDA's NASS database www.nass.usda.gov/Publications/index.asp, click on *Crops and Plants*, click on *Field Crops*, pick from the menu *Sugarcane*, and press *Search*. From *State and County Statistics* pick the starting year to be 1976 and ending year 2006. From the menu to the right, pick *United States*. Press *Get Data*. Click on the button Units as a separate column. Go to the bottom of the report you have generated and locate *Download CSV (Units as separate column within CSV)* Save the comma-delimited text file to your local disk by right-clicking on the mouse and clicking on *Save Target As*. After unzipping, you can import this file directly to Excel, and copy the appropriate ranges to MATLAB. Now you have two time series with sugarcane yields and harvested areas. I have followed this exact procedure for all other US crops discussed here.

   (a) Plot the US sugarcane yields in dry metric tonnes of biomass per hectare.

   Answer: The plot of US sugarcane yields over the last 30 years is shown in **Figure 13.21**. Note that over this time period the average yield has declined by about 3.3 tonnes of dry mass per hectare, or by ~14%.

   (b) From my paper (Patzek and Pimentel, 2006), petroleum.berkeley.edu/-papers/patzek/CRPS-BiomassPaper.pdf, find the appropriate parameters to calculate the solar energy sequestered by the sugarcane as sugar, bagasse and leaves.

   Answer: Except for the RtS ratio, all the data necessary to characterize sugarcane plants are in Table 8 in (Patzek and Pimentel, 2006). The results are listed in **Table 13.16**.

Table 13.16: Characterization of US sugarcane in 2004

Crop	Yield[a]	Area	Water[b]	HI[c]	RtS[d]	HHV[e]
	kg/ha	10^6 ha	–	–	–	MJ/kg
Sugarcane	20799	0.380	0.70	0.77[f]	0.15	17.7[g]

[a] All yields on dry-mass basis, [b] Mass fraction [c] Harvest Index, Eq. (13.1), [d] Root-to-Shoot ratio, Eq. (13.2), [e] Higher Heating Value, Chapter 3, [f] The harvest index for sugarcane is defined as the ratio of harvested stems (sugars and bagasse) to dry above-ground biomass. 77% of AG biomass are stems and 51% of stems are sugars and gum starch, see Table 18 in (Patzek and Pimentel, 2006), [g] $0.51 \times 16.5 + 0.49 \times 19.03$ (Domalski et al., 1987; Patzek and Pimentel, 2006)

Based on the data above, the solar energy sequestered by US sugar-

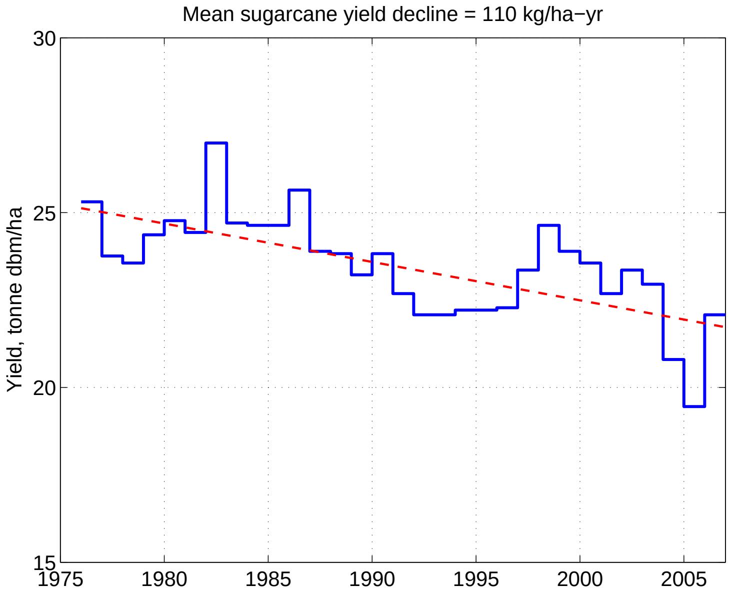

Figure 13.21: Dry stem (sucrose, glucose, fructose and starch gum + bagasse fibers) yield of sugarcane in the US. The yield has been declining by 0.11 tonnes per year on the average. Sources: USDA NASS, Table 13.16.

cane in 2004 was partitioned as follows:

i. Root energy = 0.02 EJ yr^{-1}
ii. Stem energy = 0.14 EJ yr^{-1}
iii. Leaf energy = 0.04 EJ yr^{-1}
iv. Total plant energy = 0.20 EJ yr^{-1}

(c) Do a Web search to find the root-to-shoot ratio of sugarcane.

Answer: I have found one paper for sugarcane under stress. The RtS range was 0.09 to 0.38. I chose to pick the corn value of 0.15, see Table 13.16

(d) Calculate the continuous power in W m^{-2} generated by US sugarcane above ground, roots and total.

Answer: The continuous thermal power from US sugarcane in 2004 was partitioned as follows:

i. Root power = 0.18 W m^{-2}
ii. Stem (sugar+bagasse) power = 1.17 W m^{-2}
iii. Leaf power = 0.35 W m^{-2}
iv. Total power = 1.69 W m^{-2}

(e) Calculate the continuous power from the sugar, if all sugar were converted to ethanol.

Answer: Theoretically 51% of the hydrolyzed sucrose and glucose become ethanol

$$\mathrm{C_{12}H_{24}O_{12}}(l) \rightarrow 4\mathrm{C_2H_5OH} + 4\mathrm{CO_2} + \mathrm{Heat} \tag{13.7}$$

Given the 2004 US sugarcane yield, the theoretical ethanol yield is

$$\begin{aligned}&20799\ \mathsf{kg\ biomass\ dbm\ ha^{-1}} \times 0.49\ \mathsf{kg\ sugars\ (kg\ biomass)^{-1}} \times 0.51 \approx \\ &\approx 5200\ \mathsf{kg\ EtOH\ ha^{-1}}\end{aligned} \tag{13.8}$$

Practically, 75-90% of this theoretical yield is achieved. Let's pick 85%, and the practical yield of ethanol is $0.85 \times 5200 \approx 4400$ kg of anhydrous ethanol per hectare per year.

The HHV of this ethanol is 29.6 MJ $\mathsf{kg^{-1}}$, see Table 3.2, and the continuous power drawn from the sugarcane ethanol is

$$\frac{4400\ \mathsf{kg\ EtOH\ ha^{-1}\ yr^{-1}} \times 29.6 \times 10^6\ \mathsf{J\ kg^{-1}}}{10000\ \mathsf{m^2\ ha^{-1}} \times 365 \times 24 \times 3600\ \mathsf{s\ yr^{-1}}} = 0.41\mathsf{W\ m^{-2}} \tag{13.9}$$

The historical yield of sugarcane ethanol calculated from Eqs. (13.8) and 13.9), is shown in **Figure 13.22**.

2. **Carbon sequestration in a shallow river delta**. Do a Web search on ground subsidence in the Sacramento River Delta. Find and estimate the volume of organic-carbon-rich peat subsided in the Delta over the last 100 years. Assume the undisturbed peat bul density varied linearly with depth between 160 and 220 $\mathsf{kg\ m^{-3}}$ (De Fontaine et al., 2007), organic matter content of 90%, and organic matter composition of essentially $\mathrm{CH_2O}$ (Saksman, 1937).

(a) Calculate the mass of carbon sequestered in the volume of compacted peat. Assume that 90% of compaction is due to peat oxidation and 10% to wind erosion. Try to decide if wind erosion of the peat also results in oxidation.

Answer: The Sacramento-San Joaquin River Delta is a unique and valuable resource and an integral part of California's water system, see **Figure 13.23**. It receives runoff from over 40 percent of the State's land area including flows from the Sacramento, San Joaquin, Mokelumne, Cosumnes, and Calaveras Rivers. The Delta is home to more than 515000 people[9] (2000 Census), supports agricultural and

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[9] Counties: Alameda, Contra Costa, Sacramento, San Joaquin, Solano, Yolo, and a portion of Rio Vista.

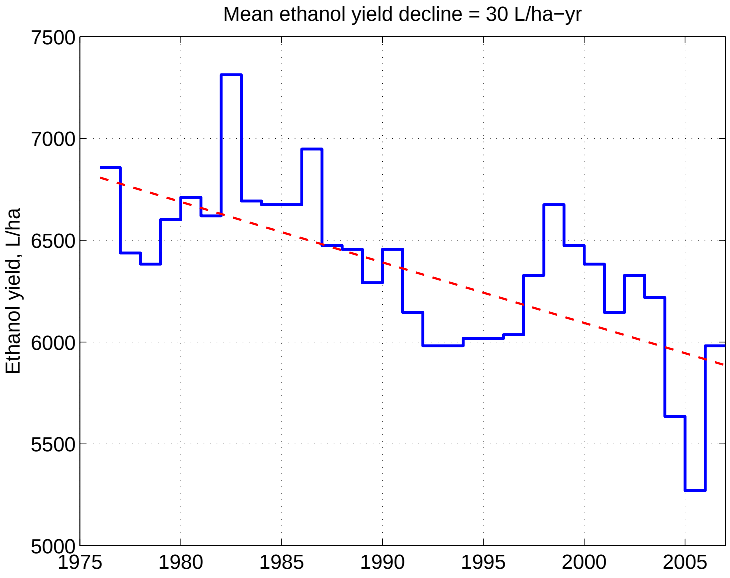

Figure 13.22: US sugarcane ethanol yield between 1976 and 2006. The yield has been declining by 30 liters per hectare and per year on the average. Sources: USDA NASS, Table 13.16.

recreational activities, provides habitat for many species of fish, birds, mammals and plants; and is the focal point for the water distribution system throughout the state.

The Delta covers 300000 hectares[10] interlaced with hundreds of waterways. Much of the land is below sea level and relies on more than 1800 km of levees for protection against flooding.

As data source, I will use the article by Jeffrey Mount and Robert Twiss, *Subsidence, sea level rise, seismicity in the Sacramento-San Joaquin Delta*, published in the San Francisco Estuary and Watershed Science, Vol. 3, Issue 1 (March 2005), Article 5, repositories.-cdlib.org/jmie/sfews/vol3/iss1/art5.

From (Mount and Twiss, 2005) it follows that anthropogenic accommodation space, or that space in the Delta that lies below sea level and is filled neither with sediment nor water, serves as a useful measure of the regional consequences of Delta subsidence and sea level rise. Microbial oxidation and compaction of organic-rich soils due to farming activity is the primary cause of Delta subsidence, see **Figure 13.24**. During the period 1900-2000, subsidence created approximately **2.5 billion cubic meters** of anthropogenic accommodation

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[10] Area (acres, 1991) 538000 agriculture 64000 cities and towns, 61000 water surface, 75000 undeveloped. Total acreage: 738000. Source: www.publicaffairs.water.ca.gov/swp/delta.cfm.

Figure 13.23: The Sacramento-San Joaquin River Delta. Source: www.beautifulvista.com/Recent_Photos/outdoors.htm.

space in the Delta. From 2000-2050, subsidence rates will slow due to depletion of organic material and better land use practices. However, by 2050 the Delta will contain more than 3 billion cubic meters of anthropogenic accommodation space due to continued subsidence and sea level rise.

During the summer of 2005, peat cores were collected on eight islands in the Delta (De Fontaine et al., 2007). The sites included four sets of both reclaimed, farmed islands and relatively undisturbed, marsh islands situated in channels adjacent to the farmed islands. This afforded a pre- and post-reclamation comparison of the peat. Laboratory analyses of the cores were conducted for bulk density, percent organic matter, and radiocarbon (for age control of the peat). The thickness of the peat on the marsh islands ranged from 4.3 to 7.8 m. The total peat thickness at the center of the farmed islands varied from 1.6 to 2.4 m, and included a compacted and oxidized zone above relatively undisturbed peat that ranged from 0.4 to 0.8 m in thickness. Mean bulk density of marsh island peat ($0.16\ \mathsf{g\ cm^{-3}}$) was lower than mean bulk density of relatively undisturbed farmed island peat ($0.22\ \mathsf{g\ cm^{-3}}$), but was significantly less than the mean bulk density of compacted and oxidized peat ($0.72\ \mathsf{g\ cm^{-3}}$) found at the surface of the farmed islands. Therefore we will assume here that the mean undisturbed peat density was $(160+220)/2 = 190\ \mathsf{kg\ m^{-3}}$).

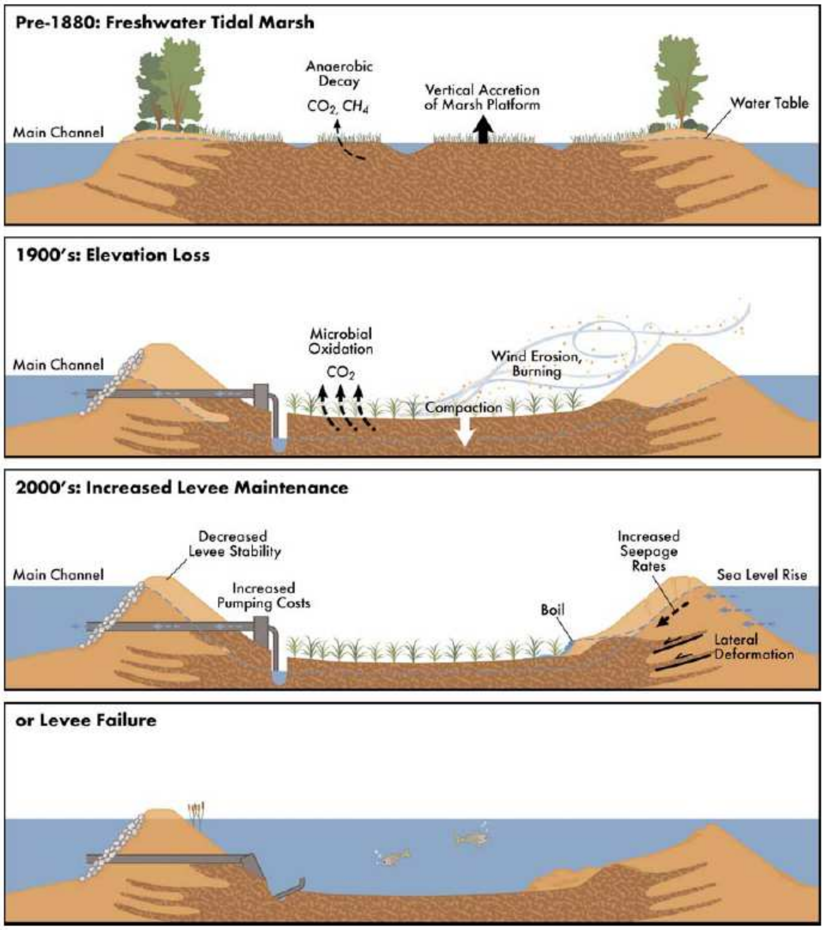

Figure 13.24: Conceptual diagram illustrating evolution of the Sacramento River Delta islands due to levee construction and island subsidence. Source: Mount & Twiss, 2005.

As bulk densities increased in the cores, percent organic matter content decreased. Higher bulk densities and lower organic content of peat on reclaimed farmed islands relative to marsh-island sites are evidence of compaction and oxidation due to reclamation and agricultural practices. The thickness of the relatively undisturbed peat that remains on the farmed islands ranged from 1.1 to 1.6 m, illustrating that little of the original peat column has been left untouched by the impacts of drainage and reclamation.

Given the assumptions in the problem statement and the discussion above, the mass of carbon released from the oxidized and compacted peat is

$$m_{\mathrm{C}} = V\rho_b f_{oc} = 2.5 \times 10^9 \times 190 \times (0.90 \times \frac{12}{30}) = 0.17\ \mathsf{GT} \quad (13.10)$$

where V is the compacted peat volume, ρ_b is the mean bulk density of the undisturbed peat, and f_{oc} is the mean organic carbon content in the peat.

(b) Calculate the amount of CO_2 released by the compacted peat.

Answer: All peat oxidation and most of erosion will result in CO_2 releases. Therefore, the mass of CO_2 released from the peat compaction is

$$m_{\mathrm{CO_2}} = \frac{44}{12} m_{\mathrm{C}} = 0.7\ \mathsf{GT} \quad (13.11)$$

(c) Comment briefly on your findings.

Answer: The carbon dioxide emissions from the Sacramento Delta subsidence over the last 100 year are equal to 1.5 months of the total US CO_2 emissions in the year 2005.

(d) Bonus: If you can, find the volume of material deposited in the Delta over the last 6000 years, and compare it with the subsidence volume.

Answer: It is important to place the amount of anthropogenic accommodation space into historic perspective. The volume of organic-rich sediment that accumulated within the Delta during the mid- to late Holocene can be approximated by summing the volume of anthropogenic accommodation space and the volume of organic-rich soils that underlie the islands. This underestimates the total volume because it does not account for material that underlies the current channel network. Based on this approach, (Mount and Twiss, 2005) have estimated that approximately 5.1 billion cubic meters of tidal marsh sediment filled accommodation space within the Delta during the past 6000 years. This represents an average annual rate of accumulation of approximately 850,000 cubic meters. During the past 100 years, oxidation, compaction, erosion and burning have reduced the volume of accumulated sediment by almost one half, which translates to an annual rate of loss almost 30 times the rate of historic accretion. Over the next 50 years rates of anthropogenic accommodation space generation will decline, but will remain more than an order of magnitude greater than historic rates of accretion, substantially increasing the forces acting on the Delta levee systems.

In his seminal study of the impacts of 19th century hydraulic mining on the Bay-Delta watershed, G. K. Gilbert (1917) estimated that mining introduced 1.2 billion cubic meters of sediment into the

Sacramento River system. As noted above, when the hydraulic mining sediment waves entered the Delta in the late 1800s, there was little accommodation space and the material by-passed the Delta. The volume of sediment created by hydraulic mining, considered one of the most destructive land use practices in the history of the Bay-Delta watershed, is less than half of the volume of accommodation space created by subsidence to date, and approximately one-third of the projected total volume in 2050.

If sea level remained unchanged, subsidence in the Delta were stopped, and current rates of inorganic deposition in the Delta were maintained, it would take 1470 years to restore elevations to mean sea level (Mount and Twiss, 2005).

3. Go to the FAOSTAT website, faostat.fao.org, click on *Production* and click on *core production data*. In *Subject* menu, highlight *Area Harvested (1000 ha)*, highlight all countries in the *country menu*, and pick the year 2005. Now, one-by-one, pick all the major agricultural commodities listed in this chapter, and also include sugarcane. Click on *download*. Accumulate the area data in a single Excel spreadsheet by cutting and pasting the columns downloaded from FAOSTAT. After your are done with all the commodities, convert the Excel text number entries to numbers. To do this place 1 in a blank cell. Copy this cell. Highlight the whole range of text numbers you want to convert, go to *Paste Special* and click on *Multiply*. Now you can sum up the areas, sort them by commodity, and plot as a single bar graph. Comment briefly on what you have found out.

   Answer: The harvested crop areas of major world crops, shown in **Figure 13.25**, encompass the total area slightly larger than the US area. The harvested sugarcane area is surprisingly small.

   The dry mass of top world's crops is shown in **Figure 13.26** and the corresponding HHV's in Figure 13.27. In addition the harvest indices for millet (proso) and oats were assumed to be 0.36 and 0.42, based on (Turgut et al., 2006; Jalani et al., 1979). The respective water contents at harvest were chosen to be 10%.

   In 2004, the US consumed 44.8 EJ of primary energy as crude oil, see Table 3.5, a little less than the 47.7 EJ produced annually from all major world crops. The remaining above-ground biomass (stems, leaves, etc.) associated with the largest crops had the HHV of 53.1 EJ, see **Figure 13.28**. Together, the largest world crops and their associated above-ground biomass had the HHV of 101 EJ in 2005. Estimating the smaller crops to yield another 9 EJ, the total world's agricultural output is about 110 EJ, equal to primary energy consumed in the US. In other words, the entire world agricultural output when efficiently burned might produce as much thermal energy as we use each year in the US. There would be no food, fiber, and other plant parts for humans, cows, pigs, horses, etc. In addition, since all above-ground biomass would be stripped from the world's fields, much of the agricultural topsoil would be exposed to rain and wind, and would quickly flow into the oceans. To feed the US appetite for primary energy in 2005, and sustain the remaining 95% of humans, we would need at least two Earths. Since the US uses 1/4 of world's primary energy, we would need to damage five Earths to run humanity on agricultural products and their thermal energy.

Note that according to Chapter 3 less than 20 $\mathsf{EJ\,yr^{-1}}$ are needed to feed the 6.5 billion people currently on the Earth. The remaining $\sim$30 EJ are used for animal feed, processed food, biofuels, and are wasted and consumed by rodents, etc.

The continuous thermal power that can be drawn from world's top crops is dominated by sugarcane at 1.08 $\mathsf{W\,m^{-2}}$. The crop mass average of 0.29 $\mathsf{W\,m^{-2}}$ is about 1/4 lower than the US average of 0.37 $\mathsf{W\,m^{-2}}$, see **Figure 13.19**.

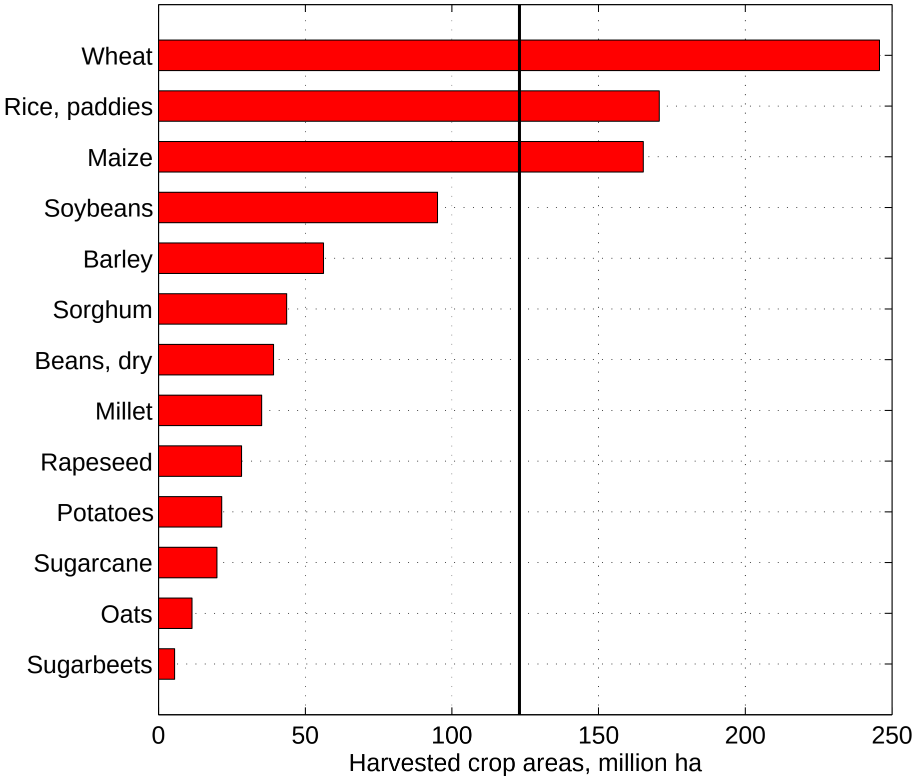

Figure 13.25: Harvested areas of world's largest crops in 2005. The total harvest area of these crops was 937 million hectares, a little larger than the US land area (916 million hectares). The black line denotes the harvested crop area in the US according to the 2002 census of agriculture. Source: FAOSTAT, accessed on April 10, 2007.

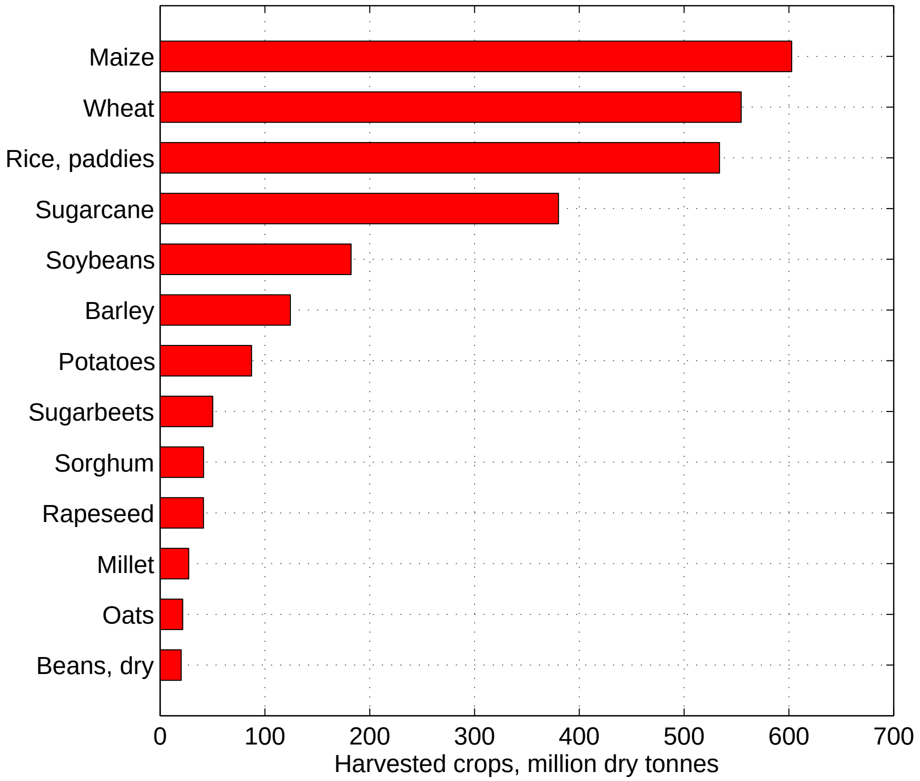

Figure 13.26: Dry mass of world's largest crops in 2005. The total harvested mass was 2.67 gigatonnes. Source: FAOSTAT, accessed on April 10, 2007, Table 13.15.

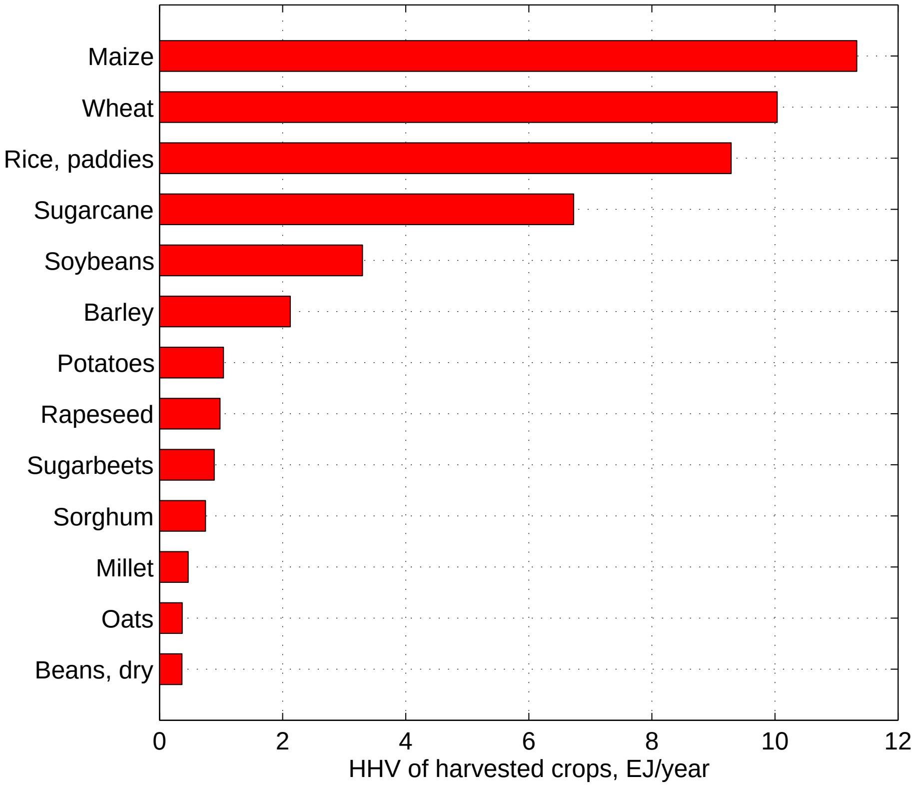

Figure 13.27: The Higher Heating Values (HHVs) of world's largest crops in 2005. The total harvested HHV was 47.7 exajoules (EJ), a little larger than the 44.8 EJ of crude oil consumed in the US in 2004. Source: FAOSTAT, accessed on April 10, 2007, Table 13.15.

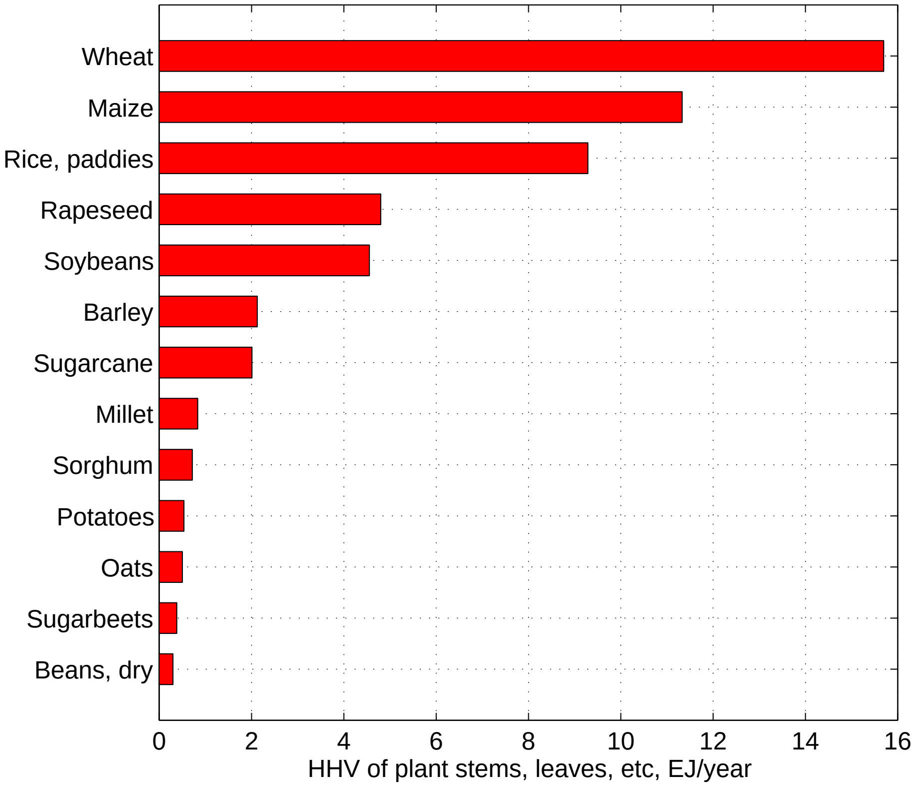

Figure 13.28: The Higher Heating Values (HHVs) of above-ground biomass (stems, leaves, etc.) associated with world's largest crops in 2005. The total remaining biomass HHV was 53.1 exajoules (EJ). Source: FAOSTAT, accessed on April 10, 2007, Table 13.15.

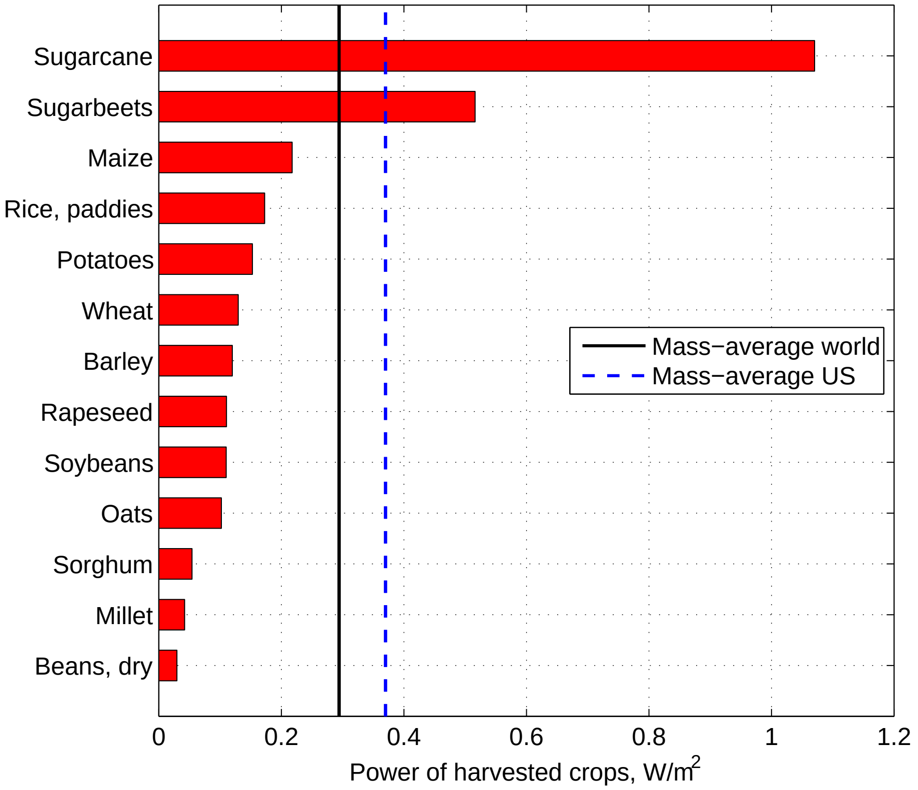

Figure 13.29: Continuous thermal power that could be drawn from the largest world crops in 2005. The plant mass-averaged power is 0.29 W m^{-2}, about 25% lower than the US average of 0.37 W m^{-2}. Sources: USDA NASS, FAOSTAT, accessed on April 10, 2007, Table 13.15.

Chapter 14

Biomass to Fuels

It is the responsibility of intellectuals to speak the truth and expose lies.
— NOAM CHOMSKY
(*The New York Review of Books*, February 23, 1967)

14.1 What Are We Going to Learn?

You are going to find out how many efficient cars can be driven using different forms of primary energy from major industrial systems, oil fields, photovoltaic cells, wind turbines, corn fields, and the tropical plantations of sugarcane, acacias and eucalypts.

14.2 Why Is It Important?

The amount of primary energy the world ecosystems can deliver for more than one year is small compared with our current run-away fossil energy use, but we vigorously deny this fundamental, indisputable fact. Quoting Harry G. Frankfurt, a retired Princeton philosopher: "The problem with ignorance and error is that they leave us in the dark. Lacking the truth that we require, we have nothing to guide us but our feckless speculations or phantasies and the importunate and unreliable advice of others." *Truth*, p. 60.

14.3 Availability of US Biomass

Today it is commonly believed that burning freshly cut plants is morally superior to burning old fossil plants. Even more curiously, some are convinced that stripping ecosystems of gigantic quantities of biomass can go on year-after-year, forever, and with no consequences. This attitude is best exemplified by the DOE/USDA report by Perlack et al. (Perlack et al., 2005) which claims that "... An annual biomass supply of more than 1.3 billion dry tons can be accomplished with relatively modest changes in land use and agricultural and forestry practices."

Based on this report others, e.g., Mr. Vinod Khosla proclaimed[1]: "Or *we could produce* 130 billion++ gallons *of ethanol*[2] per year!" Unfortunately, this is impossible for much more than one year regardless of technology.

To arrive at its conclusions, the DOE/USDA report made the following assumptions:

1. Yields of corn, wheat, and other small grains were increased by 50 percent;
2. The residue-to-grain ratio for soybeans was increased to 2:1;
3. The harvest technology was capable of recovering 75 percent of annual crop residues;
4. All cropland was managed with no-till methods;
5. 55 million acres of cropland, idle cropland and cropland pasture were dedicated to the production of perennial bioenergy crops;

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[1] Vinod Khosla's presentation, *Biofuels: Think outside the Barrel*, April 2006.

[2] The text added by T. W. Patzek is in italics.

6. All manure in excess of that which can applied on-farm for soil improvement under anticipated EPA restrictions was used for biofuel; and
7. All other available residues were utilized.

With a little thought and the calculations in Chapter 13, these assumptions can be readily disproved, see **Figure 14.1**:

1. The permanent 50 percent increase of all crop yields is impossible. The all-time record yield of corn[3] in 2004, 160.1 bushels/acre, was followed by 147.9 bu/acre in 2005, and 149.1 bu/acre in 2006. The real yields have been decreasing instead of jumping up by 50 percent. If in the next couple of years La Niña sets in, the ensuing drought in Midwest will make these yields quite high in comparison. One may look at Australia today for the effects of a major drought on crop productivity.
2. The 2:1 residue-to-grain ratio for soybeans would require a 45 percent increase of the current average harvest index of 0.42, and is not quite achievable.
3. Taking most residues from the fields would leave little or no plant matter to protect the soil from excessive wind and water erosion. The rate of erosion in US agriculture generally exceeds the rate of soil mineral deposition and humus generation.
4. Total no till agriculture would require astronomical quantities of herbicides and pesticides to kill off the "spurious" life competing with the resource-greedy, but otherwise delicate hybrid crop monocultures. Because of the comprehensive loss and poisoning of the natural environment and imported parasites (Berenbaum, 2006)[4], the honeybee population declined by 60% between 1947 and 2005. Reports of losses vary widely, ranging from losses of 30-90% of their bee colonies (Loper, 1997); some beekeepers fear loss of nearly all of their colonies in some cases. Surviving colonies are reportedly weakened and may no longer be viable to pollinate or produce honey (Johnson, 2007). Bees pollinate an estimated 15 billion dollars worth of crops every year.
5. US corn grows on over 70 million acres[5]. Dedicating 55 million acres to *Miscanthus* grass or switchgrass would eliminate plenty of other crops. The total area of the soil Conservation Reserve Program (CRP) in the US is a modest 34 million acres.

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[3] Source: US Department of Agriculture, National Agricultural Statistics Service (NASS, www.nass.usda.gov/Publications/index.asp)

[4] The 2006 National Research Council study on pollinator decline was chaired by Dr. MAY BENENBAUM of the University of Illinois, Urbana-Champagne. Previously, he was involved in the development of genetically-modified Bt-corn for Monsanto and Novartis. Bt-corn is one of the suspects in the declines of Monarch butterfly and bee populations. Is there a possible conflict of interest here?

[5] In 2007, 87 – 95 million acres are projected for corn at the expense of soybean, cotton and wheat crops.

6. The EPA requirements are perceived as restrictions. In other words, a modicum of conservation is viewed as an obstacle to feeding our thirsty cars and all remaining land (see Item 5) must go.

One simply cannot remove biomass and nutrients from an ecosystem without putting these nutrients back, protecting the soil structure, and suffering from lower yields in later crop rotations in industrial plantations. The high heating value (HHV) of 1.3 billion tons of biomass is roughly 22 EJ; and the HHV of 130 billion gallons of ethanol is 11.4 EJ. The fictitious DOE energy efficiency of converting biomass to ethanol, $11.4/22 = 0.52$, corresponds to Fischer-Tropsch synthesis and is two times higher than efficiency of the current corn-ethanol process. If one were to produce cellulosic ethanol with a 26% efficiency (Patzek, 2006a), one would have to use all above-ground biomass of all US crops, pastureland and rangeland, and annual biomass growth over 2/3 of all US forestland and timber plantations, see Figure 14.1.

In summary, the DOE/USDA vision is to capture in real time most of net growth of all biomass in the US, while at the same time mining soil, water, and air over 72 percent of our land area, including Alaska, Hawaii, and Puerto Rico. This biomass would then be devoured to feed our inefficient cars. We would have little food production, as well as little wood for paper and construction. In effect, the new brave US economy would be dedicated to feeding cars, not people.

The historical yields of two biofuels, ethanol and biodiesel, obtained from four major crops, sugarcane, oil palm, corn grain and soybean oil, are shown in **Figure 14.2**. All yields are expressed in liters of gasoline equivalent per hectare. It is obvious that the recent yields of two tropical fuels, sugarcane ethanol and palm oil biodiesel, are similar and about 2.7 times higher than the corresponding yield of corn ethanol. Biodiesel from soybeans is the worst source of automotive power. Its yield is about 10 times lower than those of the tropical biofuels.

14.4 Second Law Efficiency of Major Biomass Sources

The industrial corn, tree and sugarcane-biofuel systems – properly analyzed by PATZEK & PIMENTEL (Patzek, 2004; Patzek and Pimentel, 2006), see also Chapter 12, – are the sun-driven, man-made "machines," whose ultimate output is *shaft work*. These vast and enormously complex machines should be compared against two other, much simpler devices that also convert solar energy into shaft work: photovoltaic cells and wind turbines. Photovoltaic cells (whenever their panel areas measured in km^2 become commercially available) convert solar energy *directly* into electricity, the most valuable form of free energy, that can be further converted into shaft work with small losses. Wind turbines produce electricity from the kinetic energy of the sun-driven wind. Therefore,

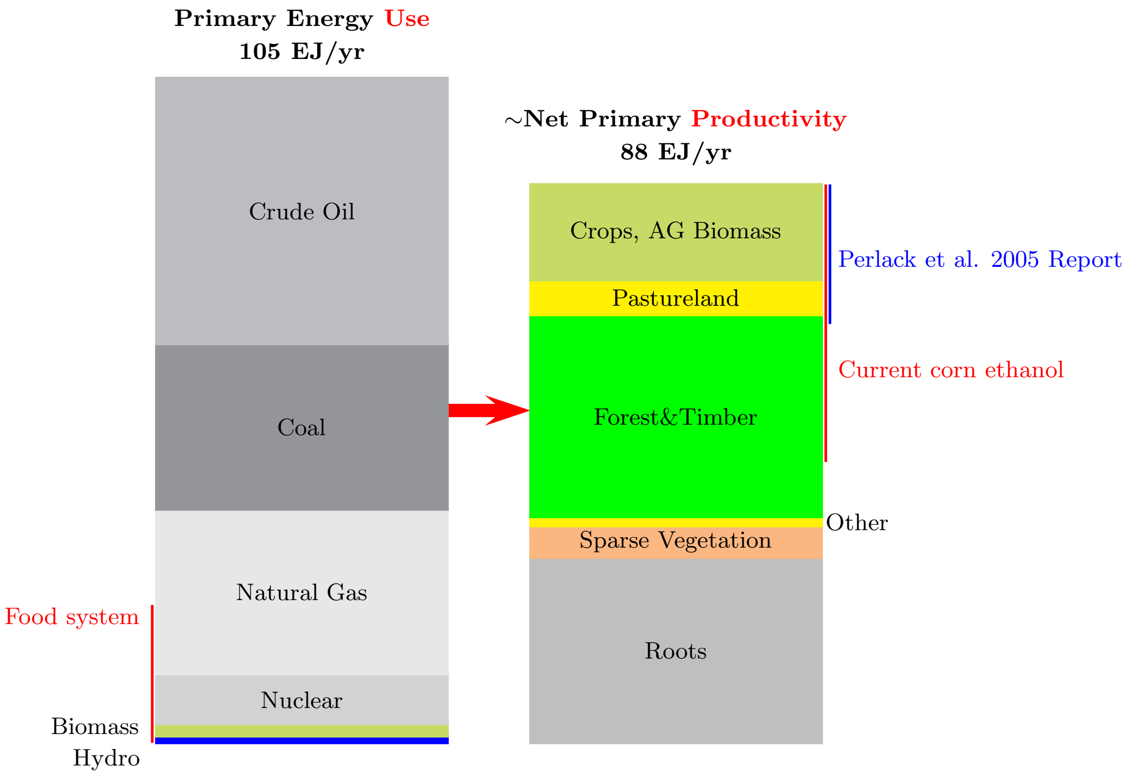

Figure 14.1: Annual fossil and nuclear fuel consumption in the US is now larger than *all* biomass energy yield over its territory. Sources: EIA; USDA NASS; (Patzek 2006c), and Chapter 13 calculations. **Left:** Primary energy use in the U.S. in 2004. Biomass burning provided about 2 percent of primary energy supply. **Right:** An optimistic estimate of annual net biomass production over the entire US area in 2004. This biomass production has been converted to equivalent energy. Over 3/4 of the biomass production is committed to food and animal feed, wood for paper, lumber and fiber, or is energy stored in plant roots and other inaccessible parts. This part of biomass production is *heavily subsidized* with fossil fuels. One half of the remainder is remote and sparse vegetation. The remainder may serve as the source of energy, but a large part of it will be used to produce biofuels. So the ultimate sustained biofuel production capacity in the U.S. is 2-3 percent of US energy consumption *today.* At its unrealistic conversion efficiency, the DOE (Perlack et al., 2005) proposal would require us to dedicate all above-ground biomass production from all US cropland, pastureland and rangeland. In 2004, crop production in the US posted an all-time record. With a more realistic process efficiency of the current corn ethanol production (Patzek, 2006c), one would also have to devote most of net timber production to biofuels. Of course, this is impossible.

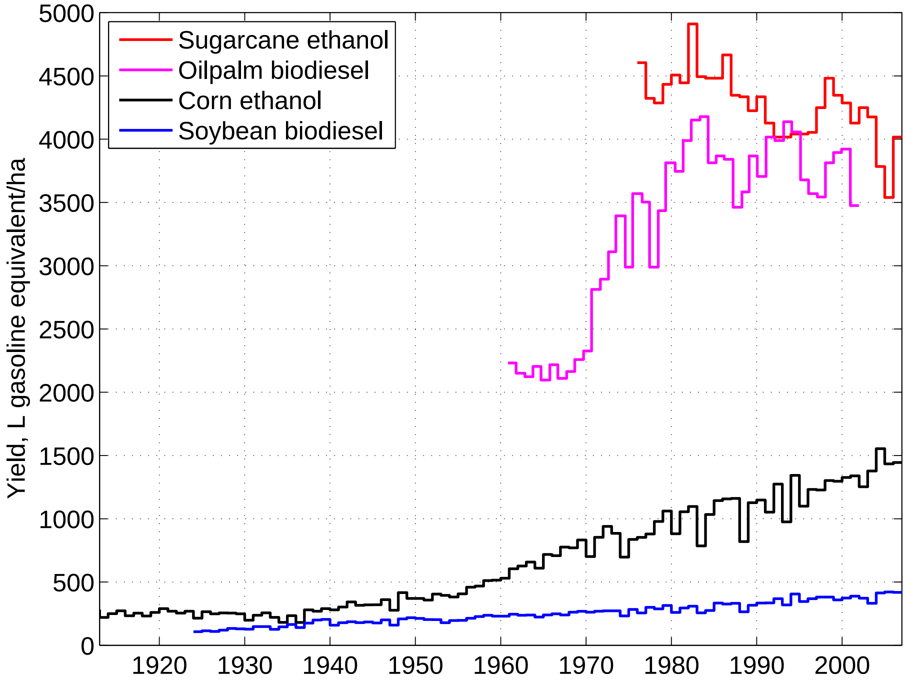

Figure 14.2: Equivalent fuel yields of three major US energy crops: sugarcane, corn and soybeans. Sources: USDA NASS, crop-to-biofuel conversion efficiencies from Problem 1e in Chapter 13 and Problem 3, and 82% conversion efficiency of conversion of soybeans in the field to finished biodiesel (Sheehan et al., 1998). For comparison, yield of finished biodiesel produced with 93% efficiency from raw palm oil in Indonesia is also shown. Source: FAO, Patzek, 2007 calculations.

Remark 3 All biofuel-producing systems should be judged on their ability to generate shaft work, not merely a biofuel. These systems consume massive amounts of free energy – by damaging the highly-structured natural systems – to produce their shaft work. But, as a rule, only the fundamentally incomplete energy balances, see (Patzek, 2004; Patzek, 2006a), are performed to evaluate merits of the industrial biofuel-producing systems. □

Therein lie the reasons for confusion surrounding the various published estimates of biofuel system efficiencies. For example, in (Dobereiner et al., 1999) it is claimed that

> . . . Brazil is the only country in the world where biofuel programmes are energetically viable. The overall energy balance of ethanol production on Brazil is 2.5. If bagasse is used to produce all factory power, the energy balance increases to 4.5 and if in addition all N fertilizers are eliminated, it increases to 5.8. . . (page 200)

The simple fact is that a mere (evidently incomplete) energy balance is insufficient to make such claims (Patzek, 2004). In addition, the authors confuse an energy *balance*, with a *ratio* of energy outputs and inputs they happen to pick. Otherwise, the numbers they cite: 2.5, 4.5, and 5.8, would have to have energy units assigned to them. Such confusion is typical of the current uninformed discussion of biofuel systems (Patzek, 2006a).

14.4.1 Efficiencies of Solar Energy Capture

It seems that we will do anything to keep on driving our cars. Therefore, the proper question to ask is this: How much continuous motive power can be extracted from 1 m^2 of land surface occupied by photovoltaic cells, wind turbines, or major energy crops: corn, sugarcane, acacias, and eucalypts? For comparison, we will also use 1 m^2 of land overlaying a medium-quality oil field produced at a constant rate to deliver automotive fuels. For each renewable energy source, we will calculate an extra land area necessary to recover all free-energy costs of producing an automotive fuel or electricity. Similarly, we will charge the oil field with all energy costs of recovering oil, transporting it to refineries, processing to gasoline and/or diesel fuel, and transporting the finished automotive fuels from the refineries to service stations. We will spend the generated automotive power on driving an efficient internal-combustion engine car, such as the Toyota Prius or a diesel engine car, and an all-electric battery car.

Average Oil Field

We start from the ancient solar energy stored in a medium-to-good quality oil reservoir similar to those in **Figure 3.3**. We assume that this reservoir is produced at a constant average rate over 20 – 30 years and 100 $\mathsf{W\,m}^{-2}$ of primary power is drawn from it continuously. This amount of power is rather small compared with real prolific oil fields, which can develop up to ∼200 – 400 $\mathsf{W\,m}^{-2}$ for years. The only problem with our oil reservoir is that after 30 years there is *no* producible oil left in it to drive internal combustion engine cars; this resource is finite and irreplaceable.

One m^2 of horizontal photovoltaic cell panels may generate 15% of the average[6] US insolation of 200 W for the US, i.e., 30 W of electricity continuously[7]. We also assume that photovoltaic cell assemblies effectively occupy twice the area of the panels.

One m^2 land occupied by wind turbines may produce continuously 1 W of electricity, see **Chapter 3**.

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[6] The 24-hour, 365-day average insolation of a flat horizontal surface anywhere in the US varies between 125 and 375 $\mathsf{W\,m}^{-2}$ (3 to 9 $\mathsf{kWh\ m}^{-2}\,\mathsf{day}^{-1}$), and is almost exactly 200 $\mathsf{W\,m}^{-2}$ on the average, see Chapter 16.

[7] Of course free energy is also used to produce solar cells. The life-cycle analysis of solar cells will be performed later.

US corn-ethanol system

The Second Law analysis of the US corn-ethanol system is based on the calculations in (Patzek, 2004), summarized in **Table 14.1**. The average corn grain harvest was assumed to be 8600 kg ha^{-1}, below the all-time record yield of 10000 kg ha^{-1} in 2004. The ethanol plants were assumed to operate at 92% of theoretical efficiency. The *net-free energy ratio*[8] of the US corn grain-ethanol system is $0.24/(0.13+0.19) = 0.77$, see Table 14.1. Notice that the Second Law analysis here cannot be translated in an equivalent net-energy ratio used in the nonphysical and incomplete analyses by DOE and USDA, see (Patzek, 2006a) for more information.

Table 14.1: Solar power capture, free energy consumption, and free energy output by US corn field-ethanol distillery systems (Patzek, 2004)

Quantity	Power	Units
Grain capture	0.44	W/m^2
Stem/leaves capture[a]	0.46	W/m^2
CExC[b] in corn production	0.13	W/m^2
CExC in ethanol production	0.19	W/m^2
Grain ethanol capture[c]	0.24	W/m^2
Stover Ethanol capture[c]	0.10	W/m^2
60%-efficient fuel cell output[d]	0.15	W$_e$/m^2
35%-efficient IC engine output	0.09	W/m^2

[a] Abbreviated as stover. 75% of corn stover is collected from the fields, a long-term environmental calamity

[b] The cumulative exergy consumption, CExC, is equal the minimum work of reversible restoration of the plantation ecosystem and its energy input sources, see Section 12.7.4

[c] Only for comparison. Fuel exergy is *not* the useful work we compare here

[d] See Appendix B

Acacia-for-energy system

The exceptionally prolific stand of *Acacia mangium* trees in **Figure 14.5**, captures 1.39 W/m^2 as stemwood+bark, and 0.31 W/m^2 as slash, which is usually destroyed by burning. Twenty percent of the stemwood mass is lost in harvest, handling and processing. Again, we do not want to just burn the wood, but we convert its free energy to electricity and/or automotive fuels. For the three scenarios discussed in (Patzek and Pimentel, 2006), the amount of solar energy captured as electricity is 0.35 W/m^2; as the FT-diesel fuel + a 35%-efficient IC engine car (equivalent to a Toyota Prius) + electricity, 0.26 W/m^2; and as ethanol, 0.11 W/m^2. The negative free energy cost of pellet manufacturing is 0.41 W/m^2 (as much as sugarcane-ethanol manufacturing), and the plantation maintenance consumes about 0.1 W/m^2 (a bit less than the 0.14 W/m^2 to run

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[8] An extension of the popular but inadequate measure of efficiency of energy systems (Patzek, 2006a).

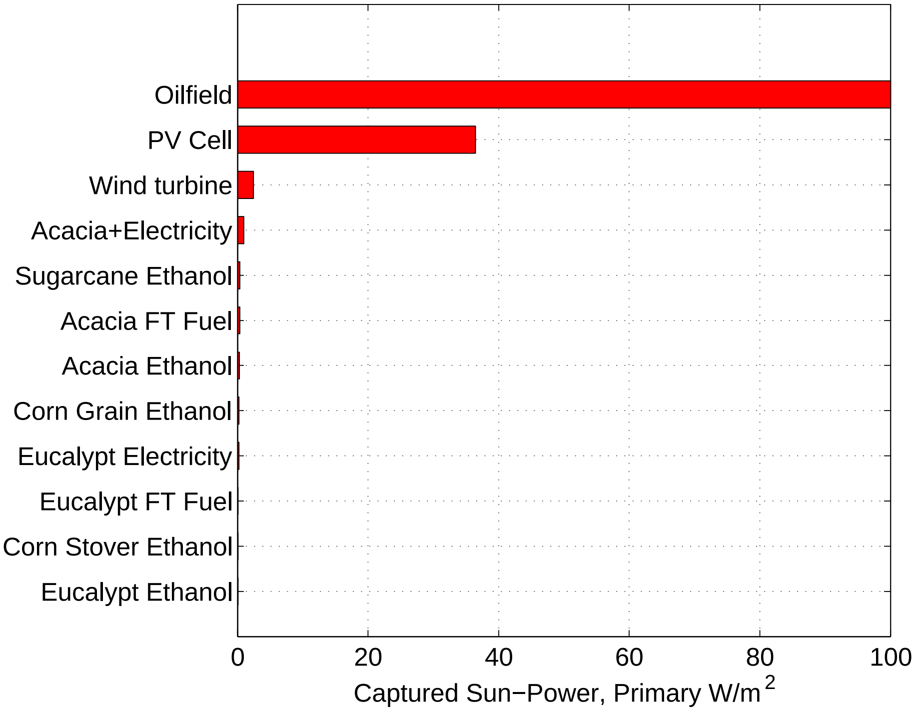

Figure 14.3: From the top: Ancient solar power extracted from 1 m^2 of a medium-quality oil reservoir by producing its crude oil for 30 years at constant rate; continuous solar power captured by a 15 W m^{-2} horizontal photovoltaic cell panel converted to primary energy by multiplying it by 2.43 (the assumed ratio of efficiencies of an all-electric car to a 40 mpg IC car); continuous primary power of a 1 W m^{-2} wind turbine; continuous solar power captured by *A. mangium*, Brazilian sugarcane, U.S. corn, and *E. deglupta* and converted to various primary energy sources, mostly biofuels. Note that the specific amounts of power outputs of these plant-energy systems are almost invisible at this scale.

a sugarcane plantation). The net solar power captured by this planation is negative, unless the free-energy cost of pellet manufacturing is cut in half.

Eucalyptus-for-energy system

The not-so-prolific stand of *Eucalyptus deglupta* in **Figure 14.6**, more representative of average plantations, captures 0.34 W/m^2 as stemwood+bark, 0.19 W/m^2 as slash. When this energy is converted to electricity, only 0.09 W/m^2 is captured. The FT-diesel fuel/car/electricity option captures 0.07 W/m^2. Finally, the ethanol/car option captures 0.03 W/m^2. The negative free energy of pellet production is 0.10 W/m^2, and the eucalypt plantation maintenance consumes 0.05 W/m^2. It seems that the net solar power captured by the eu-

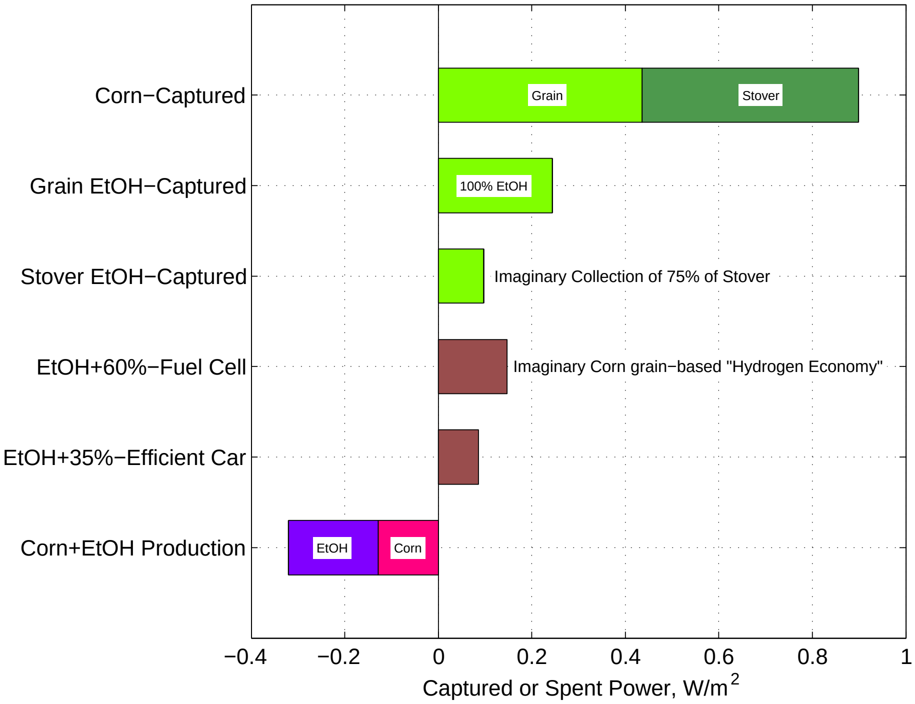

Figure 14.4: From the top: Solar power captured by 1 m^2 of an average US corn field as grain and stover; as grain ethanol in an average corn-starch refinery; as stover ethanol in an imaginary 75%-efficient lignocellulosic refinery; as an imaginary 60%-efficient fuel cell car (see Appendix B); and as 35%-efficient internal combustion engine car. The negative free energy costs of producing corn and grain ethanol are also shown. The unknown free-energy costs of running an imaginary lignocellulosic stover refinery are set to zero. Note that the *motive* power of cars is coded with the dark brown color to distinguish it from the *chemical* power of ethanol or biomass.

calypt planation is always negative, no matter what we do about wood pellets. For convenience, the acacia and eucalypt capture efficiencies are listed in **Table 14.2**.

Sugarcane-for-energy system

The prolific average sugarcane plantation in Brazil in **Figure 14.7**, captures 0.59 W/m^2 as stem sugar, 0.57 W/m^2 as bagasse, and 0.42 W/m^2 as "trash," both attached and detached. Because of the unique ability of satisfying the huge CExC in cane crushing, fermentation, and ethanol distillation (0.41 W/m^2), as well as fresh bagasse + "trash" drying (0.27 W/m^2), with the chemical exergy of bagasse and the attached "trash," sugarcane is the only industrial energy

Table 14.2: Solar power capture, free energy consumption, and free energy output by acacia and eucalypt plantation-energy systems (Patzek and Pimentel, 2006)

Quantity	Acacia	Eucalypt	Units
Stem capture	1.38	0.34	W/m^2
Slash[a] capture	0.31	0.19	W/m^2
Pellet capture	1.10	0.28	W/m^2
CExC[b] in pellet production	0.41	0.10	W/m^2
CExC in plantation	0.07	0.05	W/m^2
Electricity output	0.35	0.09	W_e/m^2
FT fuel output[c]	0.38	0.10	W/m^2
FT fuel+35% efficient IC engine output	0.13	0.03	W/m^2
FT electricity output	0.13	0.03	W_e/m^2
Ethanol fuel output[c]	0.30	0.07	W/m^2
Ethanol fuel+35% efficient car output	0.11	0.03	W/m^2

[a] This slash is no "trash" and should be left on the plantation to decompose

[b] The cumulative exergy consumption, CExC, is equal the minimum work of reversible restoration of the plantation ecosystem and its energy input sources, see Section 12.7.4

[c] Only for comparison. Fuel exergy is *not* the useful work we compare here

plant that may be called "sustainable." The sugarcane ethanol has the positive $W_u - W_R$ balance when used with 60%-efficient fuel cells, a technology that still is in its infancy, and whose real efficiency of generating shaft work is 38%, see **Appendix B**. The remainder of the "trash" must be left in the soil to decompose and improve the soil's structure. The free energy used to produce cane (0.14 W/m^2) and clean the distillery wastewater BOD (0.06 W/m^2) exceeds the benefits from a 35-% and 20%-efficient internal combustion engines (0.14 and 0.08 W/m^2, respectively). For convenience all these numbers are listed in **Table 14.3**.

14.4.2 Driving on Solar Power

In addition to the 1 m^2 of land surface used in the comparisons above to generate motive power, additional land area is needed to recover the energy and environmental costs of the power generation. This additional fractional area is calculated as follows

$$\delta A = \frac{\sum \mathsf{CExC}\text{ in all activities}}{\text{Solar power captured as biomass}} \qquad \frac{\mathsf{m}^2}{\mathsf{m}^2} \tag{14.1}$$

where CExC denotes the cumulative rate of exergy consumption in all activities related to power generation (or the minimal restoration work).

The total specific area necessary to generate the motive power is now

$$1 + \delta A \qquad \mathsf{m}^2 \tag{14.2}$$

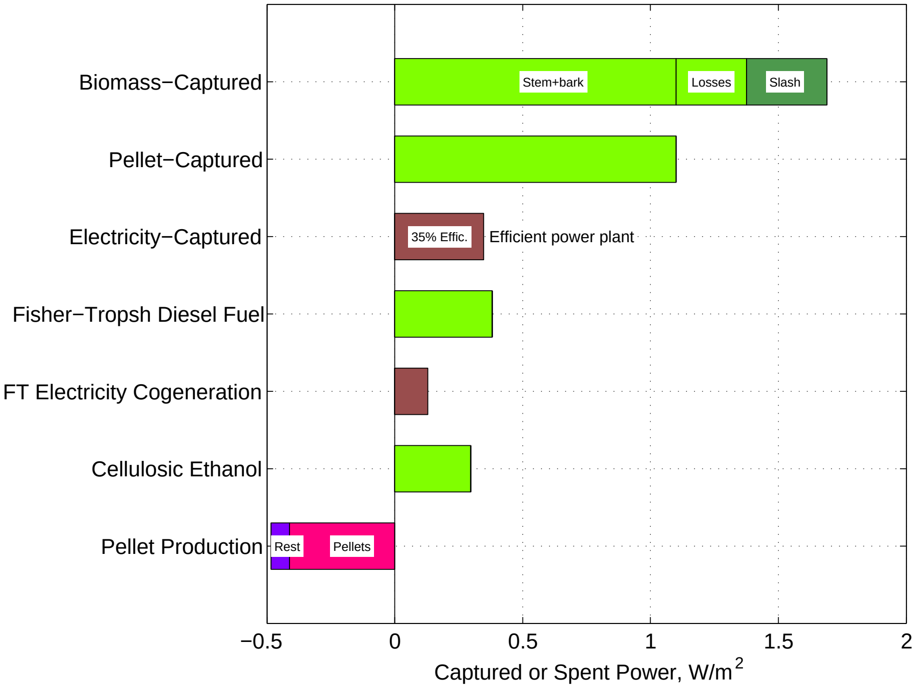

Figure 14.5: From the top: Solar power captured by 1 m^2 of the example *Acacia mangium* stand in Indonesia; as electricity generated from wood pellets in a 35%-efficient power plant; as FT-diesel fuel in a 35%efficient internal combustion engine car, and electricity; and as ethanol from the pellets powering a 35%efficient internal combustion engine car. The negative free energy costs of producing the acacia wood pellets and maintaining the plantation (Rest) are larger than our three options of generating useful shaft work from the captured solar energy. Note that the *motive* power of electricity is coded with the dark brown color to distinguish it from the *chemical* power of fuels.

To calculate how much total area of an energy system is needed to drive a single car, we will make the following assumptions:

1. Assume driving 24000 $\mathsf{km\ yr}^{-1}$ (15000 $\mathsf{miles\ yr}^{-1}$) at 5.9 $\mathsf{L\ (100\ km)}^{-1}$ (40 $\mathsf{miles\ gal}^{-1}$) in a hybrid car similar to a Honda Civic VX or Toyota Prius, or a diesel engine car.
2. Alternatively, drive an all-electric car that is $0.85/0.35 = 2.43$ times more efficient than the hybrid.
3. Account for average energy costs of producing gasoline from crude oil (17%) (Patzek, 2006a) and biofuels from biomass as in Tables 14.1 – 14.3.
4. Assume that an average solar photovoltaic panel sequesters 15% of insola-

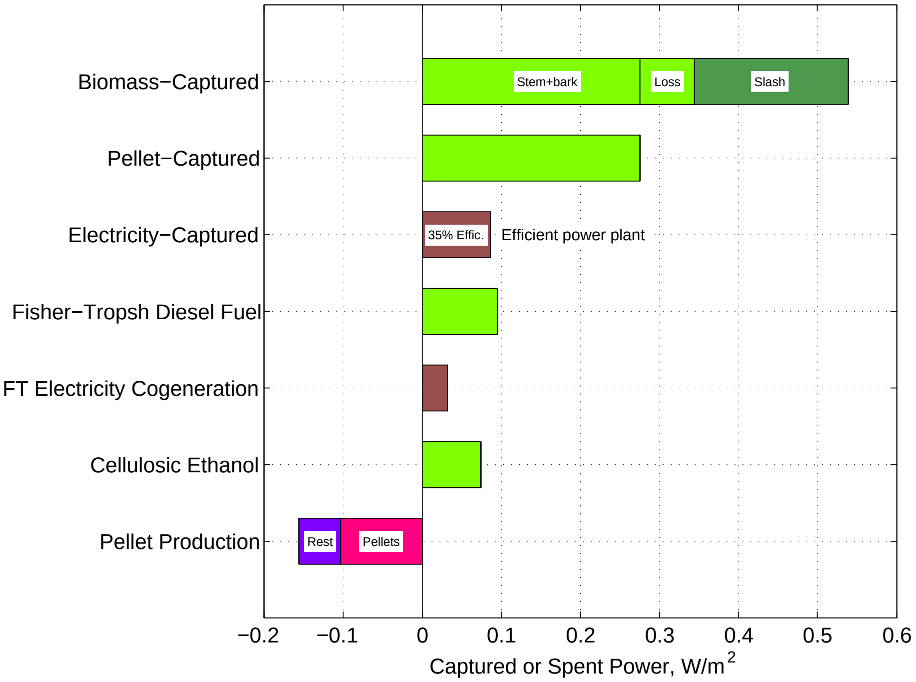

Figure 14.6: From the top: Solar power captured by 1 m^2 of the example *Eucalyptus deglupta* stand in Indonesia; as electricity generated from wood pellets; as FT-diesel fuel in a 35%-efficient internal combustion engine car, and electricity; and as ethanol from the pellets powering a 35%-efficient internal combustion engine car. The negative free energy costs of producing the eucalypt wood pellets and maintaining the plantation (Rest) are larger than our three options of generating useful shaft work from the captured solar energy. Note that the *motive* power of electricity is coded with the dark brown color to distinguish it from the *chemical* power of fuels.

tion (30 W m^{-2} on the 24-hour, annual average) and operates for 30 years. Assume that access areas, roads, and energy losses double the minimum land area occupied by the panels.

5. Assume that an average wind turbine delivers 1 W m^{-2} continuously, see Chapter 3.

6. Since photovoltaic cells and wind turbines will be used to power the all-electrical cars, convert their electrical outputs to primary energy by multiplying their ratings by 2.43.

7. Assume energy costs of manufacturing and deploying PV panels and wind turbines, 33% and 10% of their 30-year energy production.

Table 14.3: Solar power capture, free energy consumption, and free energy output by Brazilian sugarcane-ethanol system (Patzek and Pimentel, 2006)

Quantity	Power	Units
Stem sugar capture	0.59	W/m^2
Dry bagasse capture	0.57	W/m^2
Dry attached "trash" capture[a]	0.15	W/m^2
Dry mill "trash" capture	0.27	W/m^2
Ethanol capture	0.41	W/m^2
Extra electricity capture	7.7×10^{-5}	W_e/m^2
CExC[b] in cane production	0.14	W/m^2
CExC in ethanol production	0.41	W/m^2
CExC in bagasse and trash drying	0.30	W/m^2
CExC in BOD removal	0.06	W/m^2
20%-efficient IC engine output	0.08	W/m^2
35%-efficient IC engine output	0.14	W/m^2
60%-efficient fuel cell output[c]	0.25	W/m^2

[a] The detached "trash" > 1/2 of the total must be left in the soil to decompose
[b] See Section 12.7.4
[c] In (Patzek and Pimentel, 2006) we show that the 60%-efficient fuel cells do not exist, and their real efficiency is just above that of a 35%-efficient internal combustion engine, or a hybrid/diesel car

Table 14.4: Ratios of land areas needed to power cars described in Section 14.4.2 using different motive power sources

Technology	Net Ratio[a]	Gross Ratio[b]
Oilfield	1.0	1.0
PV Cell	2.7	3.0
Wind turbine[c]	39.8	37.4
Acacia+Electricity	102.0	125.5
Sugarcane Ethanol[d]	250.0	213.7
Acacia FT Fuel	263.2	323.9
Acacia Ethanol	333.3	410.3
Eucalypt Electricity	416.7	593.0
Corn Grain Ethanol	441.9	619.7
Corn Stover Ethanol	1000.0	1299.1
Eucalypt FT Fuel	1000.0	1341.9
Eucalypt Ethanol	1428.6	1917.0

[a] Ratio of the land area needed to develop the needed motive power to the equivalent oilfield area
[b] Ratio of the land area needed to develop the needed motive power and restore the power-generation free energy costs to the equivalent oilfield area
[c] Energy fraction that goes into constructing a wind turbine (0.10 of its output) is less than the energy fraction of crude oil used to produce gasoline (0.17).
[d] Energetically, sugarcane is self-sustaining until soil is eroded away and/or depleted from nutrients

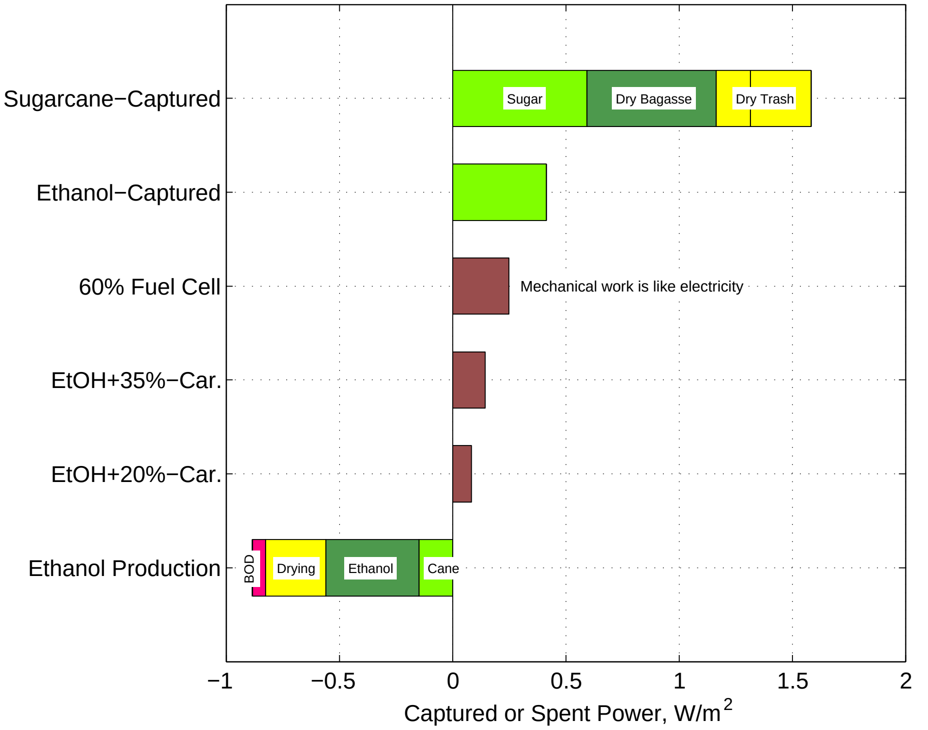

Figure 14.7: From the top: Solar power captured by 1 m^2 of the average sugarcane plantation in Brazil: as the chemical exergies of sugar, bagasse, and "trash"; as the chemical exergy of ethanol; as electricity from an imaginary 60%-efficient fuel cell (see Appendix B); as shaft work from a 35%-; and 25%-efficient internal combustion engine cars. The negative free energy costs of producing the sugarcane (Cane) and cleaning up the distillery wastewater (BOD) are larger than both internal combustion engine options, but smaller than the fuel cell option. The negative costs of ethanol distillation (Ethanol), and bagasse + "trash" drying (Drying), are paid with the chemical exergies of bagasse and attached "trash" (the left part of the rightmost bar segment at the top). Note that the *motive* power of cars is coded with the dark brown color to distinguish it from the *chemical* power of fuels.

Calculation Results

The fractional land areas needed to restore the free energy costs of power generation from 1 m^2 of land area were calculated from Eqs. (14.1) and (14.2), and Tables 14.1 – 14.3. The results are shown in **Figure 14.9**.

The net and gross ratios of land area needed to develop the motive power and pay for the free-energy costs of power generation are listed in **Table 14.4**, and displayed in **Figures 14.10** and **14.11**.

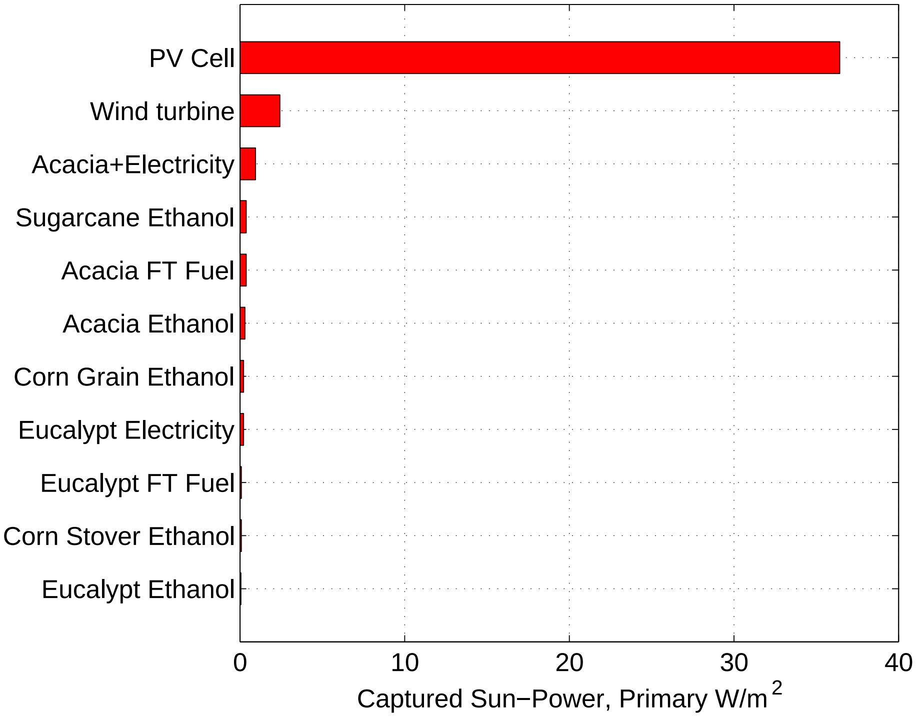

Figure 14.8: Primary continuous power delivered by renewable systems (crude oil has been excluded).

Notice that the plots in Figures 14.10 and 14.11 are semilogarithmic and the plotted areas increase by a factor of 10^4 from left to right. For example, for each 1 m^2 of medium-quality oil fields one needs 620 m^2 of corn fields to replace gasoline with corn ethanol and pay for the free energy costs of the ethanol production. Similarly, one can drive our example cars for one year from ∼30 m^2 of oil fields, 90 m^2 of photovoltaic cells, 1100 m^2 of wind turbines, and ∼18000 m^2 of corn fields, see Table 14.4 and Figure 14.11.

14.5 Conclusions

The most important lessons from the calculations presented in this chapter are as follows:

1. The solar power captured by industrial corn, tree, and sugarcane plantations is *minuscule* when compared with an oil reservoir (for a limited time only) and with solar cells (for practically infinite time). To make things worse, what little solar energy is captured by the plants goes in tandem with a disproportionate environmental damage and a negative free energy

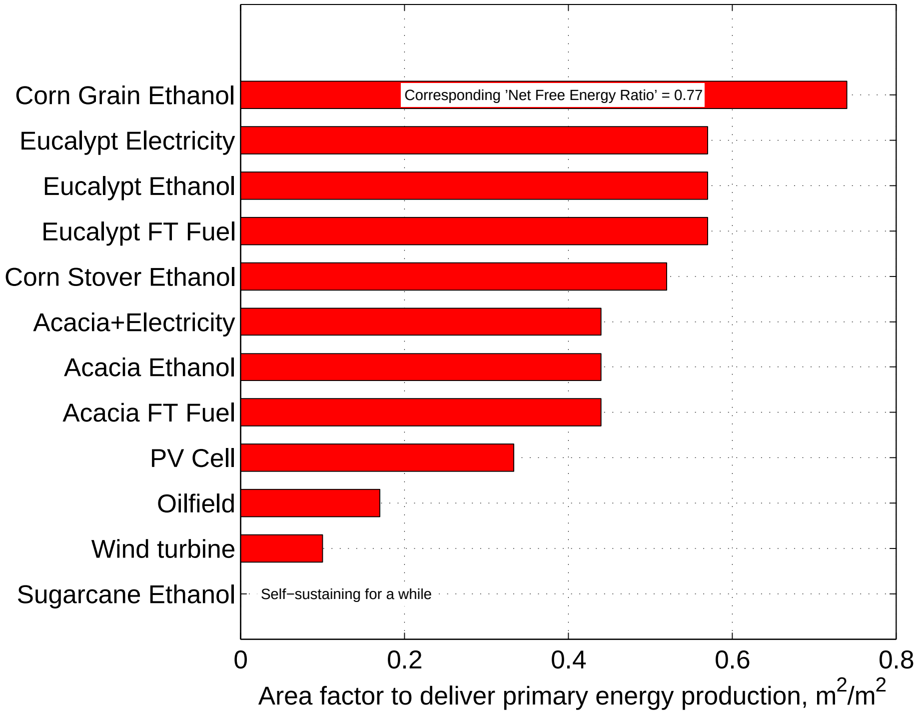

Figure 14.9: Fractional land area need to restore free energy costs of power generation from 1 m^2 of land occupied by the different energy production systems.

balance. Therefore, government and industrial funding for "renewable energy sources would be spent much more wisely on the development of large-throughput, efficient technologies of manufacturing solar cells (possibly poly-crystalline silicon-based cells).

2. One should stress the immense difficulty and costs of replacing the current large fossil fuel and nuclear power stations and oil fields with an equivalent network of distributed power sources, mostly photovoltaic cells and wind turbines.

3. Without a major cutback of the current rate of consumption of fossil fuels, we cannot even think about switching to nimbler renewable energy sources.

14.6 Problems

1. Convert 40, 50 and 60 miles per gallon (mpg) gasoline efficiencies of an internal combustion/rechargeable battery cars to km MJ^{-1} in gasoline.

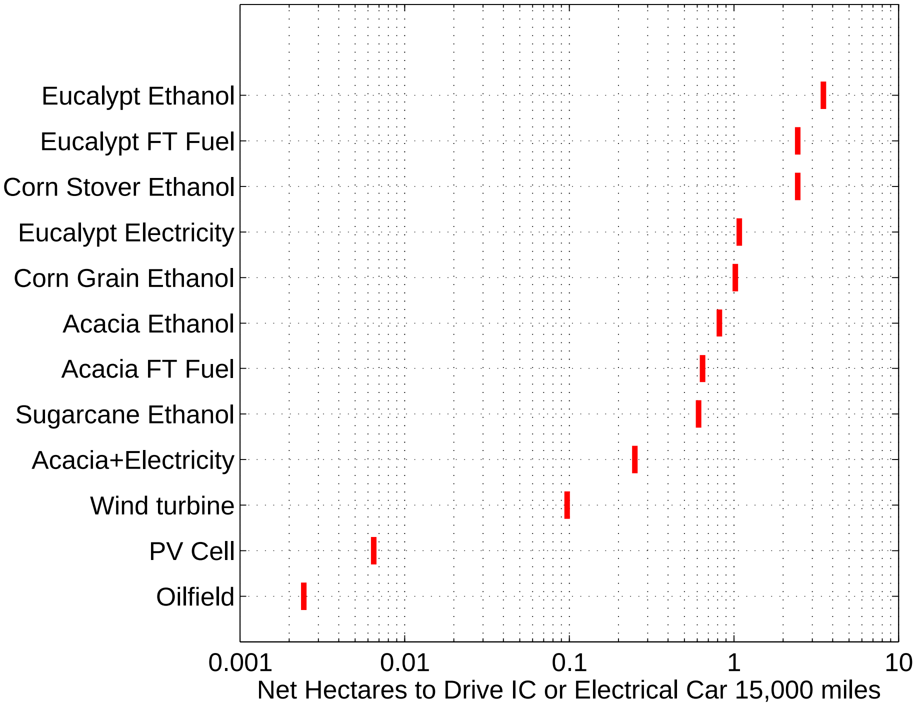

Figure 14.10: The net area of land needed just to power an efficient (40 mpg) IC engine car or an all-electric car equivalent to 100 mpg, and drive it 15000 miles per year. Note that the plot's x-axis is logarithmic and the area increases by a factor of 10000 from left to right.

Since you want this comparison be valid across fuels and energy systems, use the HHV of gasoline.

2. The Tesla Roadster[9] consumes about 110 Wh (0.40 MJ) of electricity from the battery to drive a kilometer, or 2.53 km MJ^{-1}. The energy cycle (charging and then discharging) of the lithium-ion batteries in the Tesla Roadster is about 86% efficient. This means that for every 100 mega-joules of electricity used to charge such a battery, only 86 mega-joules of electricity are available from the battery to power the car's motor.

   (a) Calculate the "electrical-outlet-to-wheel" energy efficiency of the Tesla Roadster in km MJ^{-1}.

   (b) Compare the energy efficiency of the Tesla Roadster with those of the hybrids.

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[9] *The 21st Century Electric Car*, Martin Eberhard and Marc Tarpenning, Tesla Motors Inc., 6 October, 2006.

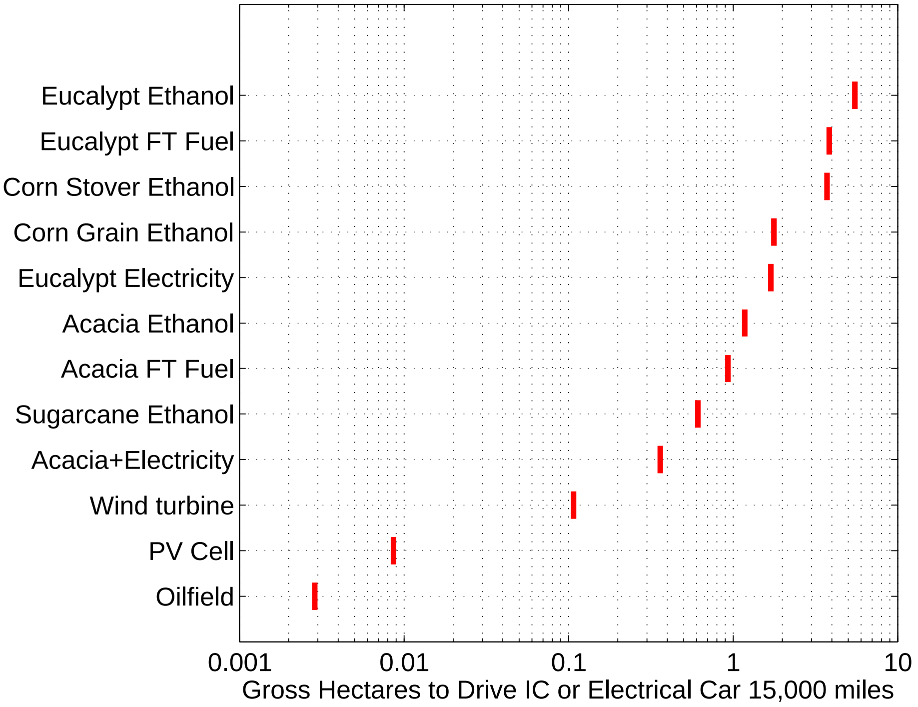

Figure 14.11: The total area of land needed to power an efficient (40 mpg) IC engine car or an all-electric car equivalent to 100 mpg, and drive it 15000 miles per year. Most of the free energy costs of fuels, fertilizers, and some environmental costs of power generation are accounted for. Note that the plot's x-axis is logarithmic and the area increases by a factor of 10000 from left to right.

(c) Is the assumption that an all electrical car is 2.4 times more efficient than a hybrid car reasonable?

(d) Is the Tesla Roadster typical of the future all-electric cars? Comment briefly.

3. Access the USDA NASS database and download historical yields of corn and the respective harvested areas. Assume that the harvested corn has had 15% of water by mass on the average, and that 66% of corn grain is starch, see **Figure 14.12**. Since ethanol (EtOH) is made from hydrolyzed starch with the stoichiometric efficiency of 0.51 (explain why), 1 kg of dry corn grain may yield $(0.66 \times 180/162) \times 0.51 = 0.374$ kg of water-free EtOH with zero losses, see **Table 13.4** for corn grain composition.

   In the US, the customary unit of reporting efficiency of corn conversion to ethanol is gallons EtOH per bushel, e.g., (Shapouri et al., 2002). With the

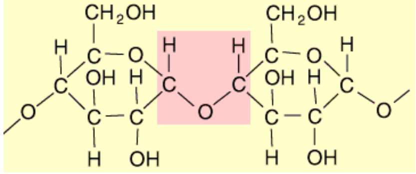

Figure 14.12: A typical starch molecule is constructed from α-glucosidic bonds (purple background), each of which links two dehydrated glucose molecules. Theses molecules form either unbranched or somewhat branched polymer chains with up to 360 or 1000 glucose units, respectively (Avers, 1976). In hydrolysis, the glucosidic bonds are broken, and each glucose unit gains one water molecule.

standard[10] EtOH density of 0.787 kg/L of anhydrous EtOH at 25^0C, the theoretical efficiency of 0.374 kg EtOH/kg dry grain (0.475 L EtOH/kg dry grain) yields 3.19 gallons EtOH/dry bushel = 2.71 gallons EtOH/equivalent bushel of corn with 15% moisture. This pure ethanol yield efficiency is further inflated by 5% by counting the mandatory 5% by volume of gasoline denaturant as ethanol. Therefore the maximum possible efficiency of denatured ethanol production is 2.85 gallons of denatured ethanol per bushel of corn with 15% of moisture.

(a) Using 92% of the theoretical ethanol production efficiency, as the historical US average, see (Patzek, 2004; Patzek, 2006b), calculate the historical volumes and HHV of ethanol from all US corn.

(b) Plot the historical yields of corn-grain ethanol in $\mathsf{kg\ ha^{-1}}$ and in $\mathsf{EJ\ year^{-1}}$.

(c) If you can find historical use of automotive gasoline, calculate the fraction of gasoline energy that could be replaced by converting all US corn into ethanol.

(d) How many 40 mpg cars could be driven on ethanol from all US corn? From EPA find the current average mileage of US automobile fleet and estimate how many average US cars could be driven on corn ethanol 15000 miles per year each?

(e) Using data from Table 14.1 and Eqs. (14.1) and (14.2) calculate the additional of corn fields needed to pay for some of the free energy costs of ethanol production.

4. Access the USDA NASS database and download historical yields of soybean and the respective harvested areas. Use data in Table 13.11 to calculate the volume of raw soybean oil in the field. Use the overall soybean oil conversion efficiency of 82% from soybeans in the field to finished biodiesel. Plot the historical yields of finished soybean diesel fuel in $\mathsf{kg\ ha^{-1}}$ and in

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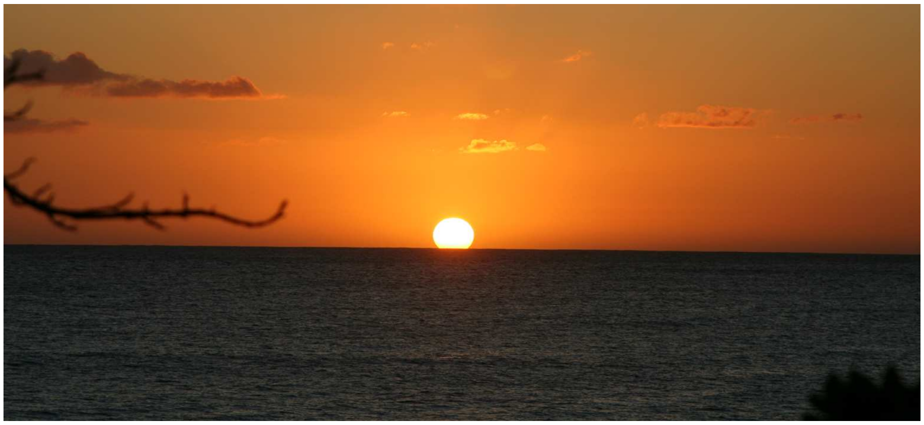
[10] Table 3.2.

$\mathsf{EJ\ year}^{-1}$. Assume the biodiesel density to be $0.9138\ \mathsf{kg\ L}^{-1}$ and its HHV to be $40\ \mathsf{MJ\ kg}^{-1}$.

Chapter 15

Black Body Radiation



Non-scientists should stop looking for shortcuts around the hard work of learning the science

— Christopher Essex and Ross McKitrick
Taken by Storm, The Troubled Science,
Policy and Politics of Global Warming (BPR Publishers, 2002)

15.1 What Are We Going to Learn?

You are going to learn about the STEFAN-BOLTZMANN Law of radiation.

15.2 Why Is It Important?

Distribution of energy of black body radiation is required to derive the energy relationship between the Sun and the Earth. Summing black body radiation over all wavelengths gives the STEFAN-BOLTZMANN law, which in turn governs radiation heat transfer between the Sun and Earth. This heat transfer has created and sustained all life on the Earth.

15.3 Background

This derivation follows Chapter XIV in *Thermodynamics* by E. A. GUGGENHEIM (1950) and *Statistical Thermodynamics* by Sir RALPH FOWLER and E. A. GUGGENHEIM (1949).

Radiation is regarded as a collection of photons. Each photon is characterized by a frequency, a direction of propagation, and a plane of polarization. In vacuum all photons have speed of light $c = 3 \times 10^8$ m/s. Each photon has specific energy u_i related to its frequency ν_i by PLANCK's relation

$$u_i = h\nu_i \quad \mathsf{J/photon} \tag{15.1}$$

and a momentum of magnitude $h\nu_i/c$. Here $h = 6.626068 \times 10^{-34}$ J s is PLANCK's constant.

It is convenient to group all photons having equal frequencies, thus equal energies, but different directions of propagation and planes of polarization. We denote by $g_i \, d\nu_i$ the number of distinguishable photons having frequencies between ν_i and $\nu_i + d\nu_i$, and energies between u_i and $u_i + du_i$.

Suppose that the radiation photons reside in a rectangular box defined by $0 \le x \le a$, $0 \le y \le b$, and $0 \le z \le c$.

Then for a wave traveling in the x-direction, the half-wave length $\frac{1}{2}\lambda$ must be an integer sub-multiple of the length a of the box, see **Figure 15.1**,

$$\frac{2}{\lambda} = \frac{l}{a}, \quad l = 1, 2, 3, \ldots \tag{15.2}$$

For a wave traveling in any direction it turns out that the boundary conditions along the box walls restrict the wavelengths to

$$\left(\frac{2}{\lambda}\right)^2 = \left(\frac{l}{a}\right)^2 + \left(\frac{m}{b}\right)^2 + \left(\frac{n}{c}\right)^2, \quad l, m, n = 1, 2, 3, \ldots \tag{15.3}$$

Hence the number of possible wavelength greater than λ_0 is equal to the number of positive integers l, m, n, satisfying

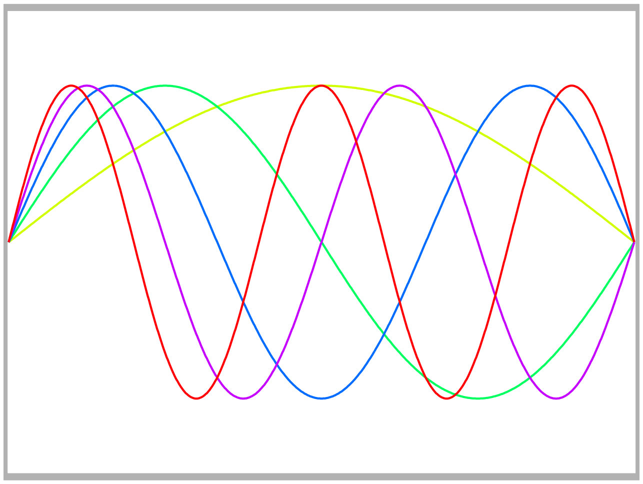


Figure 15.1: Five standing wave modes in the x-direction of a rectangular cavity.

$$\left(\frac{l}{a}\right)^2 + \left(\frac{m}{b}\right)^2 + \left(\frac{n}{c}\right)^2 \leq \left(\frac{2}{\lambda_0}\right)^2 \tag{15.4}$$

This number is equal to the number of points ξ, η, ζ with the positive integer coordinates inside the ellipsoid

$$\left(\frac{\xi}{a}\right)^2 + \left(\frac{\eta}{b}\right)^2 + \left(\frac{\zeta}{c}\right)^2 = \left(\frac{2}{\lambda_0}\right)^2 \tag{15.5}$$

and therefore to the volume of the positive octant of this ellipsoid:

$$\frac{1}{8}\,\frac{4\pi}{3}\,\frac{abc}{\left(\frac{1}{2}\lambda_0\right)^3} = \frac{4\pi}{3}\,\frac{V}{\lambda_0^3} \tag{15.6}$$

where V is the volume of the box.

It can be further shown that this dependence on V is independent on the shape of the box as soon as the wavelength becomes small compared with the dimensions of the box, and it is only such modes of the photon vibration which are numerous enough to matter.

In vacuum

$$\lambda\nu = c \tag{15.7}$$

Hence the number of possible frequencies less than ν_0 for two transverse directions of vibrations (two planes of polarization) is

$$2\,\frac{4\pi}{3}\,\frac{\nu_0^3}{c^3}V \tag{15.8}$$

and

$$g_i d\nu_i = 2\,\frac{4\pi V}{c^3}\nu_i^2 d\nu_i \tag{15.9}$$

15.4 Energy and Entropy in Terms of g_i's

Let's denote by n_i the number of photons having energies between u_i and $u_i + du_i$, and the corresponding frequencies ν_i, see Eq. (15.1). Then the total energy of all photons is

$$U = \sum_i n_i u_i \tag{15.10}$$

From the fact that the photons obey the Bose-Einstein statistics, it can be shown that the entropy of the photons is

$$\frac{S}{k} = \sum_i \ln\left[\frac{(g_i + n_i)!}{g_i! n_i!}\right] \tag{15.11}$$

Differentiating Eqs. (15.10) and (15.11) at constant g_i, i.e., constant V, we get

$$dU = \sum_i u_i dn_i \tag{15.12}$$

and

$$\frac{dS}{k} = \sum_i \ln\left[\frac{(g_i + n_i)}{n_i}\right] dn_i \tag{15.13}$$

The condition for equilibrium at a fixed V is that U be minimum and S maximum (Kestin, 1979b), page 21. Hence, for the most general variation, both expressions (15.12) and (15.13) must vanish simultaneously. Therefore the coefficients of all dn_i's must be proportional:

$$\frac{u_i}{\ln\left[\frac{(g_i + n_i)}{n_i}\right]} = \frac{u_k}{\ln\left[\frac{(g_k + n_k)}{n_k}\right]}, \quad \text{for all } i, k \tag{15.14}$$

and, consequently, using Eqs. (15.10) and (15.11)

$$\frac{u_i}{\ln\left[\frac{(g_i + n_i)}{n_i}\right]} = \frac{\sum_k u_k dn_k}{\sum_k \ln\left[\frac{(g_k + n_k)}{n_k}\right] dn_k} = k\frac{dU}{dS} = kT \tag{15.15}$$

since at constant volume

$$dU = TdS \tag{15.16}$$

From Eq. (15.15) we obtain

$$\frac{n_i}{g_i + n_i} = e^{-u_i/kT} \tag{15.17}$$

and so

$$n_i = \frac{g_i}{e^{u_i/kT} - 1} \tag{15.18}$$

and

$$U = \sum_i n_i u_i = \sum_i \frac{g_i u_i}{e^{u_i/kT} - 1} \tag{15.19}$$

For the entropy we can obtain from Eq (15.11), using a simple approximation for the factorials (see **Problem 2**):

$$\frac{S}{k} \approx \sum_i n_i \ln\left[\frac{(g_i + n_i)}{n_i}\right] + \sum_i g_i \ln\left[\frac{(g_i + n_i)}{g_i}\right] \tag{15.20}$$

Using Eqs. (15.15) and (15.17) in Eq. (15.20) we get

$$\frac{S}{k} \approx \sum_i \frac{n_i u_i}{kT} - \sum_i g_i \ln\left(1 - e^{-u_i/kT}\right) \tag{15.21}$$

For the free energy, we deduce from (15.10) and (15.21)

$$F = U - TS = kT \sum_i g_i \ln\left(1 - e^{-u_i/kT}\right) \tag{15.22}$$

15.5 Thermodynamic Functions

In the previous sections we have obtained formulæ for the energy, entropy and free energy in terms if the specific photon energies u_i and their number distribution function g_i, without making use of Eqs. (15.1) and (15.9). If we now substitute the values of u_i and g_i given by the latter two equations into Eqs. (15.21) and (15.19), we will get

$$F = \frac{8\pi V}{c^3}\, kT \int_0^\infty \ln\left(1 - e^{-h\nu/kT}\right) \nu^2 d\nu \tag{15.23}$$

$$U = \frac{8\pi V}{c^3} \int_0^\infty \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1} \tag{15.24}$$

We can also write Eq. (15.24) in the form

$$U = V \int_0^\infty U_\nu d\nu, \text{ where } U_\nu := \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1} \tag{15.25}$$

which is the original PLANCK's formula from which the quantum theory started. U_ν is the radiation energy per unit volume per unit frequency in $\mathsf{J\ m^{-3}\ s}$.

Alternatively,

$$\begin{aligned} U &= -V \int_\infty^0 U_\nu \frac{c}{\lambda^2} d\lambda, \text{ and one may define} \\ U_\lambda &:= U_\nu \frac{c}{\lambda^2} = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/(\lambda kT)} - 1} \end{aligned} \tag{15.26}$$

U_λ is the radiation energy per unit volume per unit wavelength in $\mathsf{J\ m^{-3}\ m^{-1}}$.

15.6 Evaluation of Integrals

We can rewrite Eq. (15.23) as

$$F = -\frac{8\pi V k^4 T^4}{c^3 h^3}\, I \tag{15.27}$$

where

$$I := -\int_0^\infty \ln\left(1 - e^{-\xi}\right) \xi^2 d\xi \tag{15.28}$$

Using the Taylor series for the logarithm and then integrating term-by-term, we obtain

$$I := \int_0^\infty \frac{\xi^2}{n} e^{-n\xi} d\xi = \sum_{n=1}^\infty \frac{1}{n^4} \int_0^\infty \xi^2 e^{-\xi} d\xi = 2 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi}{45} \tag{15.29}$$

Substituting Eq. (15.29) into (15.27) we finally obtain

$$F = -\frac{8\pi^5 k^4}{45 c^3 h^3}\, T^4 V \tag{15.30}$$

15.7 Stefan-Boltzmann Law

We could derive fromulæ for U and S in a similar manner, but it is easier to obtain them by differentiation of Eq. (15.30)

For historical reasons, let's write Eq. (15.30) in the following form:

$$F = -\frac{1}{3} a T^4 V \tag{15.31}$$

where a is a universal constant defined as

$$a := \frac{8\pi^5 k^4}{15 c^3 h^3} = 7.569 \times 10^{-16} \quad \mathsf{J\ m^{-3}\ K^{-4}} \tag{15.32}$$

From Eq. (15.31) we deduce immediately

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{3} a T^3 V \tag{15.33}$$

$$U = F + TS = a T^4 V \tag{15.34}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3}\frac{U}{V} \tag{15.35}$$

$$G = F + pV = 0 \tag{15.36}$$

The equation for radiation pressure can be derived from classical electromagnetic theory. The equation for the radiation energy was discovered by STEFAN and derived theoretically by Boltzmann. It is therefore called the STEFAN-BOLTZMANN law. We can see from Eq. (15.34) that aT^4 is the equilibrium value of the radiation energy per unit volume in an enclosure. If a small hole is made in such an enclosure then it can be shown by simple geometrical considerations that the radiation flux, $\mathcal{F}_U$ (radiation energy emitted through the hole per unit area and per unit time) is σT^4, where

$$\sigma = \frac{1}{4}ac = 5.6703 \times 10^{-8} \quad \mathsf{J\,m}^{-2}\, s^{-1}\, \mathsf{K}^{-4} \tag{15.37}$$

where c is the speed of light. The constant σ is called the STEFAN-BOLTZMANN constant. For details, see **Problem 8**.

15.8 Problems

1. Prove Eq. (15.5).

   Hint: We seek a standing wave solution to the three dimensional wave equation for radiation energy:

   $$\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 U}{\partial t^2} \tag{15.38}$$

   subject to the boundary condition

   $$\begin{aligned}&U(x,y,z,t) = 0 \text{ along the walls of the rectangular box:}\\ &0 \le x \le a, \quad 0 \le y \le b, \quad 0 \le z \le c\end{aligned} \tag{15.39}$$

   A nonzero value of U along the walls would dissipate radiation energy and violate the assumption of a standing wave. Since the wave is a steady oscillation, we do not need initial condition (the wave keeps on oscillating forever as a sine function of time).

   Guess a standing wave solution of the form

   $$U = U_0 \sin\left(\frac{l\pi x}{a}\right)\sin\left(\frac{m\pi y}{b}\right)\sin\left(\frac{n\pi z}{c}\right)\sin\left(\frac{2\pi ct}{\lambda}\right) \tag{15.40}$$

   Substitute this solution into the wave equation (15.38) and obtain directly condition (15.5).

2. Demonstrate the approximate equality in Eq. (15.20).

   Hint: By definition,

   $$\ln N! = \ln 1 + \ln 2 + \cdots + \ln N \tag{15.41}$$

   For a large N, the sum above may be viewed as a Riemann sum for the following definite integral:

   $$\int_1^N \ln x dx = N\ln N - N + 1 \approx N \ln N - N \tag{15.42}$$

Thus

$$\ln N! \approx N \ln N - N \tag{15.43}$$

Now use this approximation in the entropy equation (15.11) and group terms.

3. Using the solution of the previous problem, demonstrate that entropy differential dS at constant g_i, while varying n_i, is given by Eq. (15.13).

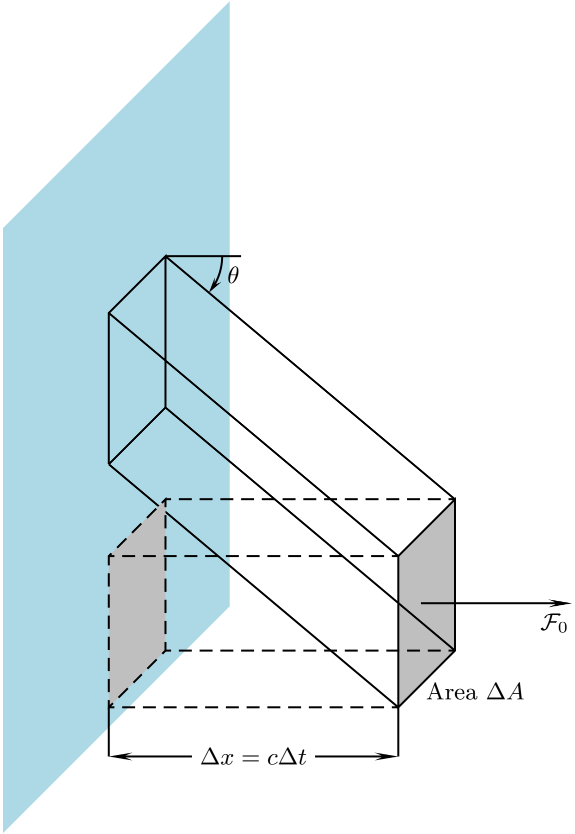


Figure 15.2: We start from radiation fluxes through two gray ends of the control box perpendicular to the hot plane in equilibrium with radiation. We then balance radiation fluxes from a tilted box, and average over all orientations.

4. Given that the coefficient ratios in Eq. (15.14) are constant (do not depend on i and k), obtain Eq. (15.15).
5. Prove Eq. (15.21).
6. Prove Eq. (15.23).

7. Prove Eq. (15.24).

8. Demonstrate that when a small hole is made in a rectangular box, the radiation flux (radiation energy emitted through the hole per unit area and per unit time) is σT^4, where $\sigma = \frac{1}{4}ac$, see **Figure 15.2.**

   Hint: For a rectangular box filled with radiation of total energy U, the radiated energy flux $\mathcal{F}_0$ (perpendicular to both gray ends) is

$$\begin{aligned} U &= \mathcal{F}_0 \Delta t \underbrace{2\Delta A}_{\substack{\text{Count}\\ \text{Both ends}}} = \mathcal{F}_0 2 \underbrace{\frac{\Delta x \Delta A}{c}}_{\text{Volume}} = \mathcal{F}_0 \frac{2V}{c} \\ \mathcal{F}_0 &= \frac{c}{2}\frac{U}{V} = \frac{c}{2} a T^4 \end{aligned} \tag{15.44}$$

   For an arbitrary tilted box, the areas of both gray ends are larger than the areas of ends perpendicular to the other edges by a factor $1/\cos(\theta)$. The time to sweep the longer tilted box is $\Delta t/\cos(\theta)$. The total flux is the average of fluxes in all directions from $-\pi/2$ to $\pi/2$ radians:

$$\begin{aligned} \underbrace{\frac{U}{\cos\theta}}_{\substack{\text{Larger}\\ \text{volume}}} \underbrace{\cos\theta}_{\substack{\text{Smaller}\\ \text{x-section}}} &= \mathcal{F}_\theta \frac{\Delta t}{\cos\theta}\frac{2\Delta A}{\cos\theta} = \mathcal{F}_\theta \frac{2\Delta x \Delta A}{c\cos^2\theta} = \mathcal{F}_\theta \frac{2V}{c}\cos^2\theta \\ \mathcal{F}_\theta &= \frac{c}{2}\frac{U}{V}\cos^2\theta = \frac{c}{2} a T^4 \cos^2\theta \\ \mathcal{F}_U &= \frac{1}{\pi}\int_{-\pi/2}^{\pi/2} \mathcal{F}_\theta d\theta = \frac{c}{2} a T^4 \, \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} \cos^2(\theta)\, d\theta \end{aligned} \tag{15.45}$$

9. Assuming that Sun surface has the black body temperature[1] of $T = 5785$ K, and using PLANCK's formula for the density of radiation energy converted to radiation flux by multiplying it by $c/2$, calculate how much energy is received by the Earth, if the average distance between the Sun and Earth is $d_{SE} = 149.598 \times 10^9$ m, and the Sun radius is $R_{\text{sun}} = 6.955 \times 10^8$ m.

   Hint: Assume PLANCK's constant $h = 6.626068 \times 10^{-34}$ J s, the speed of light in vacuum $c = 299792458$ m s^{-1}, and BOLTZMANN's constant $k = 1.3806503 \times 10^{-23}$ J K^{-1}.

   The flux of solar radiation at the edge of Earth's atmosphere is obtained from the that at the Sun's surface by applying the law of energy conser-

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[1] The Sun is not a perfect black body; instead, it is a gray body with surface emissivity of 0.93. Disregarding this small discrepancy for the time being, I have found by trial-end-error that the temperature of the Sun's surface of approximately ∼5786 K yields the solar constant of 1366 W m^{-2} when integrating from 1 to 30000 nm.

vation to radial geometry:

$$\frac{4\pi R_{\text{sun}}^2}{4\pi d_{SE}^2} \tag{15.46}$$

Thus, the function you want to plot is:

$$U_\lambda \, \frac{c}{4} \, \frac{R_{\text{sun}}^2}{d_{SE}^2} = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/(\lambda kT)} - 1} \, \frac{c}{4} \, \frac{R_{\text{sun}}^2}{d_{SE}^2} \quad \mathsf{W\ m^{-2}\ m^{-1}} \tag{15.47}$$

Plot this density function from 1 nm to 4000 nm. Calculate the area underneath the curve. It should equal approximately the solar constant at the edge of the Earth's atmosphere, ~1366 W m^{-2}. The result is shown in **Figure 15.4**. The measured solar radiation flux density is provided in **Figure 15.3**. Note close similarity of the two distributions.

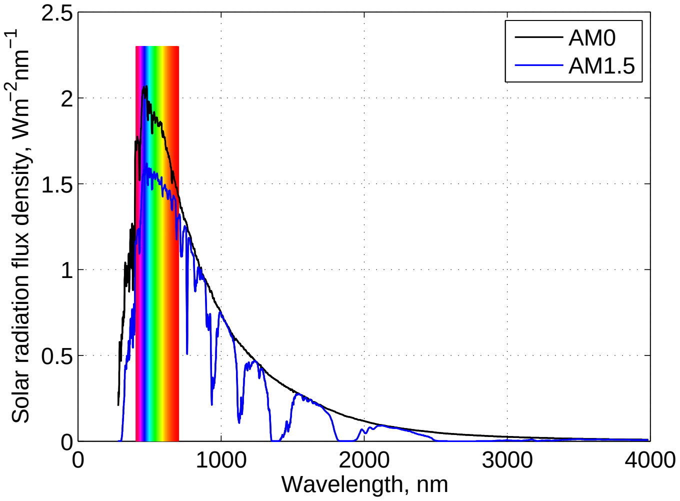


Figure 15.3: Measured solar radiation flux density functions at the edge of the atmosphere (AM0) and on the Earth surface at 37^0 latitude (AM1.5). Note the numerous absorption peaks by water vapor and carbon dioxide in the atmosphere. The area underneath the AM0 density function is 1366 W/m^2 (the solar constant), and the area underneath AM1.5 is 1010 W/m^2. The fraction of energy in visible light is 0.39 for AM0 and 0.43 for AM1.5. Source: ASTM G173-03 Tables: Extraterrestrial Spectrum, Terrestrial Global 37 deg South Facing Tilt & Direct Normal + Circumsolar; rredc.nrel.gov/solar/spectra/am1.5/. Both Etr and Global tilt data series were multiplied by 1.0074 to adjust them to the mean Total Solar Irradiance between 1978 and 2007 measured by ACRIM on the Nimbus7/ERB satellite, see www.acrim.com/Data%20Products.htm.

10. Assuming that the visible light is contained between 400 nm (purple) and 700 nm (deep red), calculate what fraction of total solar radiation falls in this range. In your calculations, use Eq. (15.47). This fraction is related to the *Photosynthetically Active Radiation* (PAR) used by plants. **Answer:** ~37%.

11. Assuming the same physical constants as in **Problem 9** and $T_E = 255$ K as the black body temperature of the outer layers of Earth's atmosphere, generate the plot in **Figure 15.5**.

    Hint: Plot the curve $U_\lambda(T_E)\ \frac{c}{4}$ as the hemispherical (omnidirectional) Earth radiation flux density. Calculate the area underneath this curve. It should be close to 236 $\mathsf{W\ m^{-2}}$. This is roughly how much power is radiated from each square meter of the Earth's surface in every direction. Note that Earth's radiation spectrum is in far infrared. Also note that the Earth is a system open to radiation flow, but closed to mass flow.

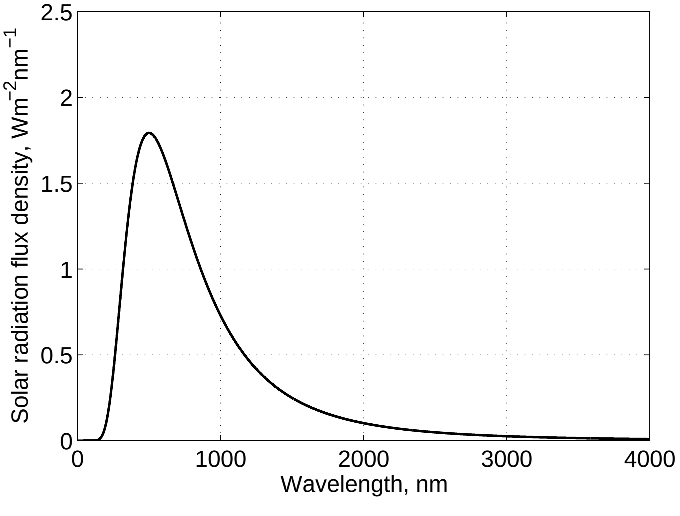


Figure 15.4: Solar radiation flux density function calculated from Eq. (15.47).

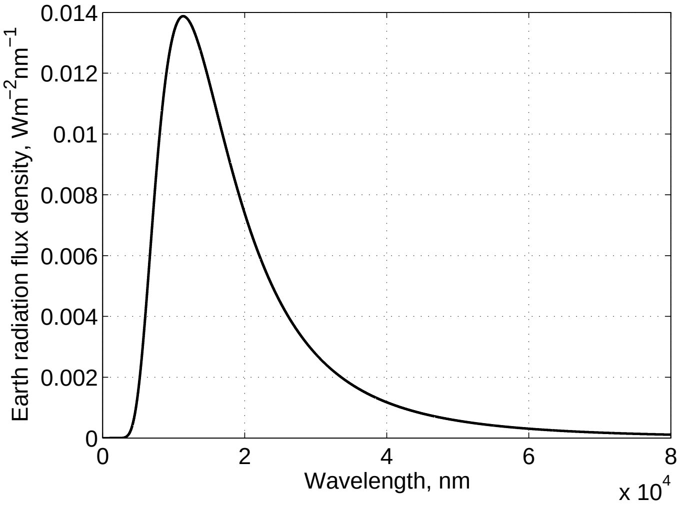
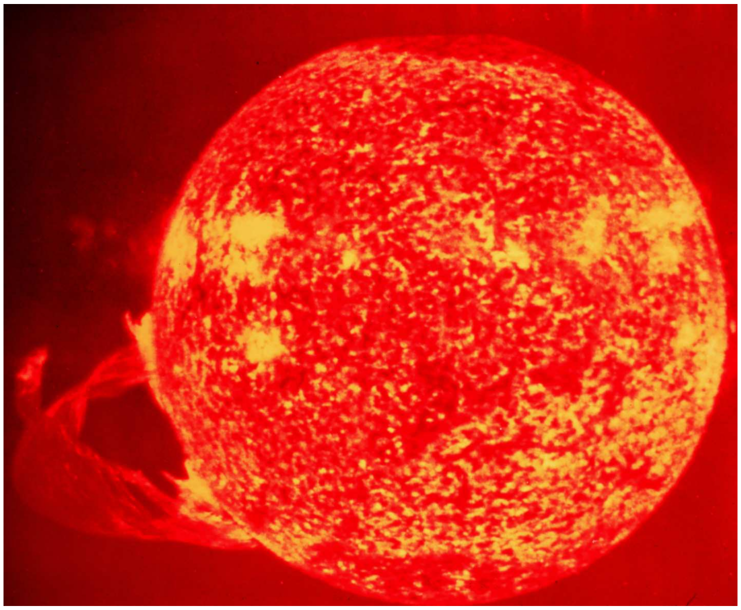


Figure 15.5: Earth radiation flux density function.

Chapter 16

Solar Power That Drives the Earth



The earth mourned, and faded away, and is weakened: the world faded away, the height of the people of the earth is weakened. And the earth is infected by the inhabitants thereof: because they have transgressed the laws, they have changed the ordinance, they have broken the everlasting covenant.

— Prophet Isaiah (c.760-690 B.C.)
Isaiah 24:4-5 (The Holy Bible)

16.1 What Are We Going to Learn?

Your are going to learn about the magnitude of solar power driving the Earth. You will learn about the various measures of this power and the common misunderstandings[1] surrounding them.

16.2 Why Is It Important?

The Earth is a finite complex system open to the flow of radiation, but closed to the flow of mass. The Earth has evolved in response to a fixed flux of solar radiation. You need to understand clearly that the finite Earth driven by the finite flux of solar energy cannot accommodate indefinite expansion of human activities, its stocks, and the associated energy and mass flows. This statement is trivial, a logical tautology, but it is vehemently denied by most economists and disregarded by most policy makers on the Earth.

16.3 Definitions

Definition 17 Irradiance, **radiant emittance**, and **radiant exitance** are radiometry terms for the power of electromagnetic radiation at a surface, per unit area, or energy flux. **Irradiance** is used when the electromagnetic radiation is incident on the surface. The other two terms are used interchangeably for radiation emerging from a surface. The SI units for all of these quantities are watts per square meter ($\mathsf{W\ m^{-2}}$) or $\mathsf{J\ s^{-1}\ m^{-2}}$. □

Definition 18 Total Solar Irradiance (TSI) is the solar irradiance at all wavelengths incident on a unit surface placed at the edge of the atmosphere perpendicularly to the direction of sunlight. It is also called the **solar constant**. An example of TSI measured by satellites over nearly three decades is shown in **Figure 16.1**. Since 1978, the average solar constant has been 1366.2 ± 0.7 $\mathsf{W\ m^{-2}}$. □

Definition 19 Average Total Solar Irradiance is defined as 1/4 of TSI $1366.2/4 \approx 342$ $\mathsf{W\ m^{-2}}$ anywhere at the edge of Earth's atmosphere and at any time, see **Problem 1** and **Figure 16.2** for details. □

Definition 20 Earth's Albedo is the ratio of reflected-to-incident flux of solar radiation at the top of the atmosphere. The Earth albedo is a function of time and space, depending in particular on the nature of cloud and ground cover.

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[1] Here is a typical nonsensical statement from US press, A.D. 2006: "The U.S. could turn off the foreign oil spigots by making fuel out of cornstalks, stover, switch grass, straw or virtually any biomass. Forget drilling thousands of oil and gas wells. Companies instead could gather the nation's abundant forest and agricultural wastes, process those to extract sugar and ferment the sugar to produce fuel." *Colorado bullish on cellulosic ethanol,* GARGI CHAKRABARTY, **Rocky Mountain News**, December 26, 2006.

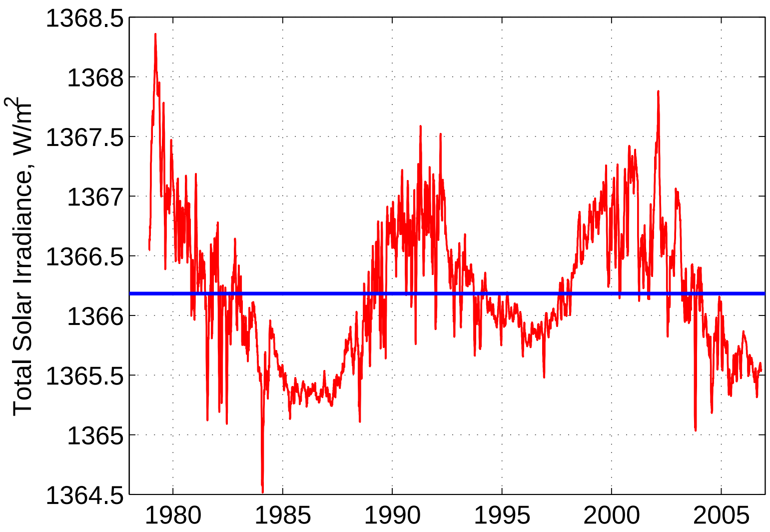

Figure 16.1: Total Solar Irradiance (TSI) between October 15, 1978, and October 5, 2006. The plotted file contains the Active Cavity Radiometer Irradiance Monitor (ACRIM) TSI composite time series acquired from Nimbus-7/ERBE, ACRIM 1, 2 & 3. Available from www.acrim.com/Data%20Products.htm, accessed on Dec. 23, 2006. The plotted TSI curve is the 11-point central running average of the ACRIM measurements. The mean TSI value is 1366.2 ± 0.7 W m^{-2}, the mean annual value anywhere along the edge of the atmosphere is $(1366.2 \pm 0.7)/4 = 341.6 \pm 0.2 \approx 342$ W m^{-2}, and the mean annual value of TSI at the Earth surface is 236 W m^{-2}.

For the Earth as a whole, the long term average planetary albedo is about 0.31. Therefore, the average solar irradiance anywhere on the surface of the Earth and anytime is $(1 - 0.31) \times 342 \approx 236$ W m^{-2}. Of course, on a very clear day, at noon, and at the equator, the instantaneous solar irradiance may be above 1100 W m^{-2}, in excess of its long term average value of 943 W m^{-2}. □

16.4 Averages of Solar Energy Flux

As discussed in Chapter 15, Problem 9, the fraction of solar energy flux intercepted by the Earth is equal to the solar energy flux density function $U_\lambda(T)$ integrated over all wavelengths, and multiplied by 1/4 of the speed of light in vacuum, c, and by the square of the ratio of the Sun radius, R_{sun}, to the average Earth distance from the Sun, d_{SE}. This quantity, gives us the total solar irradiance (TSI), see Definition 18, equal to 1366 W m^{-2}.

Because the Earth surface is curved, see Figure 16.2, each element (say, 1 square meter) of the Earth surface receives a fraction of the incident solar

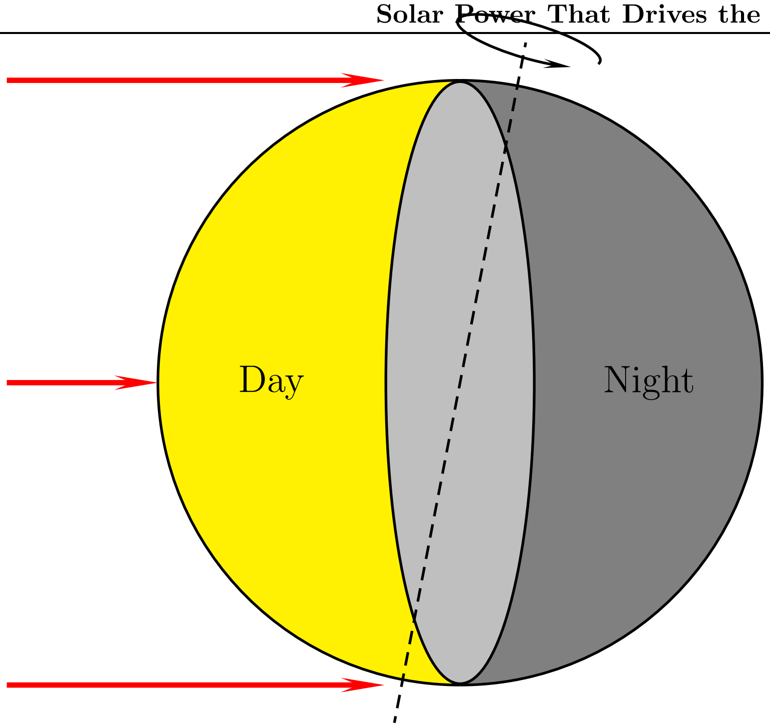

Figure 16.2: The sunlight shines onto 1/2 of the Earth area (the yellow hemisphere $2\pi R_{\mathrm{earth}}^2$), and delivers energy onto this hemisphere's projection orthogonal to the sun beam (the light gray circle with the area πR_{earth}^2, or 1/2 of the hemisphere area). Here R_{earth} is the average radius of the Earth. In addition, the Earth rotates and each hemisphere is lit by the sun only 1/2 of the time. Therefore, on the average, the solar irradiation (AM 0) is equal or $1366/4 \approx 342$ $\mathsf{W\ m}^{-2}$ anywhere at the edge of the Earth's atmosphere.

power flux equal to the projection of this element onto the direction of sunlight, see Figure 16.8. This fraction is equal to the cosine of the angle between the direction of sunlight and a line perpendicular to the surface $(-\cos(\pi - \theta) = \cos\theta)$. The average value of solar flux anywhere on the lit hemisphere at the edge of the Earth's atmosphere is therefore 1/2 of TSI. Because each hemisphere is lit 1/2 of time, the average annual solar flux anywhere at the of the atmosphere and at any time, is 1/4 of TSI. Furthermore, the Earth reflects about 31% of the incident solar flux, see Definition 20, and each square meter of the Earth's surface receives on the average 236 $\mathsf{W\ m}^{-2}$. This amount of average solar power in is equal to the Earth's radiation power out, calculated in Chapter 15, Problem 11. Therefore, the fundamental equation of steady-state climate on the Earth is

$$\dot{E}_{\mathrm{average}} \approx 235\ \mathsf{W\ m}^{-2} \tag{16.1}$$

where $\dot{E}_{\mathrm{average}}$ is the spatially and temporally averaged TSI.

16.5 A Detailed Balance of Radiation Fluxes

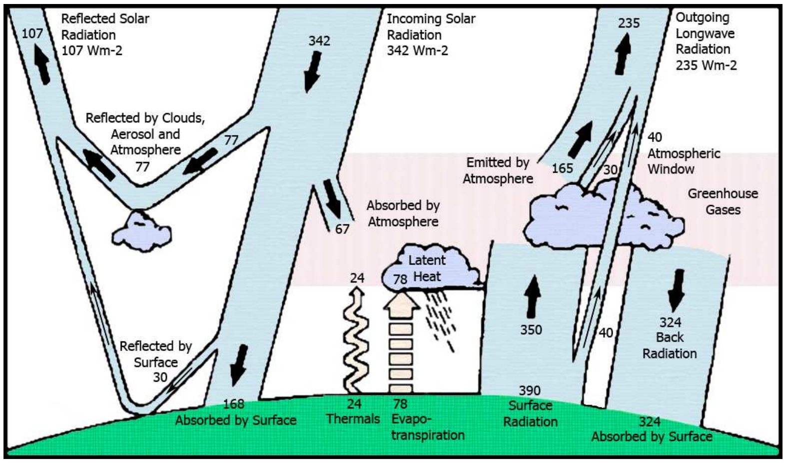

Figure 16.3: The detailed budget of radiation fluxes on the Earth is more complicated than Eq. (16.1) might suggest. Adapted from Figure 7 in Kiehl & Trenberth (1997).

A detailed estimate of the annual global energy budget of the Earth is shown in **Figure 16.3** adapted from J. T. Kiehl and Kevin E. Trenberth (Kiehl and Trenberth, 1997). The discussion below follows mostly the brilliant paper by Kiehl & Trenberth.

Satellite observations of the top-of-atmosphere earth radiation budget have greatly improved estimates of the global mean energy budget. The Earth Radiation Budget Experiment (ERBE) satellites[2] have provided nearly continuous data since 1984. The global annual mean of these data indicate that the outgoing longwave radiation is 235 $\mathrm{W\,m^{-2}}$, while the mean absorbed shortwave flux is 238 $\mathrm{W\,m^{-2}}$. Thus, the measured top-of-atmosphere energy budget balances to within 3 $\mathrm{W\,m^{-2}}$. A similar net imbalance exists for the long-term Nimbus-7 data as well. For the composite time series plot of TSI, see **Figure 18**.

The ERBE data imply a global mean clear sky outgoing longwave flux of nearly 265 $\mathrm{W\,m^{-2}}$. This flux is then adjusted for moisture content, aerosols, and cloudiness to yield $235 - 238$ $\mathrm{W\,m^{-2}}$.

The other fluxes can be classified as follows:

1. Of the 342 $\mathrm{W\,m^{-2}}$ incident on the Earth, 77 $\mathrm{W\,m^{-2}}$ are reflected by the atmosphere, and 30 $\mathrm{W\,m^{-2}}$ by the Earth surface, for the total of 107 $\mathrm{W\,m^{-2}}$ or the average Earth albedo of $107/342 = 0.31$.

2. Of the $342 - 107 = 235$ $\mathrm{W\,m^{-2}}$ of average solar radiation that power the Earth, 67 $\mathrm{W\,m^{-2}}$ are absorbed by the atmosphere and 168 $\mathrm{W\,m^{-2}}$ are

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[2] See the ERBE webpage: asd-www.larc.nasa.gov/erbe/ASDerbe.html

absorbed by the Earth surface.

3. Of the 235 $\mathsf{W\,m^{-2}}$ emitted by the upper layers of the atmosphere at black body temperature -18^0C or 255 K, 165 $\mathsf{W\,m^{-2}}$ are radiated by the air, 30 $\mathsf{W\,m^{-2}}$ by the clouds, and some 40 $\mathsf{W\,m^{-2}}$ sneak out directly from the Earth surface through the atmosphere, passing through the so-called "atmospheric window".

4. The radiation that originates near the Earth's surface and leaves the atmosphere comes from areas where there are no clouds and occupies the part of the spectrum known as the atmospheric window, taken to be the wavelengths of $8000 - 12000$ nm. The estimate of the amount leaving via the atmospheric window is somewhat *ad hoc*. In the clear sky case, the radiation in the window amounts to 99 $\mathsf{W\,m^{-2}}$, while in the cloudy case the amount decreases to 80 $\mathsf{W\,m^{-2}}$, showing that there is considerable absorption and re-emission at wavelengths in the so-called window by clouds. The assigned value of 40 $\mathsf{W\,m^{-2}}$ is simply 38% of the clear sky case, corresponding to the observed cloudiness of about 62%. This procedure emphasizes that very little radiation is actually transmitted directly to space as though the atmosphere were transparent.

5. The outgoing surface fluxes consist of surface infrared radiation (390 $\mathsf{W\,m^{-2}}$), and the evaporation ($\sim$78 $\mathsf{W\,m^{-2}}$) and convective fluxes ($\sim$24 $\mathsf{W\,m^{-2}}$). The latter two atmospheric fluxes redistribute heat across the Earth surface. They cool the tropics and heat moderate latitudes.

6. For the main outgoing flux, the surface infrared radiation of 390 $\mathsf{W\,m^{-2}}$, corresponds to a black body emission at 15^0C or 298 K. The atmosphere traps and radiates back to the Earth surface $\sim$342 $\mathsf{W\,m^{-2}}$. This is the "greenhouse effect," which keeps the Earth surface $298 - 255 = 43$ K warmer than Earth's black body temperature of the outgoing infrared radiation.

7. For the clear sky, water vapor contributes to 60% of the total radiative forcing, while carbon dioxide contributes 26% to the clear sky radiative forcing. The remaining 14% are contributed by methane, ozone, ammonia, CFC's, and other gases. In discussing increases in greenhouse gases and their impact on climate change, the dominant contribution of water vapor to the current greenhouse effect is often overlooked.

8. Thermal conduction and convection (geothermal) Earth fluxes contribute only 0.06 $\mathsf{W\,m^{-2}}$ and are neglected.

9. Photosynthesis consumes only an average of 0.08 $\mathsf{W\,m^{-2}}$.

16.6 A Functional Power Balance of the Earth

A functional power balance of the Earth, performed by M. KING HUBBERT (Hubbert, 1971), is reproduced in **Figure 16.4**. This balance splits the average solar power intercepted by the Earth into various uses: the rates of heat absorption and reflection, water evaporation and upward air convection, wind, waves, ocean currents, tides, and photosynthesis.

This balance shows clearly that the amount of solar power diverted to photosynthesis is 10% of the amount of solar power converted to wind, waves, atmospheric convection and ocean currents that in turn are minuscule in comparison with heat absorption and water evaporation.

On the other hand, the micro-scale equilibrium of *all* coupled processes that distribute solar power on the Earth is crucial in determining climate and supporting life on the Earth. Have you ever wondered about the heated arguments about the role of greenhouse gases in determining climate? The discussion is so heated because it is very difficult to close the Earth power balance to a small fraction of 1%. In addition most researchers focus on CO_2, forgetting completely about the crucial role of water vapor and droplets in determining the greenhouse effect.

16.7 Solar Radiation

Solar *irradiance* can be integrated over time and the result is solar *radiation.* Before integration, one needs to know average monthly solar irradiance. The Army and Navy maintain a large database[3] of solar irradiance in $\mathsf{kWh\ m^{-2}\ day^{-1}}$, which can be translated easily into $\mathsf{W\ m^{-2}}$. The data used here are average irradiances of zero-tilt (horizontal) flat-plate collectors. The irradiation data have been time-averaged for each month over the last 30 years. This type of data is most suitable for estimating solar irradiance and radiation during plant growth seasons.

Four examples are shown in **Figure 16.5**. The growth season was chosen to start May 1 and end September 20. The respective annual and growth-season averages are plotted as red lines. For example, the average growth-season irradiance in Des Moines is 250 $\mathsf{W\ m^{-2}}$.

16.8 Global Warming

Because the mass of Earth's atmosphere is minute compared with the mass of water in the oceans, it is possible to increase air concentrations of trace gases relatively quickly. For example, the annually-increasing concentration of CO_2 in the air, see **Figure 16.6**, can only be removed by dissolution in the ocean

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[3] *30-Year Average of Monthly Solar Radiation, 1961-1990.* Data files are listed alphabetically by state and city at rredc.nrel.gov/solar/old_data/nsrdb/redbook/sum2/state.html

water over decades or centuries, and by organic carbon burial over geological time, cf. Chapter 6.

Equation (16.1) states that the Earth is in thermal equilibrium:

$$\begin{aligned}&\text{Rate of energy input from the sun} = \text{Rate of energy radiation by the earth}\\&\dot{E}_{in} = \dot{E}_{out} = P = \text{const}\end{aligned} \tag{16.2}$$

Similarly to FRONDEL, OERTEL and RÜBBELKE (2002), I will assume that the Earth's atmosphere is a heat-transporting[4] gas layer. The surface temperature of the earth is T_0 and the PLANCK temperature of its radiation is T_{earth}. The stationary heat flow through the atmosphere occurs at a constant rate:

$$P = kA_{\text{earth}}(T_0 - T_{\text{earth}}) \tag{16.3}$$

where A_{earth} is the surface area of the earth. In this simple model, the steady-state rate of energy export from the Earth depends on the mean temperature difference between the Earth surface and the upper atmosphere. The overall heat transfer coefficient, k, depends on how effectively the atmosphere transports heat.

> With the increasing concentration of heat absorbers (the greenhouse gases) this coefficient decreases, and the Earth temperature must go up.

At steady state, Second Law of thermodynamics requires the entropy flow rate to satisfy the following equation:

$$P = T_0\dot{S}_0 = T_{\text{earth}}\dot{S}_{\text{earth}} \tag{16.4}$$

where $\dot{S}_0$ is the rate of entropy change near the Earth surface, and $\dot{S}_{\text{earth}}$ is the rate of entropy change at the outer layers of the atmosphere. Therefore, the net rate of entropy generation in the atmosphere due to energy transport is

$$\dot{S}_t = P\left(\frac{1}{T_{\text{earth}}} - \frac{1}{T_0}\right) > 0 \tag{16.5}$$

Since both $P = 235\ \mathsf{W\ m^{-2}}$ and $T_{\text{earth}} = 255\ \mathsf{K}$ are constant, it follows that as the temperature of the earth surface increases, so does the rate of entropy generation in the atmosphere. This *positive feedback* effect, or *domino effect*, will intensify the impact of human entropy production on the Earth climate. The rate of entropy generation in the atmosphere per unit surface area of the earth defines the specific atmospheric entropy generation rate:

$$\sigma_t = \frac{\dot{S}_t}{A_e} \tag{16.6}$$

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[4] Heat transport through the atmosphere proceeds through turbulent convection and mixing, water evaporation and condensation, thermal conduction, and radiation.

According to the solution of **Problem 6**, this specific rate is equal to 0.11 W/K-m^2, not bad for such a simplistic model. For comparison, STAHL (1996) reports 0.2 W/K-m^2.

According to (Brohan et al., 2006), the 1990s were the warmest decade in the series. The warmest year of the entire series has been 1998, with a temperature of 0.548^0 C above the 1961-90 mean. Ten of the eleven warmest years in the series have now occurred in the past eleven years (1995-2005). The only year in the last eleven not among the warmest eleven is 1996 (replaced in the warm list by 1990). In 2005, the global temperature anomaly was +0.47^0 C, the second highest excursion on record.

Analyses of over 400 proxy climate series (from trees, corals, ice cores and historical records) show that the 1990s is the warmest decade of the millennium and the 20th century the warmest century. The warmest year of the millennium was likely 1998, and the coldest was probably (but with much greater uncertainty) 1601. Much of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations.

We will accept global climate change and the mean global temperature increase of +0.5^0 C with respect to the years 1961-1990 as an experimental fact. Later, we will dwell on some of the dire consequences of global warming.

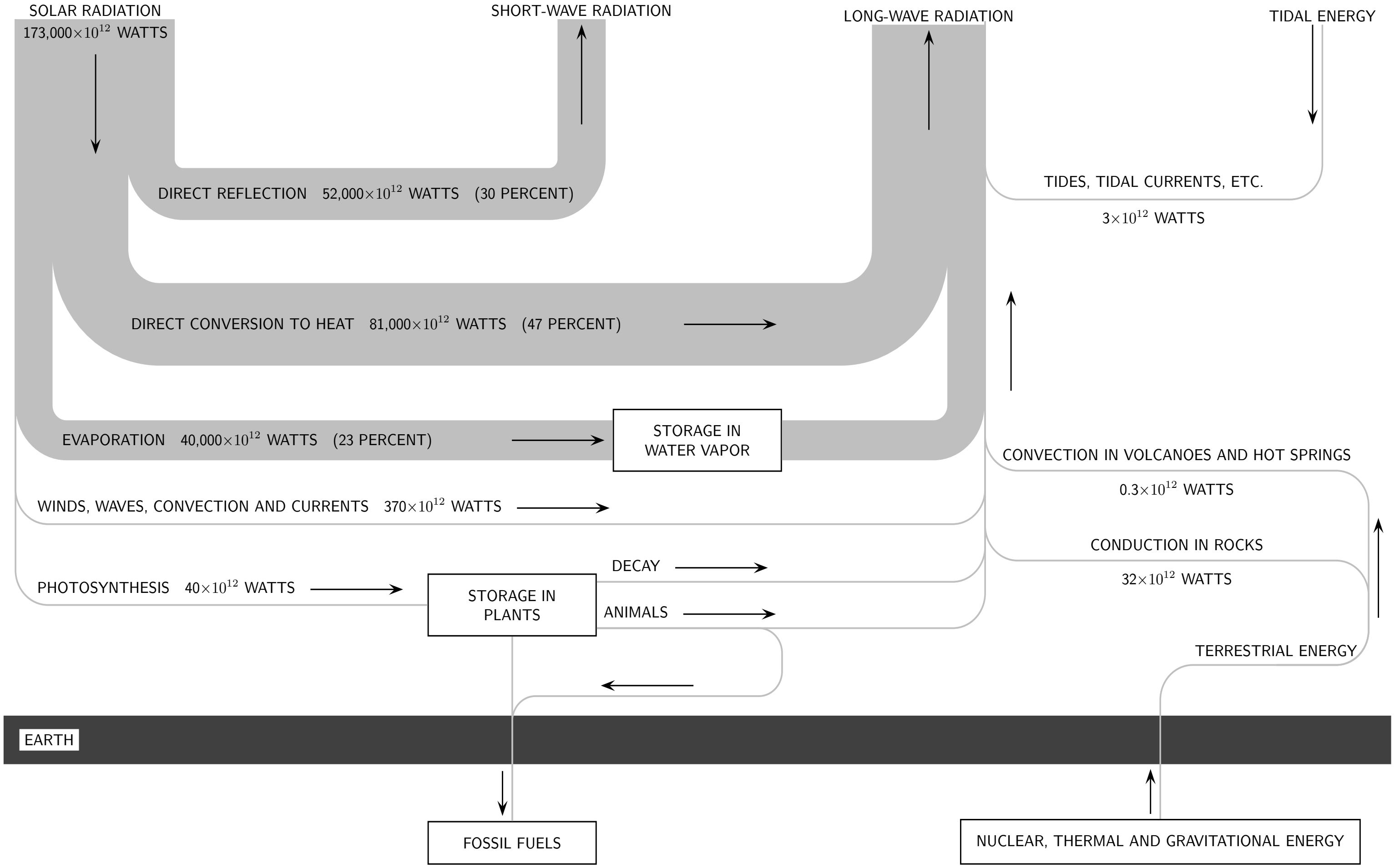

Figure 16.4: A functional balance of solar power on the Earth, performed by M. K. Hubbert (1971), shows partitioning of solar energy into the various processes that drive biosphere.

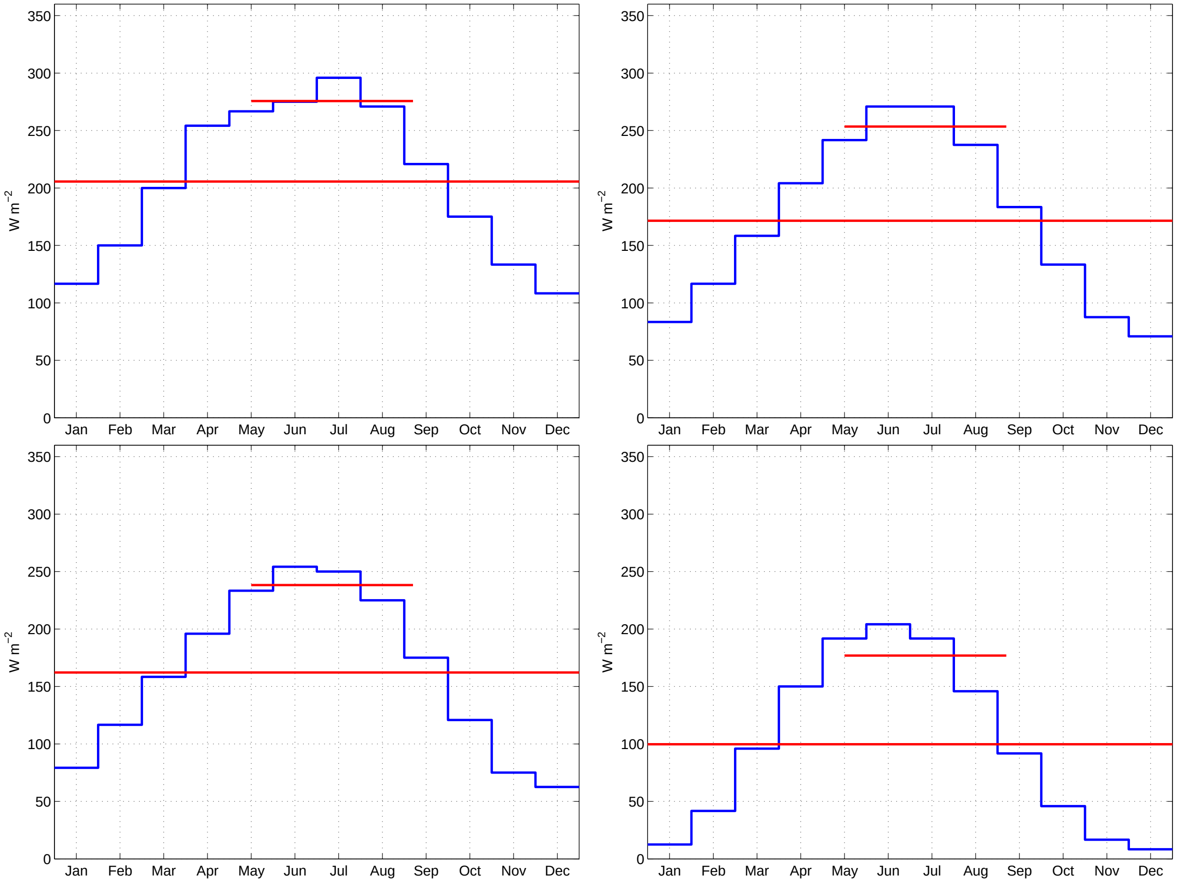

Figure 16.5: 30-year averages of mean monthly irradiances of horizontal flat-plate collectors. Clockwise from the top-left: Los Angles, CA; Des Moines, IA; Portland, ME; and Anchorage, AL.

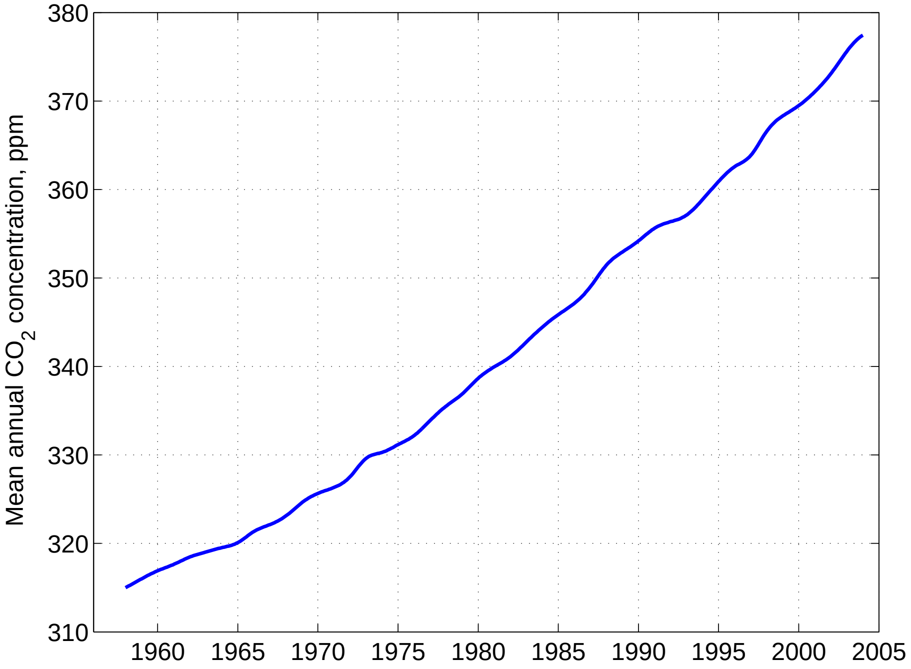

Figure 16.6: Mean CO_2 concentration in the atmosphere measured at Mauna Loa. Source: cdiac.ornl.gov/trends/co2/sio-mlo.htm, accessed December 30, 2006

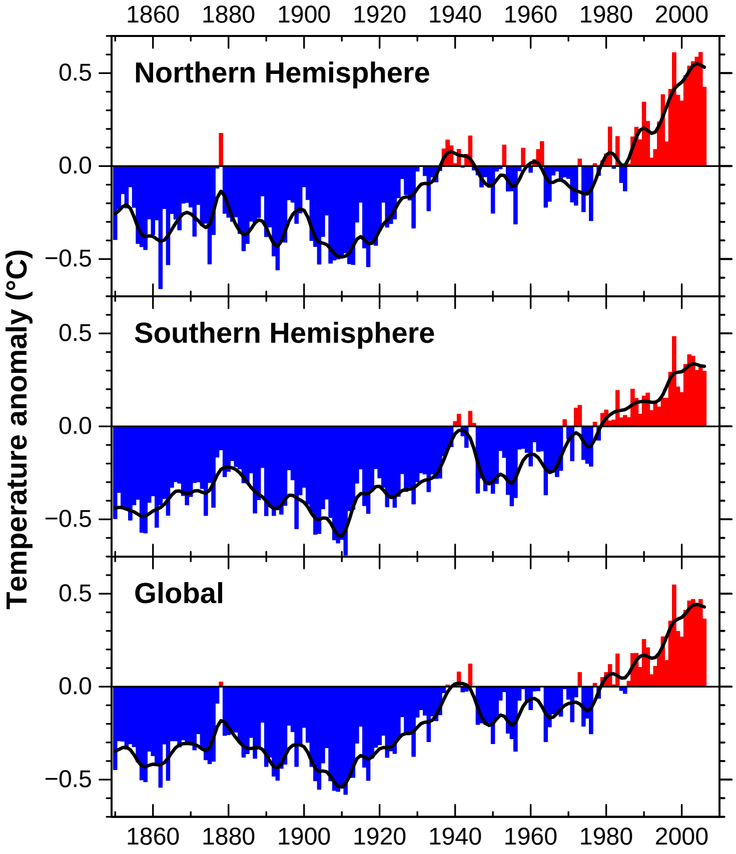

Figure 16.7: The time series shows the combined global land and marine surface temperature record from 1850 to 2005. The year 2005 was equal second warmest on record, exceeded by 1998. This time series is being compiled jointly by the Climatic Research Unit and the UK Met. Office Hadley Centre (www.cru.uea.ac.uk/cru/info/warming/). The record is being continually updated and improved (see the paper by Brohan et al., (2006)). This paper includes a new and more thorough assessment of errors, recognizing that these differ on annual and decadal timescales. Increased concentrations of greenhouse gases in the atmosphere due to human activities are most likely the underlying cause of warming in the 20th century.

16.9 Problems

1. Prove that the solar power per unit area of the lit earth hemisphere, see **Figure 16.2**, is exactly 1/4 of the the solar constant.

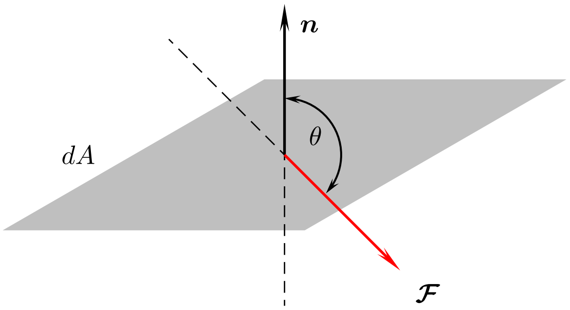

Figure 16.8: Incidence of solar radiation (irradiance) on a flat horizontal surface. The normal component of this radiation impinging on the surface is $-\boldsymbol{\mathcal{F}}\cos(\theta)$.

Hint: The normal component of solar radiation impinging on a flat horizontal surface element is, see **Figure 16.8**,

$$-\boldsymbol{\mathcal{F}}\cos\theta\;dA \tag{16.7}$$

where $dA = dx\;dy$ is the area of the element. The angle $\theta > \pi/2$, the cosine is negative, and the flux is positive.

Now imagine that the surface element $\mathbf{dA} = \mathbf{n}\;dA$ in Figure 16.8 is on a hemisphere. In a spherical-polar coordinate system, the element's area is equal to

$$\mathbf{dA} = r^2 \sin\theta\;d\phi d\theta\;\boldsymbol{e}_r \tag{16.8}$$

and it points in the radial direction $\boldsymbol{e}_r$. The solar power flux is $\boldsymbol{\mathcal{F}} = -\mathcal{F}\;\boldsymbol{e}_z$. Integration of the solar flux over the hemisphere yields the following average value

$$E = \frac{\mathcal{F}}{2\pi R^2_{\text{earth}}} \int_0^{2\pi} d\phi \int_0^{\pi/2} R^2_{\text{earth}} \sin\theta\cos(\pi-\theta)\;d\theta \tag{16.9}$$

Here $\boldsymbol{e}_z$ and $\boldsymbol{e}_r$ are the unit vectors in the z-direction and the r-direction of the coinciding cartesian and spherical coordinate systems, respectively. Both coordinate systems have origin at the center of the sphere.

Sketch the geometry, the angles, derive this integral more carefully, and state your assumptions. Then show that this integral is 1/2. The Earth rotates with a period of 24 hours and the lit hemisphere is exposed to sunlight for 12 hours on the average, or 1/2 of the time. Hence another factor of 1/2 in **Figure 16.3**.

2. In Earth orbit the solar radiation density is called AM0 (air mass zero). On the surface of the Earth, the solar radiation spectrum is changed by absorption in the atmosphere and it also depends on the length of the light path through the air. This length varies approximately with the inverse cosine of the latitude, see **Problem 1**. The irradiation at the equator it is called AM1 (perpendicular incidence), in Central Europe it is AM1.5. What is the latitude that justifies the name AM1.5?

   Answer: 47.20N.

3. Calculate the average solar power delivered to the edge of the atmosphere and to the surface of the Earth. Express this power in tera watts (TW) or 10^{12} W. State clearly your assumptions and use the Earth radius of 6.371×10^6 m.

   Hint: This question is answered in **Figure 16.4**.

4. Using **Figure 16.3** show that the incoming and outgoing power fluxes balance at the surface of the Earth.

5. Based on what you have learned thus far, comment briefly on Footnote 16.1. Why did I call the quoted excerpt "nonsensical"? Your comments should be based on science (physics, chemistry, biology, etc.), and not on political "science" or economics.

6. Calculate the specific rate of entropy generation in the Earth's atmosphere, given by Eq. (16.6).

Chapter 17

The Extraordinary Water

When we try to pick out anything by itself, we find it hitched to everything else in the Universe.

— John Muir
My First Summer in the Sierra (Boston: Houghton Mifflin, 1911)

17.1 What Are You Going to Learn?

In this lecture you will learn about the extraordinary properties of water in its three states: solid ice, liquid, and vapor. Our interest will be limited to the near-earth surface conditions; roughly, the total pressures of 0.5-100 bars, and the temperatures ranging from -50 to 100^0C. The water properties of interest in this course are listed in **Table 17.1**.

Table 17.1: Physicochemical properties of water

Property	Comparison with Other Substances	Importance to Environment
Molecular structure	Strong hydrogen bonds among water molecules, see **Section 17.4**	Results in unusual properties: high melting and boiling points, large latent heats, and specific heat capacity
Density	Maximum density at 4^0C, not at freezing point; expands upon freezing, see **Section 17.5**	In fresh water lakes prevents freezing up and causes seasonal stratification
Melting and boiling points	Abnormally high, see **Section 17.6**	On the earth, water exists as a liquid
Heat capacity	Highest of any liquid but ammonia, see **Section 17.7**	Moderates global temperatures, prevents climate extremes
Heat of vaporization	One of the highest known, see **Section 17.8**	Controls heat transport in atmosphere and oceans, moderates climate
Surface tension	Very high, see **Section 17.9**	Regulates drop formation, allows for tall plants
Absorption of radiation	Large in infrared and ultraviolet regions; less in visible light, see **Section 17.10**	Controls biological activity (photosynthesis) in water bodies and atmospheric temperature
Solvent properties	Excellent solvent for ionic salts and polar molecules, see **Section 17.11**	Transport of dissolved nutrients in hydrologic cycle and biological systems

17.2 Why Is It Important?

Life on the earth would be impossible without water. Before we get busy with the details of how water flows through porous media, you should understand what water is, and what role it plays on the planet Earth. The mass of all water on the earth is about 0.02% of the planet mass, and about 0.9% of the earth's crust[1] mass. Most scientists think that water quantity on the earth has hardly changed over the last 3.8 billion years, and water was part of our planet from the very beginning, see HOLLAND (Holland, 1984) and the references therein.

Almost all water that feeds our civilization is underground, in natural lakes, and in man-made reservoirs. In fact, the mass of groundwater down to the depth of 4000 m is almost 60% of the mass of water locked in ice, the single biggest repository of fresh water on the earth. How groundwater moves in the subsurface and what happens to it because of human activities will be discussed in this course.

17.3 How Much Water Is There on the Earth?

According to the distinguished Swiss researchers, Profs. LAURA SIGG and WERNER STUMM (Sigg and Stumm, 1994), water on the earth is distributed as in **Table 17.2**.

Table 17.2: Water in the hydrosphere

Parameter	Value	Units
Total Earth area	5.1×10^{14}	m^2
Ocean area	3.6×10^{14}	m^2
Land area	1.5×10^{14}	m^2
Earth mass	$59{,}720{,}000 \times 10^{17}$	kg
Earth crust mass	$1{,}552{,}720 \times 10^{17}$	kg
Atmosphere mass	52×10^{17}	kg
Ocean mass	$13{,}700 \times 10^{17}$	kg
Groundwater 0 – 750 m	42×10^{17}	kg
Groundwater 0 – 4,000 m	95×10^{17}	kg
Water in ice	165×10^{17}	kg
Water in lakes and rivers	1.3×10^{17}	kg
Water in atmosphere	0.105×10^{17}	kg
Water in biosphere	0.006×10^{17}	kg
Total stream discharge	0.32×10^{17}	kg/yr
Precipitation=evaporation	4.5×10^{17}	kg/yr

Imagine a 16-gallon jug as representing the total water supply on the planet. The entire fresh water supply would then be about 5 cups. However, more than 3 cups of this water is bound in glaciers. When you remove the additional water

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[1] The solid outer "skin" of the earth, up to 40 km thick.

sources deep in the earth's crust, along with what is contained in the top soil and the atmosphere, and the amount of the water we have already polluted, then the useable water amounts to a small fraction of 1 cup. To understand better what this fraction might be, solve Problem 1.

17.4 Molecular Structure of Water

At room conditions ($P = 1$ atm and $T = 20^0$C), water is a transparent liquid, colorless in thin layers and blue-green in thick layers. The physical characteristics of water have been used to define several physical units and constants. For example, the normal freezing temperature of water (in equilibrium with air and under the pressure of 1 atm) defines 0^0C, and its normal boiling point defines 100^0C. The CGS unit of mass, 1 gram, is equal to the mass of 1 cm^3 of water at 4^0C (its maximum density). 1 calorie[2] (1 cal_{15}) is equal to the amount of heat necessary to raise the temperature of 1 g of liquid water at 14.5^0C by one degree Celsius. . . .

17.4.1 The van der Waals Intermolecular Forces

All like molecules attract each other to some degree. This *weak attraction* – called the van der WAALS attraction – is the result of interactions of the nuclei and electrons of like molecules. The protons in one molecule attract the electrons in another one, and this attraction prevails over the electron-electron and nucleus-nucleus repulsions. The van der WAALS forces act across the distances of the order of molecule size, 1-10 Å(1 nm = 10^{-9} m = 10 Å), and are further differentiated into the *dispersion* (LONDON) and *dipole-dipole* forces, for details see e.g., (Hill and Petrucci, 1999). Because of its shape and charge separation, **Figure 17.1**, water molecules are highly *polar*, i.e., are *permanent electric dipoles.* The water dipole moment, μ_e, is the product of the charge δ and the distance d: $\mu = \delta d$; $d = .10$ nm = 1 Å in **Figure 17.2**. 1 DEBYE (1 D)= 3.34×10^{-30} Coulomb-meter. The dipole moment of the water molecule at room conditions is 1.84 D.

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[2] Other calories have been based on the initial temperatures of 0^0C, 3.5^0C, and 19.5^0C. Still another definition made the calorie 1/100th of the quantity of heat needed to raise the temperature of 1 gram of water from 0^0C to 100^0C. The values produced by the various definitions differ by somewhat less than 1%. 1 *thermochemical calorie* (cal_{th}), used in some branches of chemistry, was defined by the U.S. Bureau of Standards in 1953 as = exactly 4.1840 joules. In 1929, the International Steam Table Conference (London) defined the *international calorie*, cal_{IT}, as 1/860 of the international watt hour = 4.1860 international joules. The adoption of the absolute system of electrical units changed these values to 1/859.858 watt hours and approximately 4.18674 joules. At present, 1 *International Steam Table calorie* = exactly 4.1868 joules (Fifth International Conference on the Properties of Steam, London, 1956). This value was suggested by E. J. LE FEVRE because it is evenly divisible by 9, which in pre-computer days facilitated conversions between specific heats described in kilocalories per kilogram-degree Celsius and those in Btu per pound-degree Fahrenheit (Schmidt, 1959).

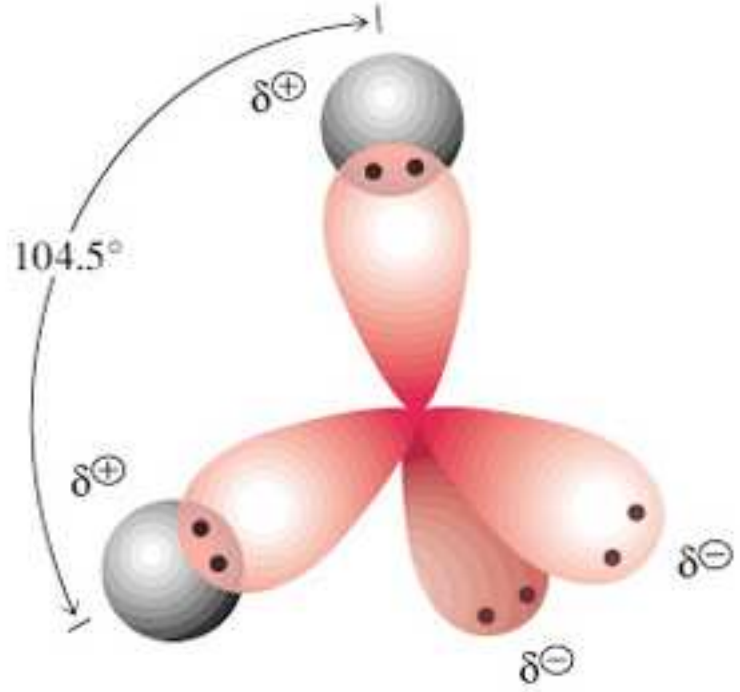

Figure 17.1: The structure of a water molecule. The electron configuration of a water molecule is tetrahedral, while the molecular structure is "bent" to yield a 104.5 degree angle between the hydrogen atoms. These hydrogen atoms have a partial positive charge. Oxygen also has 2 unbonded pairs of electrons that participate in hydrogen bonds because of their partial negative charges. The sp^3 hybrid orbital structure of oxygen in water leads to the formation of 4 hydrogen bonds by water. Reproduced from *Principles of Biochemistry* by H. ROBERT HORTON (editor), 3rd Edition, Prentice Hall, New York, 2001. For more on the sp^3 orbitals go to www.mhhe.com/physsci/chemistry/essentialchemistry/flash/hybrv18.swf.

17.4.2 Hydrogen Bonds

The very special properties of water are caused by the unusually strong attraction among its molecules. This special attractive force is called the *hydrogen bond*. A hydrogen bond between molecules is an intermolecular force in which a hydrogen atom covalently bonded to a nonmetal atom in one molecule is simultaneously attracted to a nonmetal atom in another molecule (Pauling, 1953; Hill and Petrucci, 1999), see Figure 17.2 and **17.3**.

The model of ice in **Figure 17.4**, shows how hydrogen bonds hold water

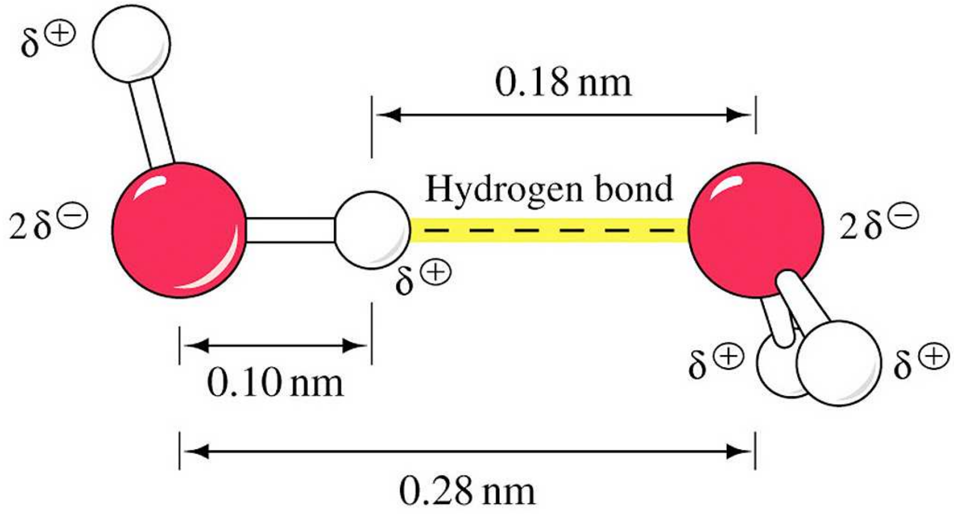

Figure 17.2: Hydrogen bonding between two water molecules. A partly positive hydrogen atom of one water molecule attracts the partly negative unbonded electron pair in the oxygen atom, forming a hydrogen bond. The distances between the atoms of the two water molecules in ice are shown. Hydrogen bonds are indicted by dashed lines highlighted in yellow. The bond angles between the two water molecules are determined by the electron configuration, *sp*3, of oxygen in water. Reproduced from *Principles of Biochemistry* by H. ROBERT HORTON (editor), 3rd Ed., Prentice Hall, New York, 2001.

molecules in a rigid but open structure. Oxygen atoms in ice are arranged in layers of distorted hexagonal rings. Hydrogen atoms lie between pairs of oxygen atoms, closer to one (covalent bond) than to the other (hydrogen bond).

17.5 Water Density

As ice melts, some of the hydrogen bonds break, and water molecules move into the holes that were in the ice structure. As a result, the water molecules are closer together in liquid water than in ice, and there is a 10% volume contraction when ice melts. Thus water in equilibrium with ice near melting point is *denser* than ice, see **Figure 17.5**. This behavior is most unusual; almost all other substances shrink and become denser as they freeze. High pressures disrupt hydrogen bonding and water swelling upon freezing. Thus the greater the pressure, the lower the temperature at which ice melts, and the slope of the fusion curve in phase diagram of water is *negative*, see **Figure 17.6**.

When liquid water is heated just above the melting point, more hydrogen bonds are broken, the water molecules become even more closely packed, and the density of water reaches its peak at $3.98 \approx 4^0$C. Above 4^0C, the water

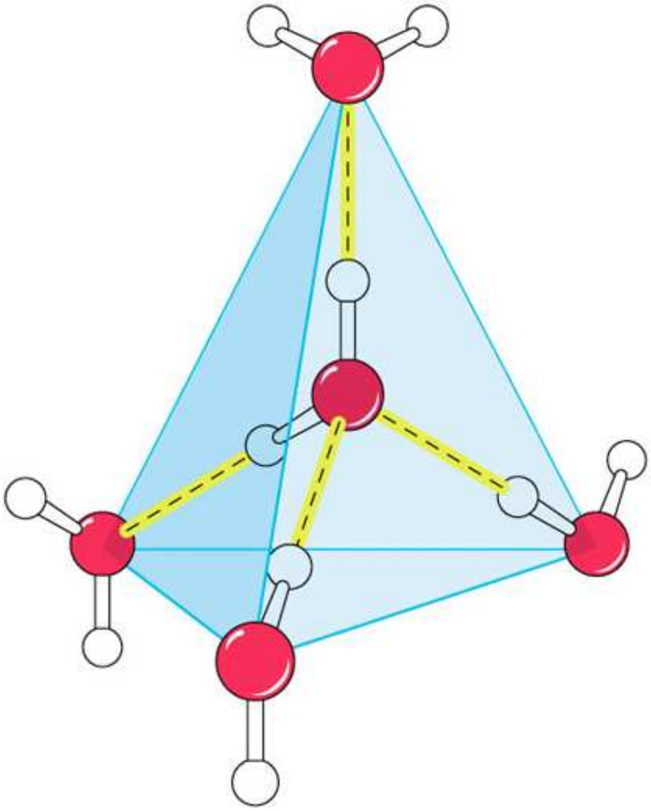

Figure 17.3: Hydrogen bonding by a water molecule. A water molecule can form up to four hydrogen bonds simultaneously. The oxygen atom of a water molecule is the hydrogen bond acceptor for two hydrogen atoms. Each O-H group serves as a hydrogen bond donor. The tetrahedral structure of the water hydrogen bonds is a consequence of the *sp*3 hybridization of the oxygen's electrons. The two hydrogen bonds between the oxygen and the hydrogen atoms on another water molecule utilize the two partly-negative pairs of unbonded electrons on oxygen. Reproduced from *Principles of Biochemistry* by H. ROBERT HORTON (editor), 3rd Ed., Prentice Hall, New York, 2001.

density decreases as one would expect from a "normal" liquid.

The increase of water density between 0-4^0C explains why freshwater lakes do not freeze over during winter. When water temperature falls to below 4^0C, the warm denser water sinks to the bottom, and the colder water freezes first. In addition, the less-dense ice floats on top of the water. The top layer of ice further insulates the water beneath, and prevents freezing solid, except for very shallow bodies of water and harsh climates. In addition, because fresh water has a maximum density at 4^0C, both warmer and cooler water can overlay stably the 4^0C water layer, leading to stable stratification of lake water both in winter

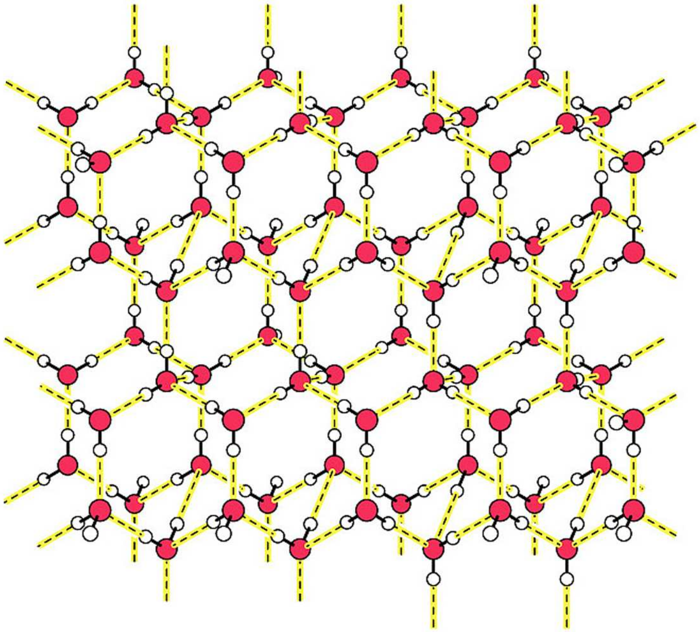

Figure 17.4: Molecular structure of ice. Water molecules in ice form an open hexagonal lattice in which every water molecule is hydrogen bonded to four others. The geometric regularity of these hydrogen bonds contributes to the strength of the ice crystal. The hydrogen bonding pattern of water is more irregular than that of ice. The absolute structure of liquid water has not been determined. All hydrogen bonds are satisfied in ice. The structure of ice at 0^0C is less dense than that of liquid water at 0^0C due to its open lattice. Reproduced from *Principles of Biochemistry* by H. Robert Horton (editor), 3rd Ed., Prentice Hall, New York, 2001.

and summer. Seawater does not behave like fresh water. Because of the high salt content, the density of seawater only decreases with increasing temperature.

Water expansion upon freezing drives the physical weathering of rocks (mechanical rock breakdown without chemical reactions). Repeated freezing and thawing is quite efficient in shattering rock, as evidenced by the rubble that covers high mountains, **Figure 17.7**.

17.6 Water Melting and Boiling Points

Compared with hydrides of the heavier members of the oxygen group (Sulfur S, Selenium Se, and Tellurium Te), water has an extraordinarily high melting and freezing points, see **Figure 17.8**. Not surprisingly, a number of substances having considerably higher molecular masses than water are gases at room temperature, e.g., the nonpolar CO_2 and SO_3. The only intermolecular forces acting

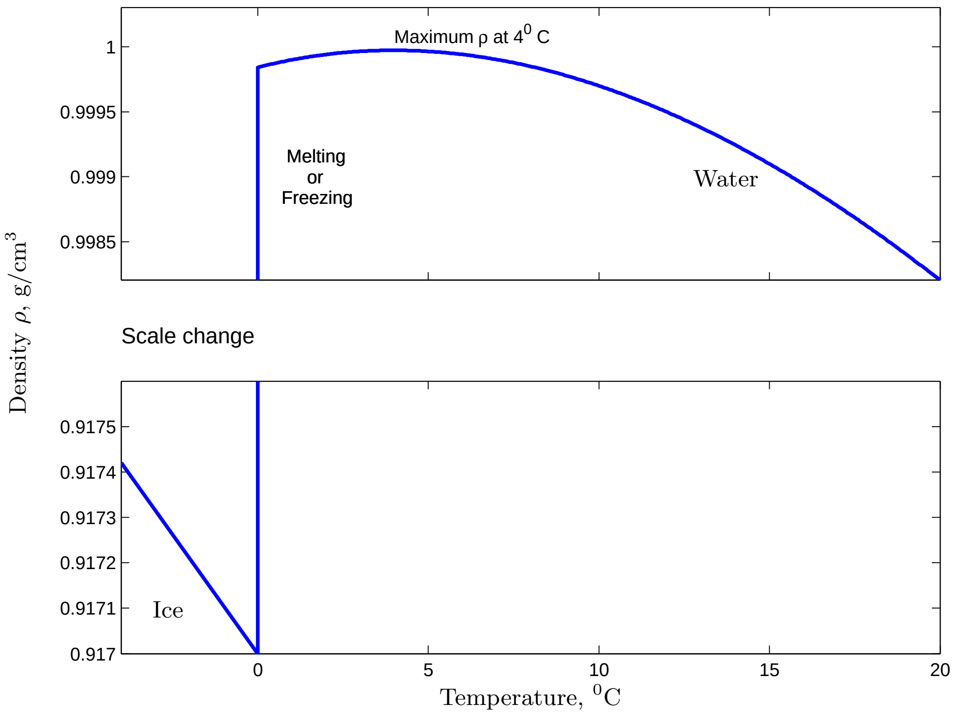

Figure 17.5: Density of water and ice as a function of temperature near the triple point. Note that water attains maximum density at 4^0 C, and is near the triple point has is less dense than water. Data from L. PAULING (Pauling, 1953).

in these gases are dispersion forces. Even some polar substances, such as SO_2, are gases at room temperature. In contrast, ethanol just like water remains liquid at room temperature because of strong hydrogen bonding among molecules.

The elevated meting and boiling points of water allow it to exist as liquid on the earth surface. The liquid water is necessary to all life.

17.7 Water Heat Capacity

The heat capacity of water, i.e., the amount of energy in kJ required to heat up a unit mass of water in kg by one Kelvin, is higher than that of any other liquid but ammonia **Figure 17.9**. Again, a lot of energy must be added to water to break hydrogen bonds among the water molecules without increasing their kinetic energy or temperature. Because of hydrogen bond breaking water can absorb a lot of heat for a small temperature change.

The temperatures of large standing bodies of water, lakes and the oceans, are relatively constant because of the high heat capacity of water. Thus water

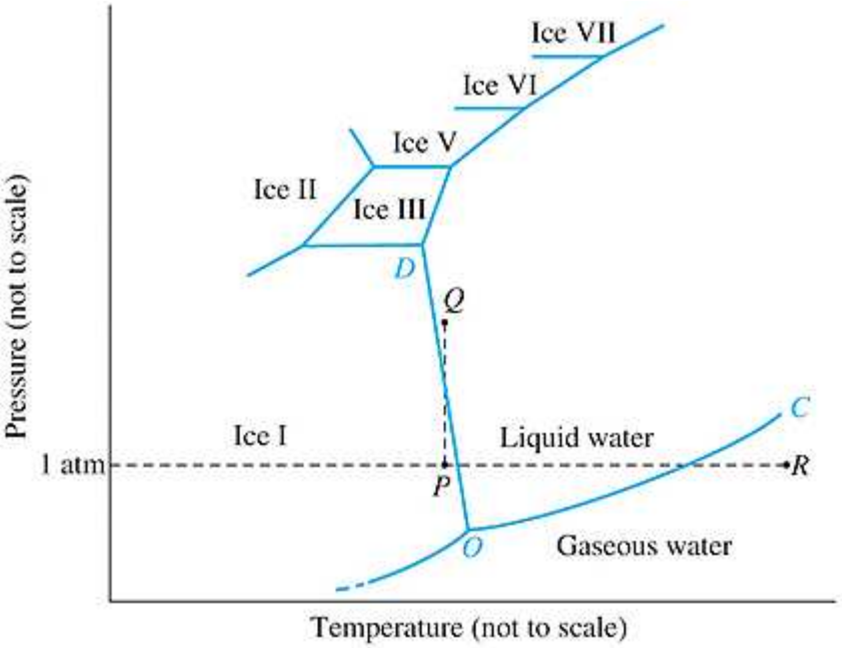

Figure 17.6: Phase equilibrium diagram for water. Point O, the triple point, is at 0.0098 ^{0}C and 4.58 mm Hg. The critical point, C, is at 374.1 ^{0}C and 218.2 atm. The negative slope of the fusion curve OD is exaggerated in this diagram, reproduced from (Hill and Petrucci, 1999).

serves as a thermal buffer protecting life from possibly devastating temperature fluctuations.

17.8 Water Latent Heats of Phase Change

The *specific latent heat of evaporation*, H_v, is the amount of energy required to convert a unit mass of liquid into vapor at the same temperature. For water $H_v = 540$ cal/g or 2260 J/g @ 100^{0}C and 2440 J/g @ 25^{0}C, is largest among liquids, **Figures 17.10 – 17.11**. The latent heat of evaporation is the energy required for the water molecule to escape the attractive forces of other molecules. This process requires breaking of hydrogen bonds, in addition to overcoming the usual van der WAALS forces. When water vapor condenses into liquid it releases the same amount of heat.

The water cycle on the earth depends on the heat of vaporization and condensation of water. Liquid water absorbs heat at one place on the earth and evaporates; the vapor is transported by the wind to a different place; and the vapor releases its latent heat when it is cooled and condenses. The high latent heat of evaporation of water allows for huge amounts of heat to be exchanged.

Figure 17.7: Physical rock weathering by the repeatedly freezing and thawing water. This photo was taken by T. W. Patzek on the way to the top of Mount Whitney, CA.

Evaporation dissipates about 1/4 of solar radiation, thus moderating and stabilizing the earth's surface temperature without changing ocean temperatures.

The specific latent heat of fusion is the amount of energy required to melt a unit mass of solid to liquid at the same temperature. The latent heat of fusion of water, 80 cal/g or 335 J/g, is the second largest[3] after hydrogen peroxide, H_2O_2, which also has plenty of hydrogen bonds. Thus, in the global water cycle, ice plays a proportionally large role in stabilizing the earth surface temperature.

17.9 Surface Tension

Regardless of the nature of intermolecular forces in a bulk liquid, molecules in the interior of the liquid are attracted to more neighbors, than those at the

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[3] We only look at substances that exist as liquids at room temperature.

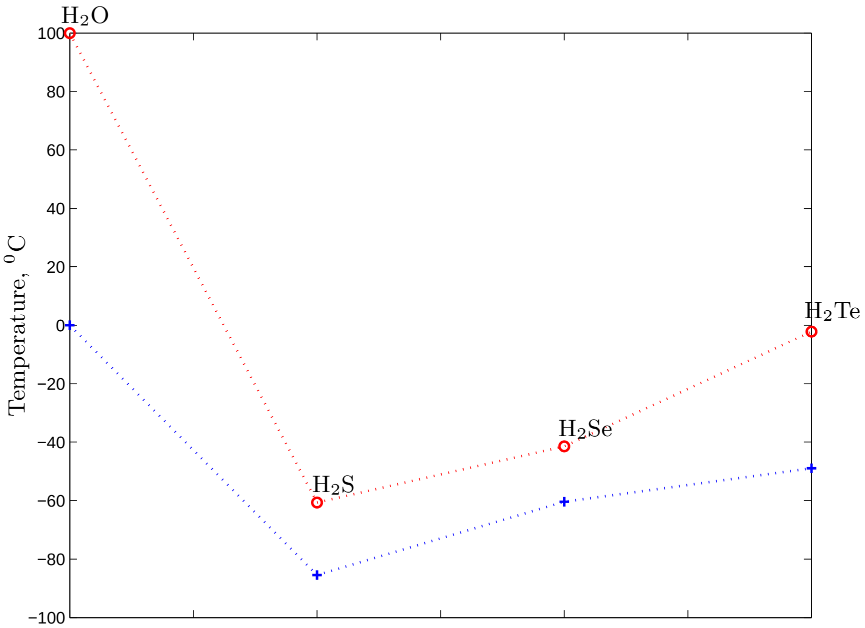


Figure 17.8: Melting (bottom) and boiling (top) temperatures for oxygen hydride homologs. The abnormally high values for water (also for NH_3: $T_m = -78^0$C, $T_b = -33^0$C) are caused by hydrogen bonds.

surface, **Figure 17.13**. Molecules crowd into the interior of the liquid to the greatest extent possible, and minimize the area of contact with other substances: the *interfacial area*. A sphere has the smallest possible ratio of surface-to-volume, hence free liquid drops are spherical. It takes energy to bring a liquid molecule to the surface. *Surface tension* is the amount of energy required to extend the liquid/gas interface by a unit area; hence its units are J/m^2 or N/m. For convenience, milliNewton/meter = mN/m = dyne/cm are commonly used.

Water has the second highest surface tension after mercury, **Figure 17.14**. Strong intermolecular hydrogen bonding makes it more difficult to extend the water/gas interface, than those of liquids dominated by dispersion forces alone.

A liquid/gas interface under tension behaves as a tight “skin” surrounding the bulk liquid. So, for example, a steel needle can rest on the water surface, **Figure 17.15**, even though it is 7.8 times denser than water and should sink.

When a drop of liquid spreads across a solid surface, we say that the liquid *wets the surface*. In addition to gravity, two other forces determine if a drop spread on a surface: the *adhesive* and *cohesive* forces. Adhesive forces are intermolecuar forces between unlike molecules, whereas cohesive forces are those between like molecules. If the adhesive forces between a liquid and solid are stronger than the cohesive forced in the liquid, the liquid will wet the surface.

Water on a leaf can either wet it or not if the leaf is coated with wax, see

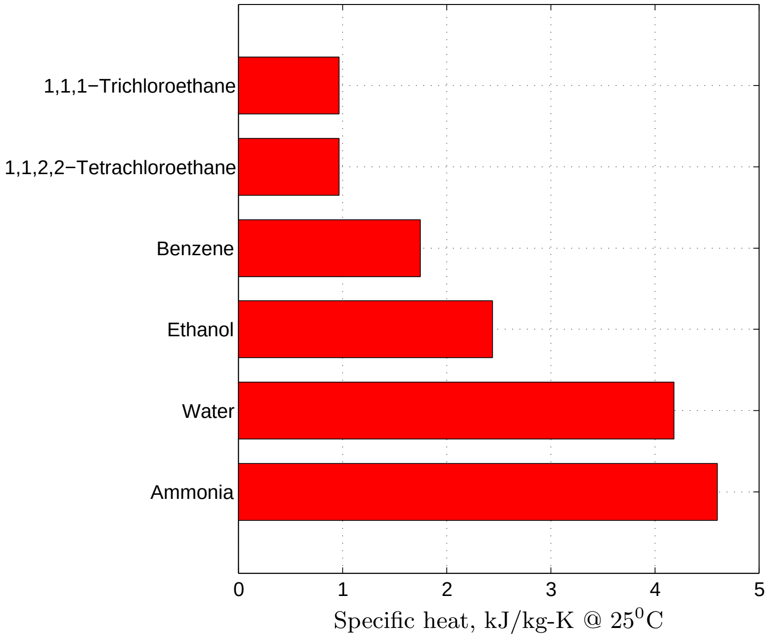


Figure 17.9: Specific heat capacities for liquids at 25^0C The specific heat of ammonia is shown at 0^0C (ammonia boils at -2^0C).

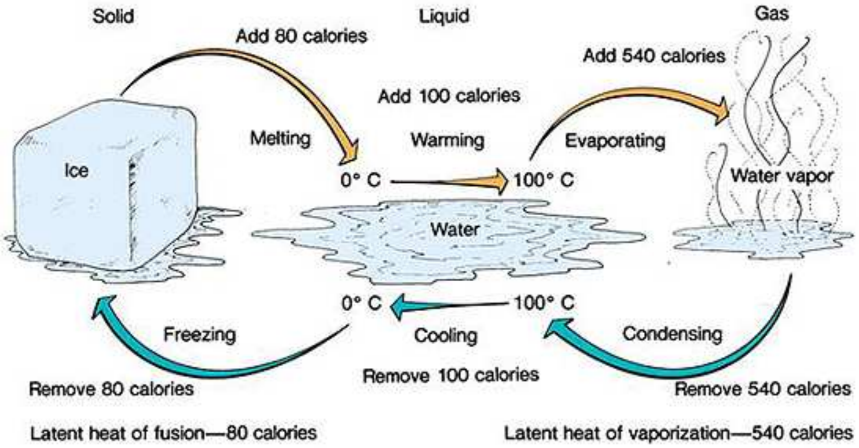


Figure 17.10: Phase changes for 1 gram of water at 1 atm. All heats are expressed in calories: 1 cal = 4.184 J = 3.965667×10^{-3} Btu.

Figure 17.16.

If a liquid wets the surface of a solid container, a glass capillary or a void in porous rock, the liquid is drawn up to some extent. The interface between the liquid and a gas above it forms a *concave* surface. In contrast, if the liquid does not wet the solid surface, the liquid/gas interface is *convex*, **Figure 17.17**.

As the liquid/air meniscus becomes more curved, the force pulling the concave meniscus up or the convex meniscus down becomes stronger. Therefore, water may rise considerably in a clean glass capillary of small diameter, **Figure 17.18**.

Capillarity and gravity govern the *immiscible flow* of air and water in the vadoze zone, the separate-phase contaminant (e.g., gasoline on water) migration in the subsurface, and the oil and gas flows in petroleum reservoirs. These subjects will be discussed later in the course.

17.10 Water Absorption Spectrum

The wavelength of visible light ranges from roughly 400 nm (blue) to 700 nm (red), see **Figure 17.19**. Water absorbs light vigorously on both ends of the visible light range, but especially in the near infrared range (Hale and Querry, 1973), **Figure 17.20**. This property of water is very important in keeping the earth surface relatively warm.

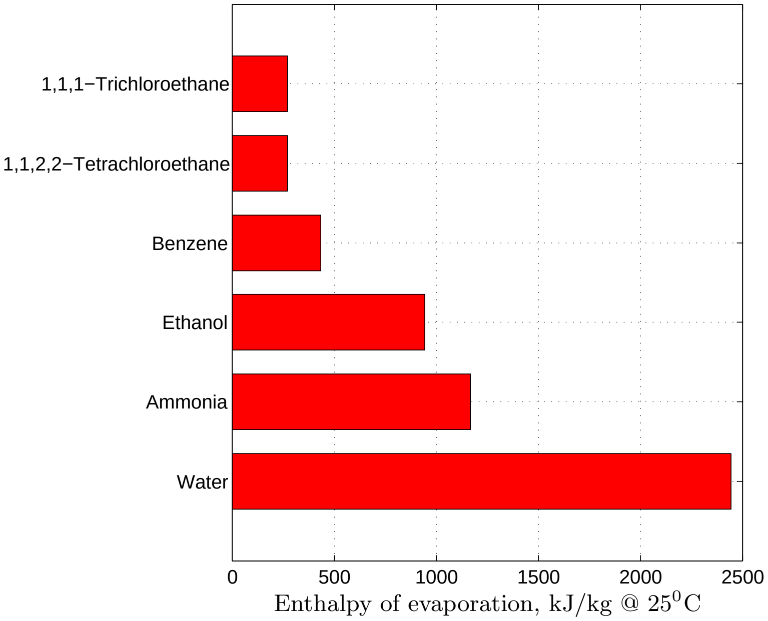


Figure 17.11: The enthalpy (latent heat) of evaporation at 25^{0}C.

17.11 Water as a Solvent

One of the most extraordinary properties of water is its ability to *dissolve* so many substances into *aqueous solutions*. A *solution* is a fluid phase consisting of two or more unlike molecules, which do not readily transform from one to another. A more prevalent solution component is called *solvent*, and the other components are *solutes*. For example, air is a *gaseous solution* of nitrogen, oxygen, carbon dioxide, noble gases etc.; soda water is a *liquid solution* of water and carbon dioxide; and bronze is a *solid solution* of 97% copper, 2.5% zinc and 0.5% tin. We defined a substance as *insoluble* in water if its solubility is much less than 1 g in 100 ml, and we define is as *soluble* otherwise. A substance whose solubility is about 1 g per 100 ml is termed *weakly soluble*.

Ocean water consists of thousands of components: metallic and nonmetallic ions, complex organic ions, and many organic substances. In this solution life began. With time, many organisms encapsulated their own aqueous solutions inside them, and left the oceans. Humans consists mostly of aqueous solutions in our tissues and blood.

The *dielectric constant* of water indicates how well it dissolves salts. This parameter measures how much water reduces the attraction between oppositely charged ions. Water is highly polar, see Section 17.4.1, has the dielectric constant equal to 80 (Pauling, 1953), and reduces the ionic attraction forces by this

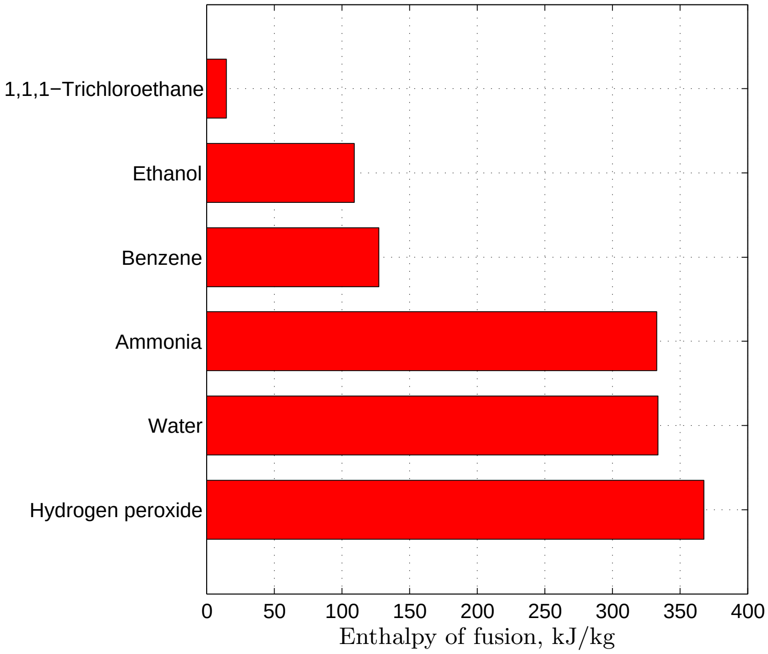


Figure 17.12: The enthalpy (latent heat) of fusion at normal melting temperatures.

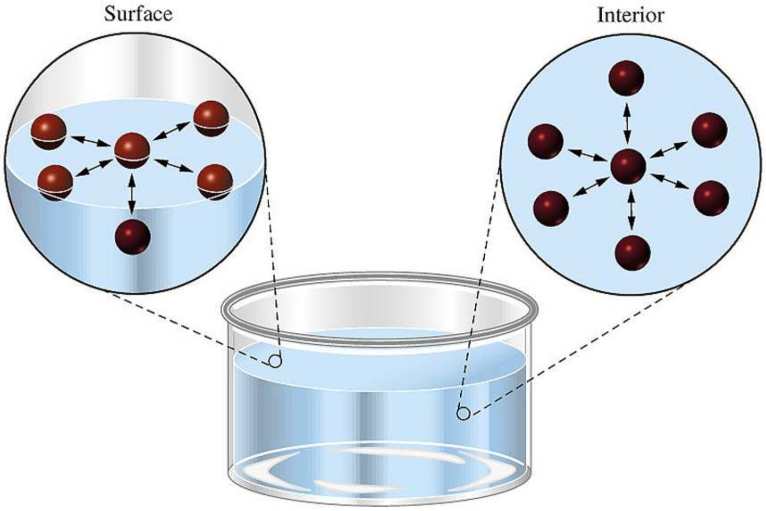


Figure 17.13: Molecules at the interface between a liquid and gas are attracted only by other liquid molecules at and below the interface. Molecules in the interior of a liquid experience forces from close-by molecules in all directions. Reproduced from (Hill and Petrucci, 1999).

factor.

17.11.1 Solubility of Salts and Hydroxides

Most ionic substances dissolve in water by forming hydrated ions, **Figure 17.21**. Water molecules surround each ion in solution and screen the interionic interactions. These hydration forces may be so strong that water molecules continue to accompany ions after precipitation, e.g., in gypsum $CaSO_4 \cdot 2H_2O$.

The water solubility of key inorganic substances is as follows:

- All *nitrates* are soluble, e.g., KNO_3.
- All *chlorides* (e.g., NaCl), *bromides* (e.g., $CaBr_2$) and *iodides* (e.g., KI) are soluble, with the exception of those of silver (Ag), mercury (Hg), and lead (Pb^+).
- All *sulfates* are soluble, except for $BaSO_4$, $SrSO_4$ and $PbSO_4$. $CaSO_4$, Ag_2SO_4 and Hg_2SO_4 are weakly soluble.
- All *hydroxides*, except for the alkali metal hydroxides, are *insoluble*.
- All *carbonates* (e.g., $CaCO_3$) and *phosphates* (e.g., $Ba_2(PO_4)_3$) are insoluble, except for those derived from the alkali metals (e.g., Na_3PO_4).
- All *sulfides*, e.g., FeS, are insoluble, except for those derived from the alkali metals (e.g., Na_2S), and the alkaline earth metals.

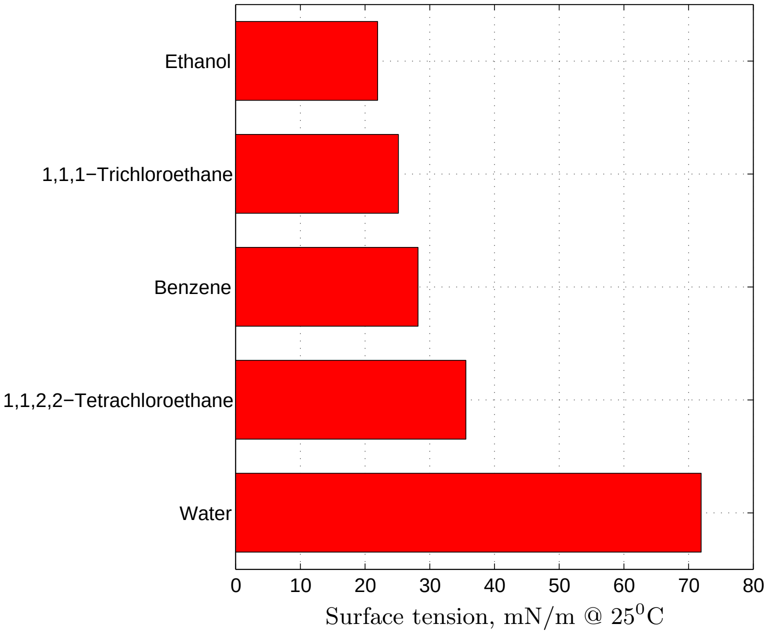


Figure 17.14: Surface tensions for liquids at 25^0C. Mercury (Hg) has the highest surface tension of 485.5 mN/m.

17.11.2 Solubility of Polar Substances

In addition to ionic salts, water dissolves polar molecules, such as sugars, alcohols, amino acids, ammonia, resins etc.. The ability of water to dissolve polar organic molecules is essential to life, and its ability to dissolve ammonia provides nitrogen to plants.

17.12 Problems

1. Using the data in Table 17.2, assuming the water density to be ≈ 1 kg/L, and rescaling the volume of all water on the Earth to 16 gallons (1 gal = 3.785 L), show that
    (a) All fresh water volume is equal to about 5 cups (1 US cup = 8 oz, 16 oz of water = 1 lbm = 0.454 kg).
    (b) All fresh water $0-750$ m, all water in lakes and rivers, and all water in the atmosphere and biosphere is less than 1 cup. (How much exactly?)
    (c) Calculate what fraction of the cup is there in all rivers in lakes.
    (d) Estimate how much water in shallow aquifers is available for human consumption.

Figure 17.15: The surface tension of water supports a steel needle, which otherwise would sink immediately. Reproduced from (Hill and Petrucci, 1999).

Figure 17.16: Strong adhesive forces cause a film of water to spread on a clean glass surface (left). When glass is coated with oil (right), adhesive forces between oil and water cannot overcome the cohesive forces in water and water does not wet the altered glass surface. Reproduced from (Hill and Petrucci, 1999).

(e) Guess how much water in rivers, lakes, and shallow aquifers is now contaminated or inaccessible.

(f) Estimate what fraction of a single cup is available for human consumption. Express your results in drops (1 drop = 0.000217 cup [US]).

(g) Do a Web search and estimate what fraction of fresh water is used for agriculture in the US.

Carefully show your steps, assumptions, and data sources.

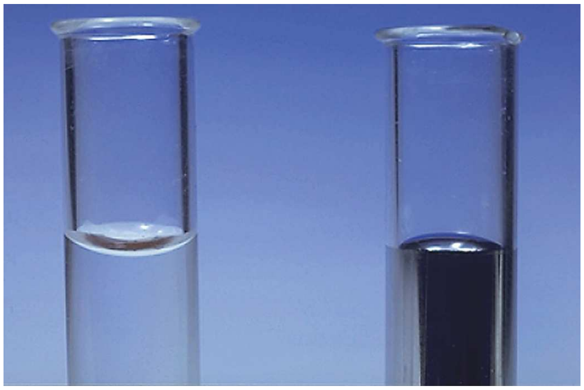


Figure 17.17: Water wets glass and forms a concave water/air interface (left). Mercury does not wet glass, and forms a convex mercury/air interface (right). Reproduced from (Hill and Petrucci, 1999).

2. Explain briefly what would it take for the needle in Figure 17.15 to sink.
3. Using physical arguments, explain why a thick body of water is blue?
4. Summarize the influence of hydrogen bonds on the properties of water.
5. If 23% of the solar energy absorbed at the earth's surface (0.5 cal/cm^2-min) is used to evaporate water, estimate how much water per minute can be evaporated on average over the entire surface of our planet.

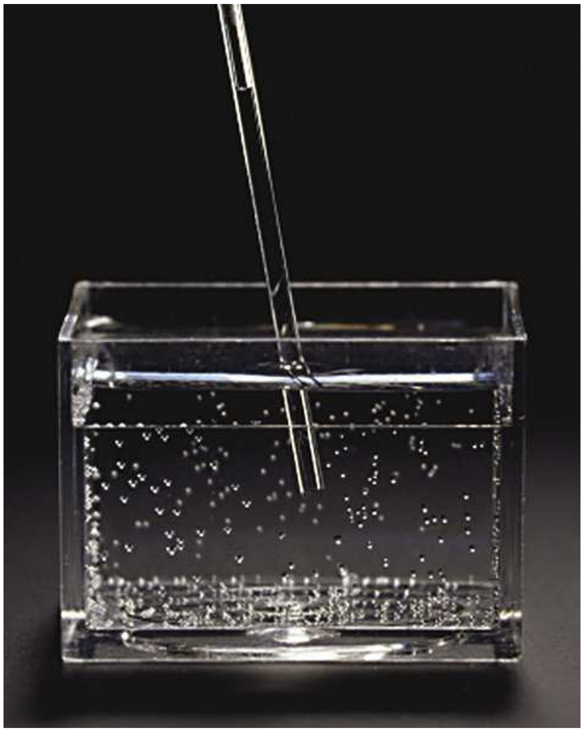
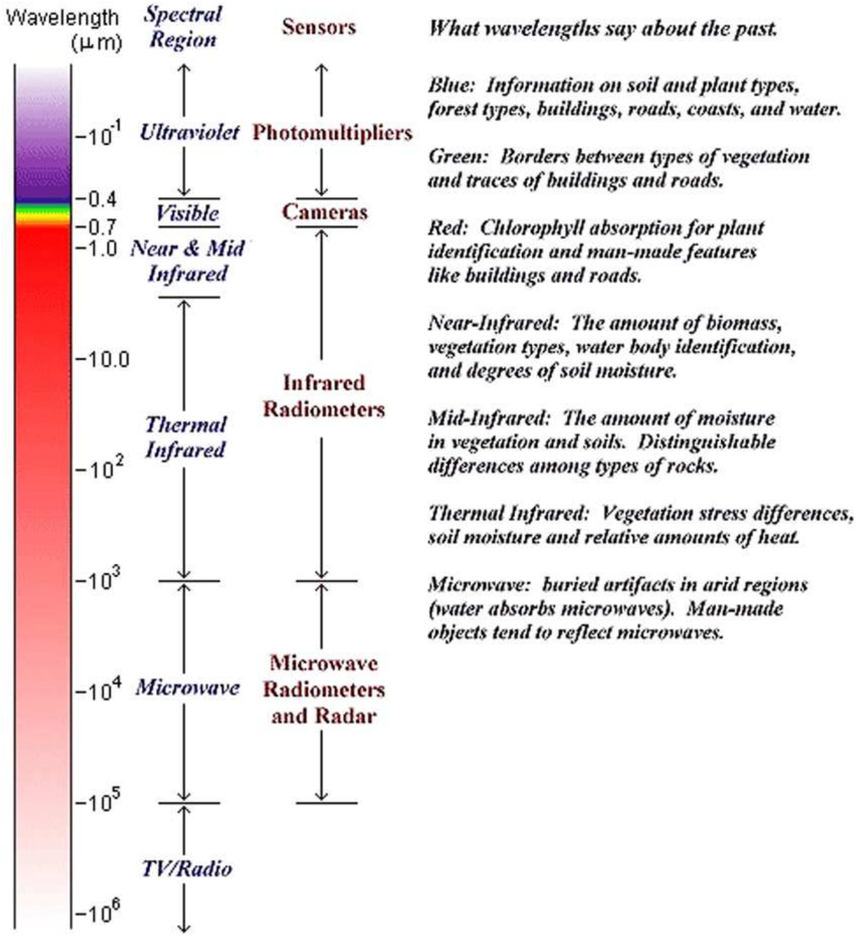


Figure 17.18: The spread of a film of water up the glass capillary wall produces a pressure drop across the water/air meniscus. This pressure drop is called the *capillary pressure*. Atmospheric pressure pushes a column of water up, until its weight acting down balances exactly the capillary force acting up. Reproduced from (Hill and Petrucci, 1999).



What wavelengths say about the past.

Blue: Information on soil and plant types, forest types, buildings, roads, coasts, and water.

Green: Borders between types of vegetation and traces of buildings and roads.

Red: Chlorophyll absorption for plant identification and man-made features like buildings and roads.

Near-Infrared: The amount of biomass, vegetation types, water body identification, and degrees of soil moisture.

Mid-Infrared: The amount of moisture in vegetation and soils. Distinguishable differences among types of rocks.

Thermal Infrared: Vegetation stress differences, soil moisture and relative amounts of heat.

Microwave: buried artifacts in arid regions (water absorbs microwaves). Man-made objects tend to reflect microwaves.

Figure 17.19: Electromagnetic wave spectrum. The different wavelengths are used in satellite imaging.

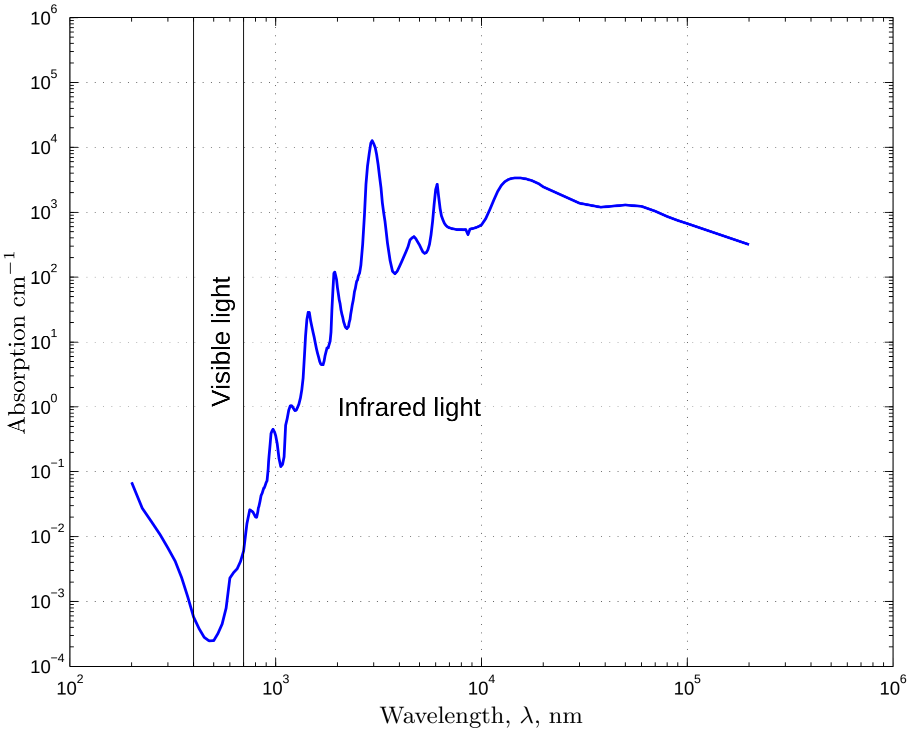


Figure 17.20: Light absorption by water (Hale and Querry, 1973). For a thorough compendium of water absorption data, go to omlc.ogi.edu/spectra/water/-abs/index.html.

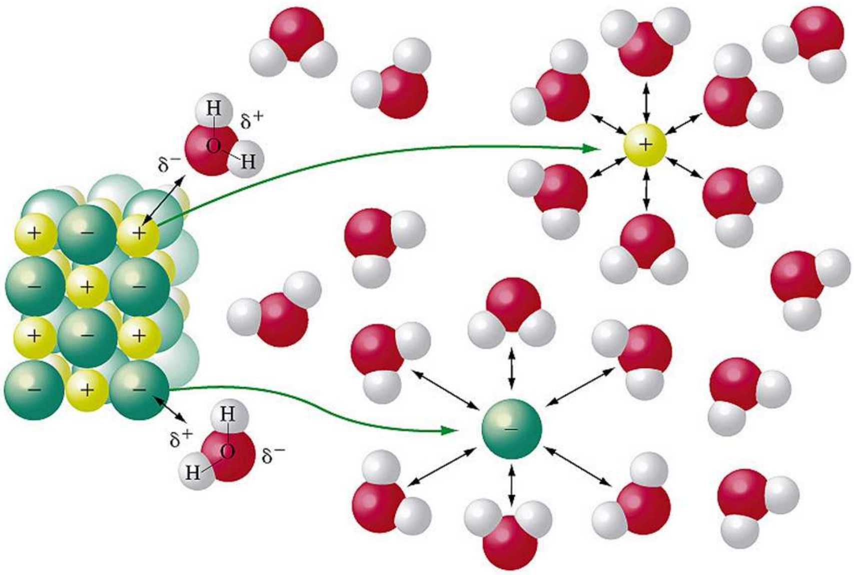


Figure 17.21: An ionic crystal dissolving in water. Clustering of water dipoles around the surface of the ionic crystal and the formation of hydrated ions in solution are the key factors in the dissolving process. Reproduced from (Petrucci et al., 2001).

Chapter 18

Photosynthetic Efficiency of Plants

In thermodynamics, you have to get to the point where you understand what any damn fool means no matter what he says

— PROF. A. R. GORDON
(*Lecture Notes*, Department of Chemistry, University of Toronto)

18.1 What Are We Going to Learn?

Your are going to learn about the maximum and achievable fractions of solar energy flux captured by plants and converted into biomass.

18.2 Why Is It Important?

In order to compare plant biomass systems with other systems that sequester solar energy – such as photovoltaic cells, passive solar systems, wind turbines, wave-energy systems, ocean thermal energy conversion (OTEC) systems, etc. – we must know the fraction of solar energy converted to biomass.

18.3 Definitions

Definition 21 **Photosynthetically Active Radiation**, often abbreviated as PAR, designates the wave lengths of solar light from 400 to 700 nanometers used by plants in the process of photosynthesis. This spectral region falls in the range of light visible to the human eye. Photons at shorter wavelengths tend to be so energetic that they can damage cells and tissues; fortunately they are mostly filtered out by the ozone layer in the stratosphere. Photons at longer wavelengths do not have enough energy to allow photosynthesis to proceed. Through almost 3 billion years of evolution, plants have developed capacity to scatter these photons away, hence the very high reflectance and transmittance of live green leaves, and light filtered through dense plant canopies. □

18.4 Background

It is often pointed out that agriculture converts less than 1% of the energy of sunlight falling on fields to biomass during one calendar[1] year. From such observations, it is inferred that there are remarkable opportunities for the improvement of agriculture. However, as I will show here, the real efficiency of converting light energy to biomass is quite high, if this efficiency is understood as the ratio of actual conversion to the maximum possible conversion.

18.5 Asymptotic Efficiency of Photosynthesis

To calculate the highest possible efficiency of photosynthesis, we will calculate the fraction of the solar energy flux at the Earth surface that could in principle be sequestered by plants if light were the sole limiting factor. Both water and water-dissolved nutrients are present in quantities sufficient to satisfy all plant

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[1] Average growth season of corn and soybean is ~120 days. Therefore, conversion of the sequestered corn or soybean biomass to one calendar year is achieved by the multiplication by $120/365 = 0.33$.

growth demands, and we disregard energy costs of respiration that keeps plants alive. The analysis in this section is asymptotic in its nature and holds only for very low light intensities. In other words, the real life efficiency of photosynthesis by plants in a field will be perhaps 10 times lower than the upper bound obtained here.

The discussion in this section follows along the line of reasoning developed in *Photosynthesis, Productivity, and Yield* by Norman E. Good and Duncan H. Bell in (Good and Bell, 1980).

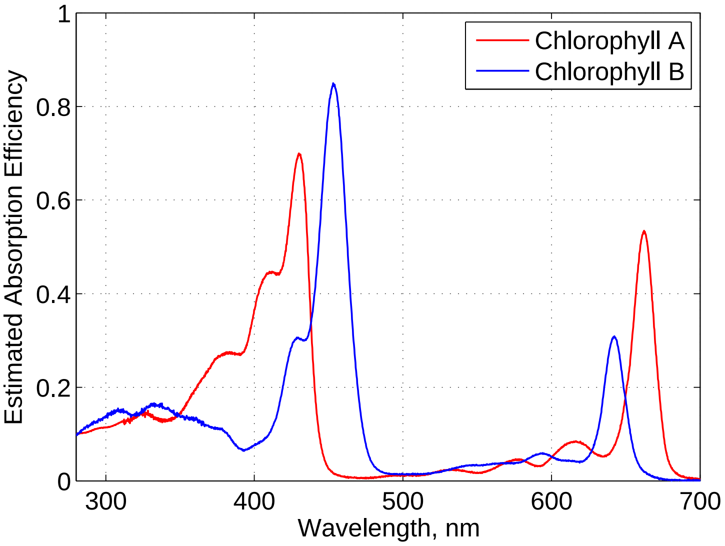

Figure 18.1: These experimental light extinction spectra of Chlorophyll A and B in diethyl ether were measured by Junzhong Li (1997). These sepctra have been scaled to their maximum absorption coefficients reported in the photosynthesis literature, e.g., Taiz & Zeiger (1998).

18.5.1 Light Absorption

Photosynthesis starts by the absorption of quanta of visible light by pigments present in plant leaves. These pigments are mostly Chlorophyll A and B (and C) and the carotenoids[2].

Light Absorption Spectra by Chlorophyll A and B

Chlorophyll A and B absorb blue and red light quanta, and reflect the rest of the incident light (this is why plant leaves are green). The molar extinction coefficients of Chlorophyll A and B dissolved in diethyl ether are posted

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[2] Alpha-carotene, beta-carotene, cryptoxanthol, luteol, and zeaxanthol, see (Zscheile et al., 1942).

at http://omlc.ogi.edu/spectra/PhotochemCAD/html/index.html. Chlorophyll A in diethyl ether has a short-wavelength peak molar extinction coefficient of 111700 $\mathsf{mol}^{-1}\mathsf{cm}^{-1}$ at 428 nm (Strain et al., 1963). Chlorophyll B has a short-wavelength peak molar extinction coefficient of 159100 $\mathsf{mol}^{-1}\mathsf{cm}^{-1}$ at 436 nm (Vernon and Seely, 1966). The wavelengths of the peaks depend on the solvent and are different for methanol. Others have reported the absorption maxima of Chlorophyll A (in methanol?) at $\lambda = 430$ and $\lambda = 662$ nm, and those of Chlorophyll B at $\lambda = 453$ and $\lambda = 642$ nm. The two groups of results are reconciled with a right-shift by 2.25 nm of the Chlorophyll A spectrum in diethyl ether, and by 17.25 nm for Chlorophyll B. In **Figure 18.1**, both experimental curves have been shifted to reflect the most commonly reported values.

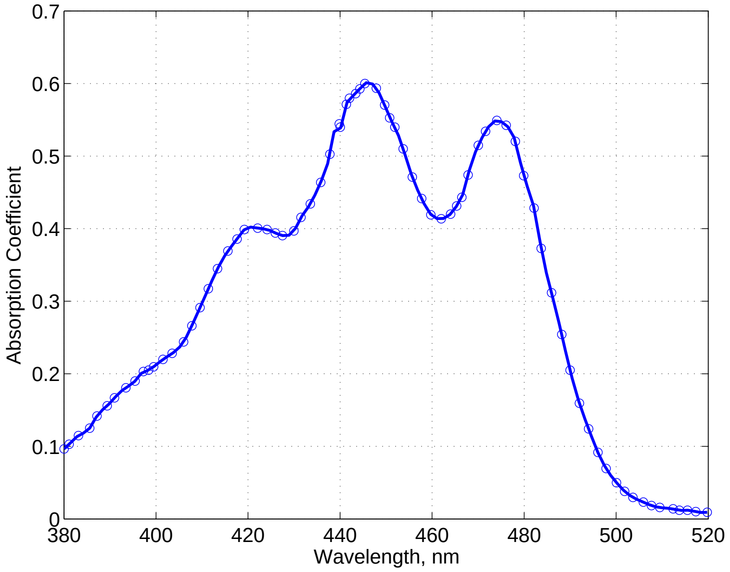


Figure 18.2: This absorption spectrum of α-carotene in hexane was measured by F. P. Zscheile et al. (1942). It has been scaled to the maximum absorption coefficient reported in literature, e.g., Raven et al. (1992).

Absorption Spectrum by α-Carotene

Light absorption spectra of carotenoids were measured with great care by F. P. Zscheile et al. (1942). An example of the α-carotene absorption spectrum, scaled to the commonly reported values of the peak absorption coefficient (Raven et al., 1992), are shown in **Figure 18.2**. Note that α-carotene absorbs light at the short wavelengths, with the peak absorption at 446 nm (blue light).

Photosynthetic Action by the Leaves of a Plant

Light quanta are delivered directly and indirectly to the photosynthetically active pigments mentioned above. Each quantum, if absorbed by an appropriate pigment, is capable of exciting one chlorophyll molecule, which then can give up an electron to be used in the reduction of carbon dioxide. Next, the electron-depleted chlorophyll molecule takes up another electron that comes originally from water, and the chlorophyll is restored to its original condition. When enough electrons have thus been transferred via chlorophyll excitations from water to carbon dioxide, the water is converted to oxygen and the carbon dioxide is converted into glucose, and then carbohydrates (starch) and fats.

Four electrons from water are required to reduce one molecule of carbon dioxide to carbohydrate. Therefore, one might assume that four quanta of light would suffice, since ordinarily one quantum moves one electron. But this is not the case. The electron transport pathways in photosynthesis are such that *two* quanta of light are required to move one electron along Photosystems I and II, see, e.g., (Taiz and Zeiger, 1998). In practice, a plant needs even more electrons $(10-13)$ to finally reduce one molecule of carbon dioxide (Balegh and Biddulph, 1970).

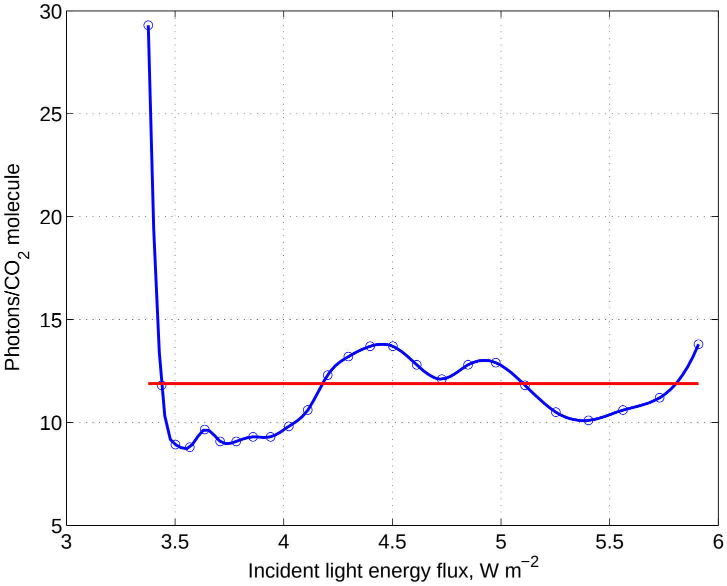


Figure 18.3: The average photon efficiency of photosynthesis in a bean plant leaf is 12 (11.88). This photon efficiency was measured at very low intensity of incident light. At these experimental conditions photon availability is the limiting factor.

The average number of photons required to reduce one molecule of CO_2, 12 $h\nu/CO_2$, in **Figure 18.3** is close to those for unicellular organisms. Quantum numbers determined for leaves of higher plants are in good agreement with that shown in Figure 18.3. BRIGGS (as cited by KOK (1959)), using gas analysis to measure the oxygen exchange of *Phaseolus*, *Sambucus*, and elm leaves, observed values approaching 11 $h\nu/\text{CO}_2$. GABRIELSEN (as cited by GAFFRON (1963)), using gas analysis to measure CO_2 exchange with leaves of several higher plants, found quantum numbers between 10 and 12 $h\nu/\text{CO}_2$. WASSINK (as also cited by KOK (1959)), using manometric techniques to determine quantum numbers for several horticultural plants, reported values between 11 and 13 $h\nu/\text{CO}_2$.

To calculate the maximum theoretical efficiency of photosynthesis, we will make the following three assumptions:

1. One mole of carbon dioxide reduced to glucose stores about 472.2 kJ mol^{-1} CO_2, see **Problem 2**.
2. Eight photons per molecule of the photosynthetically-reduced CO_2 is the theoretical minimum. The measured photon numbers are 10-13 $h\nu/\text{CO}_2$.
3. The average wavelength of photosynthetically-active solar light (AM1.5) is 550 nm, see **Problem 1**, and corresponding energy of 1 mole of average photons is 217 kJ mol^{-1}

Therefore, the *maximum intrinsic* efficiency of photosynthesis is

$$\eta_{\text{PSI/II}} = \frac{472.2 \text{ kJ mol}^{-1} \text{ reduced CO}_2}{8 \times 217 \text{ kJ mol}^{-1} \text{ absorbed PAR photons}} = 0.27 \tag{18.1}$$

where PSI/II denotes the intrinsic efficiency of Photosystems I and II.

Thus, at most 27 percent of the absorbed PAR becomes biomass. With 12 photons per molecule of CO_2, this efficiency is only 18%.

PAR and Absorption

Now I will ask the following two questions:

- What fraction of the photons in incident sunlight is in the photosynthetically-active range (PAR)? and
- What fraction of the photosynthetically-active photons is actually absorbed by the plants, as opposed to being reflected, transmitted and dissipated to heat?

The product of these two fractions of all sunlight is used with at most 27% efficiency to reduce CO_2.

It turns out, that the fraction of photons with wavelengths between 400 and 700 nm in the standard AM1.5 atmosphere is 43%, see **Problem 3** and also (Yocum et al., 1960). Finally, it is inevitable that some of these useful photons will be reflected and transmitted. If all the visible photons were absorbed, the fields would look perfectly black, not green, brown, etc., see **Figure 18.4**.

Figure 18.4: A corn field on a sunny day. Notice light transmission through the leaves, and multiple reflections.

Also, there would be total darkness in the shade of the crop. Reflectivity and transmission vary from crop to crop and with the stage of development of the crop (Yocum et al., 1960). But plants adjust their leaf positions so that a field crowded with plants absorbs solar energy as efficiently as a single plant leaf, see **Figure 18.5**.

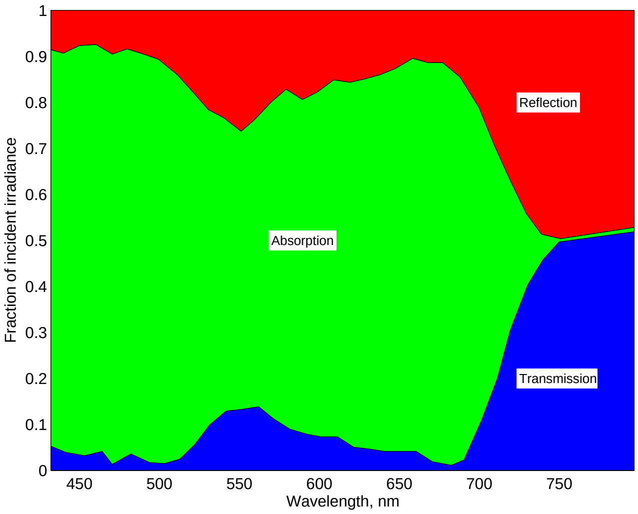
Observed reflections of PAR from fields range from 5 to 10%, see Figure 18.5. If we take 5% to be the minimum reflection and allow another 5% for transmission through the crop canopy (another minimum according to Figure 18.5), it follows that only $43 - 10 \times 0.43 = 39\%$ of the total incident solar light can be used for photosynthesis, even if the entire field is packed with vegetation. This estimate is in excellent agreement with the measured average quantum yield of 26 herbs (38%) under carefully controlled conditions (Inada, 1976), see **Figure 18.6** .

Taking the measured quantum yield as an upper limit, efficiency of photon absorption by a canopy is at most:

$$\eta_{\text{absorption}} = 0.38 \, \frac{\textsf{flux of PAR photons absorbed by leaves}}{\textsf{flux of all photons in AM1.5 irradiance}} \qquad (18.2)$$

An Upper Limit of Photosynthetic Efficiency

The overall maximum efficiency of photosynthesis is the product of efficiencies (18.1) and (18.2):



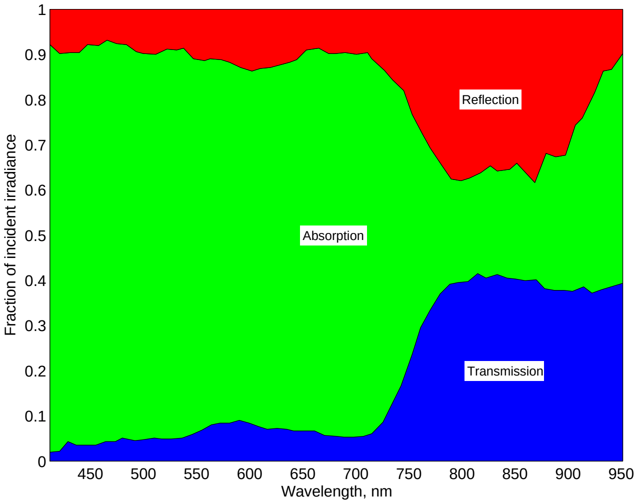


Figure 18.5: **Top:** Transmission, reflection and absorption spectra of a corn leaf from 400 to 800 nanometers, as determined in an Ulbright sphere (Yocum et al., 1964). **Bottom:** The same spectra from 400 to 950 nm for a corn field on a clear day (Yocum et al., 1964). Note that all leaves of corn plants in the field have *better* irradiance absorption characteristics than a single corn leaf. Because of the multiple reflections and fractal character of leaf positions and orientations, the corn field and one leaf are almost self-similar.

$$\eta_{\text{photosynthesis}} = 0.27 \times 0.38 = 0.10\,\frac{\textsf{Glucose power flux}}{\textsf{Incident AM1.5 irradiance}} \tag{18.3}$$

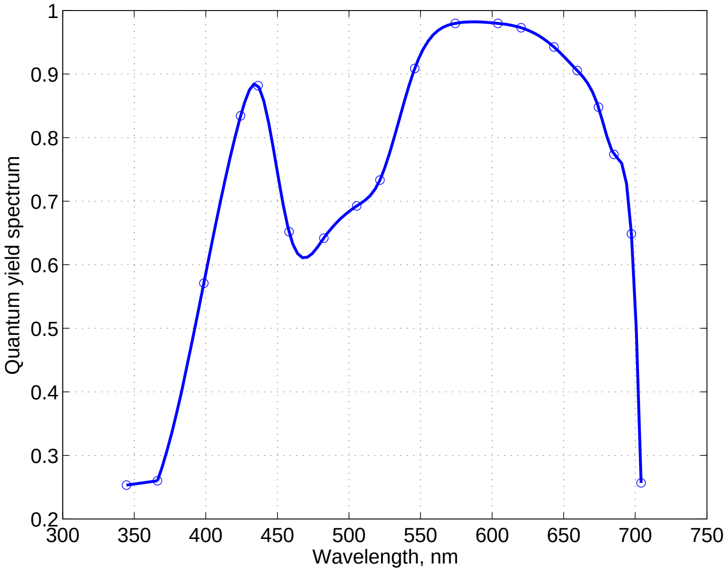


Figure 18.6: Average quantum yield spectrum of 26 herbaceous plants. When this spectrum is used to weigh energy in the AM1.5 solar spectrum, 38% of the incident solar light is used for photosynthesis. Source: Figure 4c in Inada (1976).

in a field or forest covered with dense vegetation. A likely practical upper bound photosynthesis efficiency is $0.18 \times 0.39 = 0.07$ of solar irradiance at low-photon density.

It is important to understand that *nothing whatsoever* can be done about Eq. (18.3), the upper limit of photosynthetic efficiency, until Nature develops an entirely different mechanism of photosynthesis. This new photosynthesis process would have to cope differently with high light intensities, concentrating CO_2 in the leaves, water management, heat dissipation, and a plethora of other irreversible effects. The development of this new process is highly unlikely. Starting with cyanobacteria and algae, Nature has spent almost 3 billion years perfecting photosynthesis as we know it today.

It is also important to realize that the high efficiency above disregards the respiration costs, light saturation effects, water and nutrient limitations, and other irreversibilities. In fact, the photosynthetic efficiency in Eq. (18.3) can only be approached at very low light intensities and low rates of photosynthesis, where the correction for respiration becomes large.

It is currently fashionable to equate the complex ecosphere with the simplistic technosphere. Synthetic biology is offering the false promise of instantaneous improvements on the eons of evolution. Quite ordinary men, who think that the scientific method has somehow transfigured them into little godlings, now claim that new life and better photosynthesis will be "manufactured" in their laboratories just like microprocessors, and promptly released into the wild. The hubris[3] of these men exceeds almost anything claimed by science heretofore. But the misinformed and uneducated society, and the desperate, greedy corporations praise this hubris and reward it with unlimited funding and high scientific awards. As in a Greek tragedy, the outcome is known and inevitable, but the heros do not know it.

18.6 Real-life Efficiency of Photosynthesis

The question I pose now is this: What fraction of the incoming solar energy can a field full of living plants convert into chemical energy of plant grain, stems, leaves, and roots?

To answer this question, I will use eddy-covariance estimates of the sequestered CO_2 flux over a corn field in Kansas on a beautiful, sunny day of August 15, 1961. We will then extrapolate the plant mass produced during that day to 120 days of average sun irradiation, and plentiful water and nutrients. As we will see, the newer field experiments in 1998-2002 (Lindquist et al., 2005), have reached 60-80% of our projected efficiency, but at a cost of heroic measures: continuous irrigation and high nutrient amounts, $225 - 298$ kg N ha^{-1}, 45 kg P ha^{-1}, 85 kg K ha^{-1}, and 8 kg Zn ha^{-1}, as well as field chemicals, chlorpyrifos, 1 kg a.i. ha^{-1}; alachlor, 1.4 kg a.i. ha^{-1}; and atrazine, 0.85 kg a.i. ha^{-1} (a.i. = active ingredient).

The CO_2 intake for the Kansas corn field, measured by LEMON (1965) and by MUSGRAVE and MOSS (1961), see **Figure 18.7**, has been translated into the sequestered starch energy flux using the results of Problem 2 and is shown in **Figure 18.8**.

We want calculate the average corn plant efficiency for an average 12-hour day. At sunrise and sunset the solar irradiance is zero, and it is at $I_{\max} = 1100$ Wm^{-2} at noon, see **Figure 18.9**. Solar irradiance varies as $\sin(\pi x/T)$, where $x = 0$ corresponds to sunrise and $x = T$ corresponds to sunset, say $T = 12$ hrs. To find the area of the tails, we should integrate from 0 to $\arcsin(600/1100) = \arcsin(0.55)$ and multiply the result by two. The central area is the difference between the integral from 0 to T and the area of the tails. Therefore, on a perfectly sunny summer day, with ample soil water, and ample soil nutrients,

---

[3] *Hubris* denotes overconfident pride and arrogance; it is often associated with a lack of knowledge, no interest in exploration of history, combined with a lack of humility. The remorseless goddess *Nemesis* in the Greek mythology was the spirit of divine retribution against those who succumb to hubris. Her name is related to the Greek word $\nu\epsilon\iota\mu\epsilon\iota\nu$, meaning "to give what is due".

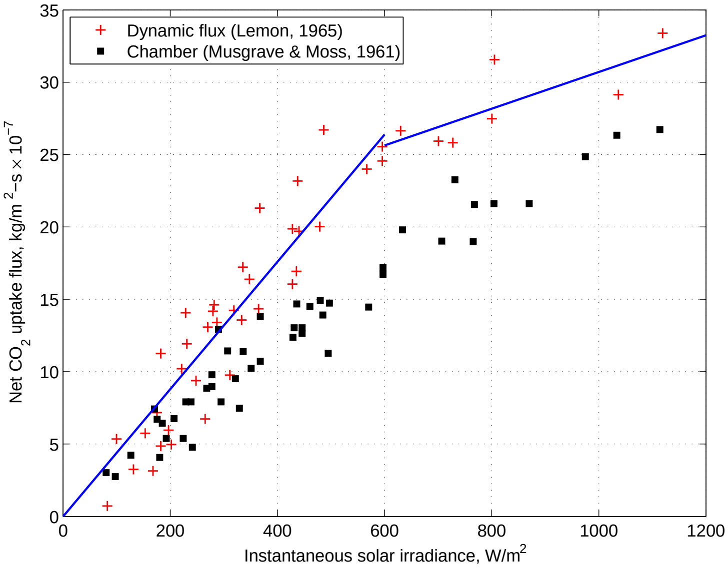


Figure 18.7: The net uptake of carbon dioxide by a corn field at various light intensities. The highest solar irradiance, $600 - 1100$ Wm^{-2}, corresponds to noon conditions on the sunny August 15, 1961. The low-irradiance regime slope slope $b_l = 0.044$, 95% confidence $b_{l,\min} = 0.043$ $b_{l,\max} = 0.047$. The high irradiance slope is $b_h = 0.013$, and the intercept is $a_h = 18.02$. The slope units are kg CO$_2$ $\times 10^{-7}$ J^{-1}. The intercept units are kg CO$_2$ $\times 10^{-7}$ m^{-2} s^{-1}. Adapted from the dynamic CO$_2$ flux data in LEMON (1965), Figure 8. The diamonds represent the data from a controlled chamber experiment by MUSGRAVE and MOSS (1961) on July 26, 1961.

the ideal efficiency of a maturing corn plant is

$$\begin{aligned}
&\text{Total irradiation in one day} = \frac{I_{\max} T}{\pi} \int_0^{\pi} \sin(x)\, dx = \frac{2 I_{\max} T}{\pi} \\
&\eta = \frac{\text{Energy stored as glucose}}{\text{Total irradiation in one day}} = \frac{1}{2}\Bigg[2 b_l \int_0^{\arcsin(0.55)} \sin(x)\, dx + \qquad (18.4) \\
&b_h \int_{\arcsin(0.55)}^{\pi - \arcsin(0.55)} \sin(x)\, dx + \frac{a_h}{I_{\max}} (\pi - 2 \arcsin(0.55)) \Bigg]
\end{aligned}$$

From **Figure 18.8** it follows that in the morning and the evening (up to, or down from 600 Wm^{-2}), a corn field has energy efficiency of 0.05, and over the rest of the day this efficiency decreases to 0.02.

Now we assume after TRANSEAU (1926) that transpiration is $1/8 = 0.125$ of photosynthesis, and it is active 24 hours/day. Therefore, the overall net synthesis is $1.125 - 0.125 \times 2 = 0.875$ of the net synthesis shown in Figure 18.8. We also assume after WHITE et al. (White and Johnson, 2003) that corn grain

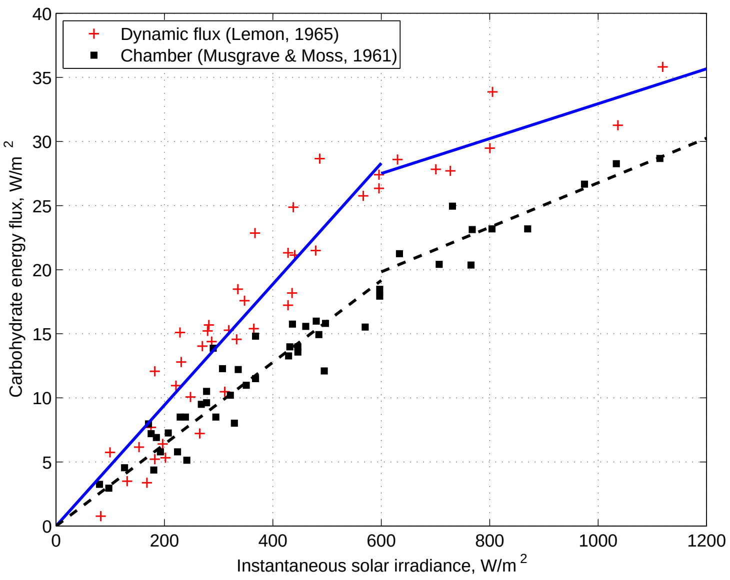


Figure 18.8: Carbohydrate (starch) buildup in a corn field at various light intensities. The highest solar irradiance, $600 - 1100$ Wm^{-2}, corresponded to cloudless noon conditions on August 16, 1961. The low-irradiance regime slope $b_l = 0.047$, 95% confidence $b_{l,\min} = 0.044$, $b_{l,\max} = 0.050$. The high-irradiance slope is $b_h = 0.014$, and the intercept is $a_h = 19.33$ Wm^{-2}. The slopes are dimensionless. The measured CO_2 fluxes in Figure 18.7 were converted to the starch energy flux using Problem 2. This conversion shows that corn sequesters as biomass energy about 5% of the solar irradiance in the morning and evening, and about 1.4% closer to noon. The data by MUSGRAVE and MOSS (1961) have different slopes. Their low-irradiance slope is $b_l = 0.032$, 95% confidence $b_{h,\min} = 0.030$, $b_{h,\max} = 0.034$. The high-irradiance slope $b_h = 0.017$, and the intercept is $a_h = 9.42$.

is 0.42 of the dry mass of mature corn plant, including roots. Finally, we assume that the average duration of corn growth season in Iowa is 120 days and the average irradiance is 254 Wm^{-2}, see **Figure 16.5** in Chapter 16.

With the average net glucose synthesis efficiencies listed in the caption of Figure 18.8, and the averaging procedure described in Eq. (18.4) and Figure 18.9, we obtain the following results:

- The irradiance-weighted corn plant efficiency is 0.037 (dynamic) and 0.028 (chamber).
- The net weighted corn plant efficiency at 12.5% respiration losses is 0.032 (dynamic), 0.025 (chamber).
- The GJ/ha-yr sequestered as corn grain are 353 (dynamic) and 273 (cham-

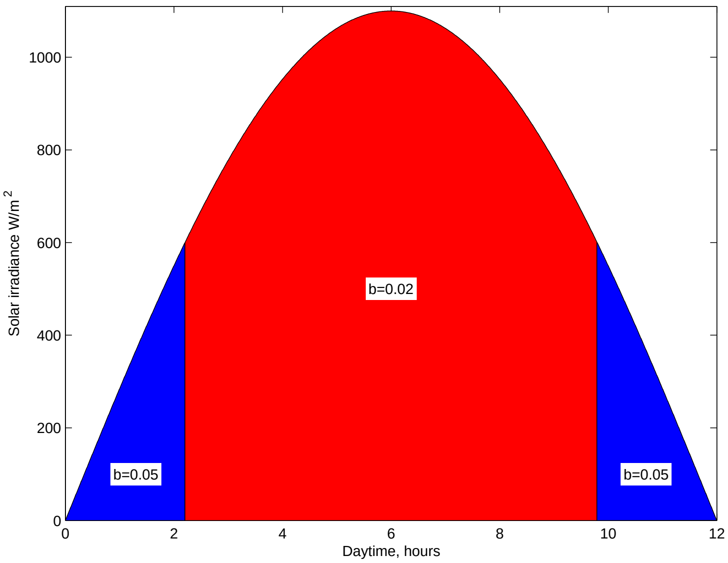


Figure 18.9: Consistently with Figures 18.7 and 18.8, we average the corn plant efficiency by calculating the area-weighted average of solar irradiance from the 0 to 600 W/m^2 (left and right tail), and the central irradiance from 600 to 1100, and back to 600 W/m^2. The solar irradiance follows the sine curve. We assign the solar energy sequestration efficiency of 0.05 (plus the scaled intercept) to both tails, and of 0.02 to the strong irradiance over the rest of the day.

ber), respectively.

- The corresponding kg/ha-yr of corn grain with 15% moisture are 22100 (dynamic) and 17100 (chamber), respectively.

- The corresponding bushels/acre-yr of corn grain with 15% moisture are 352 (dynamic) and 272 (chamber), respectively.

- One could argue that a tighter estimate of the largest possible yield would be with 100 days of growth of plants above ground. All the estimates above would then be 20% lower.

The chamber roof screened solar radiation, and I prefer to use the results of the dynamic eddy-covariance method for further extrapolations.

Because light absorption characteristics of a single corn leaf and an entire corn field are almost identical, see **Figure 18.5**, the additional amount of energy sequestered by increasing plant density should be relatively small, because each plant in a denser packing will obstruct its neighbors from accessing sunlight.

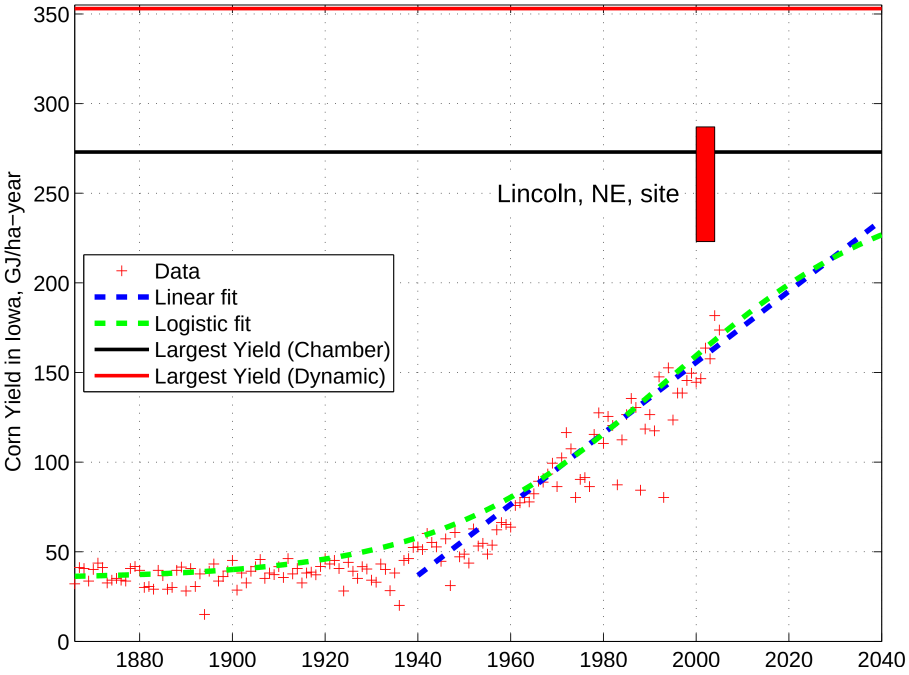


Figure 18.10: Historical corn crops in Iowa, their logistic fit, and the straight line fit usually presented by economists, who imply that corn yield can grow indefinitely in the future. The red rectangle brackets yields from the irrigated, highly-fertilized site in Lincoln, NE. Heroic agricultural practices achieve 80% of the maximum practical corn yield. Note that bushels per acre are numerically equal to GJ ha^{-1}.

18.6.1 Record crop in 2004

In 2004, the all-time high crop yield in Iowa was 181 bushels per acre, 51% of our practical photosynthetic limit at the 30-year average insolation. It is unlikely that this limit will ever be achieved, see **Figure 18.10**.

Five years of corn field studies in Lincoln, Nebraska, (Lindquist et al., 2005; Dobermann et al., 2005) have shown that the above-ground mass of corn is a linear function of the absorbed PAR:

$$\text{Total dry mass above ground kg m}^{-2} = 0.00384 \times \text{absorbed PAR} \qquad (18.5)$$

The highest possible yield in 2004, translates to 2.9 kg m^{-2}, of above-ground biomass, 53% of which is grain, or 18 000 kg ha^{-1} of grain with 15% moisture (287 bu/acre). The highest measured crop yield was therefore $18000/22100 =$ 0.80 of our projection.

The highest measured photosynthetic efficiency of a corn field has been

$$1.3 \times 0.00384\,\frac{\text{kg all biomass}}{\text{MJ absorbed PAR}} \times 15.77\,\frac{\text{MJ}}{\text{kg biomass}} \times$$
$$0.38\frac{\text{MJ absorbed PAR}}{\text{MJ irradiance during growth season}} \times \frac{120}{365} = 0.03 \times 0.33 = 1\% \tag{18.6}$$

The annualized crop-mass average of photosynthetic efficiency for all US agriculture was 0.2% in 2004, i.e., 0.36 $\mathsf{W\,m^{-2}}$ of seed/grain biomass output vs. 200 $\mathsf{W\,m^{-2}}$ of average insolation. All agricultural biomass (aboveground plants and their root systems) sequestered 0.66 $\mathsf{W\,m^{-2}}$ or 0.33 % of average insolation. See Chapter 13 for details.

18.7 Problems

1. The photosynthetically active radiation (PAR) is often expressed as μmol m^{-2} s^{-1} of photons. By using the standard relationship for the photon energy (see Chapter 15, Eq. (15.1)):

   $$u = \frac{hc}{\lambda} \tag{18.7}$$

   and the distribution function density per unit wavelength for solar light at moderate latitudes (AM1.5), provided to you as a MATLAB file, calculate:

   (a) Average wavelength of visible light (400 – 700 nm). Give your averaging formula.

   (b) Average energy flux of 1 μmol m^{-2} s^{-1} of photons between 400 and 700 nm. Express your answer in W m^{-2}.

2. Convert the photosynthetically reduced CO_2 into glucose energy. Use 15.74 MJ kg^{-1} as the net free chemical energy of glucose in photosynthesis, see Table 21 in Patzek (Patzek, 2004). (Note that about 0.7 MJ/kg of glucose is used up to concentrate carbon dioxide in the leaves.)

   Answer: 472.2 kJ mol^{-1} CO_2 = 472.2/4.184 ≈ 113 thermochemical kcal mol^{-1} CO_2 = 472.2 MJ kmol^{-1} CO_2.

3. Calculate the fraction of energy of the standard AM1.5 (provided as a MATLAB file) between 400 and 700 nm. Give the formula you will use in the calculations.

   Answer: 42.66% (and 39% for AM0).

4. Find out what are stromatolites and what do they have in common with ancient photosynthesis? How old can they be?

Chapter 19

Water and CO_2 Management by Plants

All truly wise thoughts have been thought already thousands of times; but to make them truly ours, we must think them over again honestly, till they take root in our personal experience.

— Johann Wolfgang von Goethe, (Unsourced)

19.1 What Are We Going to Learn?

From Chapter 18 you have learned that photosynthesis in plants, (i) has low intrinsic efficiency, (ii) occurs only when photosynthetically active photons are absorbed by a plant leaf, and (iii) only some of the absorbed photons carry photochemical reactions. In this chapter, you will learn about the limitations imposed on photosynthesis by CO_2 diffusion into the leaves and water transpiration out of the leaves.

19.2 Why Is It Important?

Both carbon dioxide and water are necessary for photosynthesis, but in significantly different amounts. Carbon dioxide is a reagent, whose photosynthetic reduction produces sugars. The rate of its consumption is equal to the rate of photosynthetic production of glucose. In contrast water is both a donor of electrons and an environment in which all reactions occur. Because the air taken in by a plant to acquire carbon dioxide is often dry, and the leaves heat up in the sun, plants of necessity lose a lot of water to acquire whatever little carbon dioxide they need. In short, about 1000 moles of water are lost to reduce one mole of carbon dioxide. You need to understand why this is so.

19.3 Leaf Stomata

Stomata, shown in **Figure 19.1**, are small pores on the surfaces of leaves and stems, bounded by a pair of guard cells, that control the exchange of gases - most importantly water vapor and CO_2 - between the interior of the leaf and the atmosphere. In this capacity they make major contributions to the ability of the plant to control its water use and to gain carbon. Gas exchange is regulated by controlling the aperture of the stomatal pore and the number of stomata that form on the epidermis. Environmental signals such as light intensity, the concentration of atmospheric carbon dioxide, and plant hormones, control stomatal aperture and development. The acquisition of stomata and an impervious leaf cuticle are considered to be key elements in the evolution of advanced terrestrial plants, allowing them to inhabit a range of different, often fluctuating environments but still control water content (Hetherington and Woodward, 2003).

19.3.1 Countercurrent Diffusion of CO_2 and Water

Since CO_2 and water vapor flow in the opposite directions through the same stomatal pores, their mass fluxes are coupled. The steady state flux of water through a stoma and into the air is

$$\mathcal{F}_{\mathrm{H_2O}} = \mathcal{D}_{\mathrm{H_2O}} \frac{[\mathrm{H_2O}]_{\mathrm{inside}} - [\mathrm{H_2O}]_{\mathrm{outside}}}{L} \quad \mathsf{mol\ m^{-2}\ s^{-1}} \tag{19.1}$$

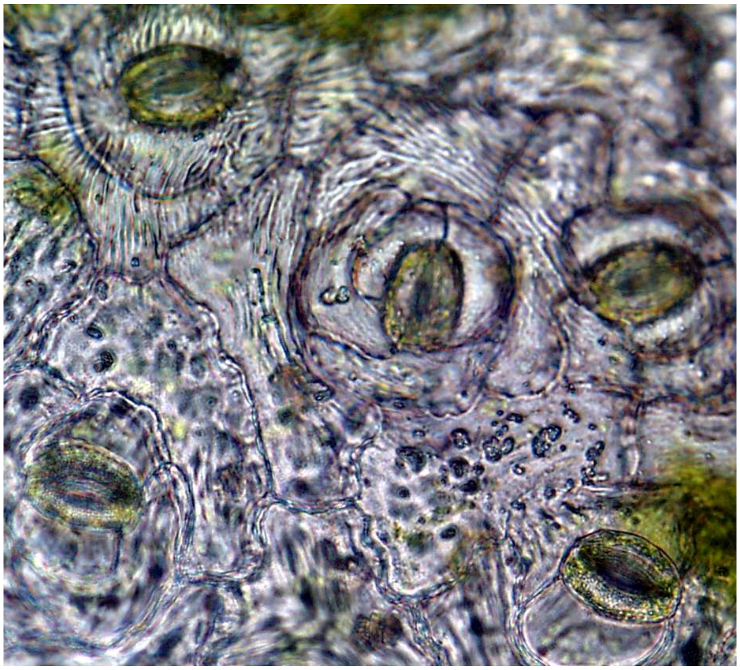


Figure 19.1: Stomata in a leaf of hibiscus, 400x. The inner greenish "lips" of a stoma are two guard cells that control aperture, and the outer ovals are made of two subsidiary calls. Source: College of St. Benedict/St. John's University; Biology Department; Collegeville, MN 56321, employees.csbsju.edu/ssaupe/-biol327/Lab/stomata/stomata-images.htm.

where $\mathcal{D}$ is the effective molar diffusion coefficient, L is the stoma length, and the square brackets denote the molar concentration of water vapor in the gaseous mixture in the stoma.

Similarly, the steady state flux of carbon dioxide through a stoma and into the leaf is

$$\mathcal{F}_{\mathrm{CO_2}} = \mathcal{D}_{\mathrm{CO_2}} \frac{[\mathrm{CO_2}]_{\mathrm{outside}} - [\mathrm{CO_2}]_{\mathrm{inside}}}{L} \quad \mathsf{mol\ m^{-2}\ s^{-1}} \tag{19.2}$$

The ratio of these two fluxes is

$$\frac{\text{moles of H}_2\text{O out}}{\text{moles of CO}_2\text{ in}} = \frac{\mathcal{D}_{\mathrm{H_2O}}}{\mathcal{D}_{\mathrm{CO_2}}} \frac{[\mathrm{H_2O}]_{\mathrm{inside}} - [\mathrm{H_2O}]_{\mathrm{outside}}}{[\mathrm{CO_2}]_{\mathrm{outside}} - [\mathrm{CO_2}]_{\mathrm{inside}}} \tag{19.3}$$

The ratio of the molecular diffusion coefficients is also the ratio of water and carbon dioxide mobilities, which can be calculated from the kinetic theory of gases. At constant temperature, both water and carbon dioxide have the same mean kinetic energies ($= 3kT/2$), and

$$\frac{1}{2} m_{\mathrm{H_2O}} v_{\mathrm{H_2O}}^2 = \frac{1}{2} m_{\mathrm{CO_2}} v_{\mathrm{CO_2}}^2 \tag{19.4}$$

where m_{H_2O} and m_{CO_2} are masses of the both molecules and v_{H_2O} and v_{CO_2} are their mean velocities of translational motion. Therefore

$$\frac{\mathcal{D}_{H_2O}}{\mathcal{D}_{CO_2}} = \frac{v_{H_2O}}{v_{CO_2}} = \sqrt{\frac{m_{CO_2}}{m_{H_2O}}} = \sqrt{\frac{44}{18}} = 1.56 \tag{19.5}$$

19.3.2 H_2O and CO_2 Flux Estimates

Now we can estimate the actual ratio of water consumption and carbon dioxide sequestration. I will make very favorable (limiting) assumptions to calculate the smallest possible ratio of these fluxes:

- The maximum concentration of CO_2 near the leaves is equal to the mean CO_2 concentration in the atmosphere, see **Figure 16.6**: $[CO_2]_{\text{outside}} =$ 375 ppm (ppm = parts per million or mg/L of air).
- In C_3 plants, the lowest possible CO_2 concentration in the leaves (the "compensation point") is ∼50 ppm (Zeltich, 1971). Below this concentration, photosynthesis stops and switches to photorespiration during which the plant takes in oxygen and produces CO_2. In C_4 plants, the possible lowest concentration of CO_2 is ∼10 ppm (Zeltich, 1971). In real life, both C_3 and C_4 plants maintain much higher CO_2 concentrations to help the kinetics of CO_2 reduction. We will assume $[CO_2]_{\text{inside}} = 200$ ppm for C_3 plants and 100 ppm for C_4 plants.
- The leaves and the air are at 30^0 C.
- The relative humidity of the air is 50% (pretty high most of the time).

If one applies these assumptions and Eq. (19.5) to Eq. (19.3), one obtains

$$\frac{\text{moles of } H_2O \text{ out}}{\text{moles of } CO_2 \text{ in}} = 190 \text{ for } C_3 \text{ plants and } 120 \text{ for } C_4 \text{ plants} \tag{19.6}$$

see **Problem 1** for details. Thus, under most favorable conditions, plants trade at least 120 moles of water for each mole of CO_2 sequestered. In reality, these ratios are about 5-7 times higher.

At field conditions, plants use most of the transpired water for cooling purposes, not to sequester CO_2. All of the energy of absorbed sunlight, including photosynthesis, must be balanced by infrared radiation from the leaves and heat transfer to the air through convection and evaporation of the transpired water. Much work has been done in this area, see, e.g., (Uchijma, 1963), but it goes beyond the scope of this course.

19.4 Water Requirements of Crops

Definition 22 Water requirement, W, is the ratio of weight of water absorbed by the plant during its growth period to the weight of dry matter harvested. Only in the case of root crops is the weight of underground parts included (Shantz and Piemeisel, 1927). □

Between 1911 and 1917, Professor H. L. SHANTZ & Ms. LYDIA N. PIEMEISEL conducted an extensive study of water requirements of 288 sets of crop plants in 1800 pots (Shantz and Piemeisel, 1927). Some of their results are listed in **Tables 19.1** and **19.2**. Since 1917, plant breeding has focused on improving the relative proportions of grain to stem + leaf mass, drought tolerance of plants, and their ability to survive crowding in the field.

Table 19.1: Water requirements by crops. Averages for 1911 – 1917, Table 27 in (Shantz and Piemeisel, 1927)

Name	kg/kg[a]	±STD	mol/mol[b]	±STD
Alfa-alfa	859	10	1432	17
Oats	602	11	1003	18
Barley	511	8	852	13
Wheat	484	11	807	18
Corn	368	9	613	15
Millet	273	3	455	5
Sorghum	270	3	450	5
Potatoes[c]	329	6	548	10
Crimson Clover[d]	517	19	862	32

[a] kg of water per kg of dry mass

[b] mole of water per mol of carbon dioxide

[c] Potato tubers, 1915 average, Table 14

[d] 1914 average, Table 13

Table 19.2: Water requirements by grain. Averages for 1911 – 1917, Table 29 in (Shantz and Piemeisel, 1927)

Name	kg/kg[a]	±STD	mol/mol[b]	±STD
Oats	1644	35	2740	58
Wheat	1338	45	2230	75
Corn	1958	159	3263	265
Millet	926	55	1543	92
Sorghum	1061	122	1768	203
Potatoes[c]	945	134	1575	223

[a] kg of water per kg of dry mass

[b] mole of water per mol of carbon dioxide

[c] Potato tubers, 1915 average, Table 15

In comparison, recent measurements (Henderson et al., 1998) of water requirements of 30 varieties of sorghum plants in Australia yield $W = 2040$

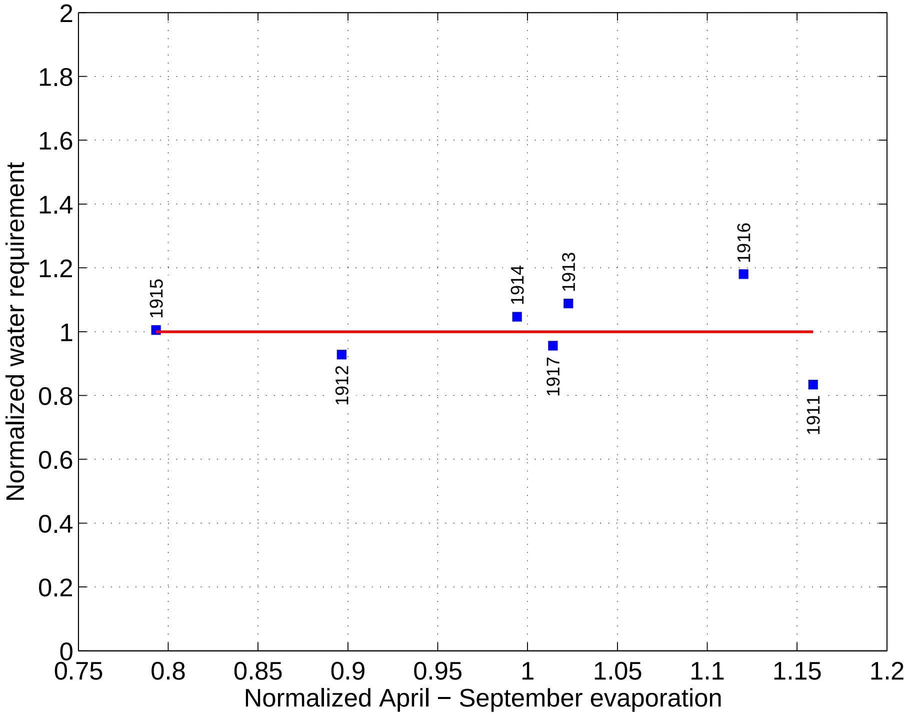


Figure 19.2: Corn water requirement vs. evaporation. The cumulative evaporation between April and September was normalized by its mean. The water requirement was correlated as $\log W_{\text{corr}} = a \log(e_v) + b$, where e_v is the time series of April - September water evaporations divided by their mean. The plotted red curve is W/W_{corr} versus e_v. It is obvious that accounting for the variability of evaporation (rain fall) explains most of the variability of the reported corn harvests between 1911 and 1917.

mol H_2O mol^{-1} CO_2 in the glasshouse, and $W = 3570$ mol H_2O mol^{-1} CO_2 in the field. The range of water requirements was twice the mean. Australia has a much drier, hotter climate and higher transpiration rates than Colorado. This observation should serve as a warning, as the climate warms up, plants will transpire more water for the same crop yield. Soybean water requirements are about 3700 kg of water per kg of grain (Specht et al., 2001).

In Colorado, plant water requirements between 1911 and 1917 were correlated with evaporation from a free water surface. For example, the average water requirements for corn plants varied between 280 kg/kg (466 mol/mol) and 495 kg/kg (825 mole/mol) and were clearly correlated with the cumulative evaporation, see **Figure 19.2**.

The maximum biomass production fluxes for C_4 and C_3 plants, expressed in μmol CH_2O m^{-2} s^{-1} (equal to the number of μmol of sequestered CO_2 and C), are plotted versus the maximum stomatal conductance flux in mol H_2O m^{-2} s^{-1} in **Figure 19.3**. Note that C_4 plants are about 2 times as efficient as C_3 plants in managing water. Also note that as crop yields increase, the incremental (marginal) water requirement becomes very large.

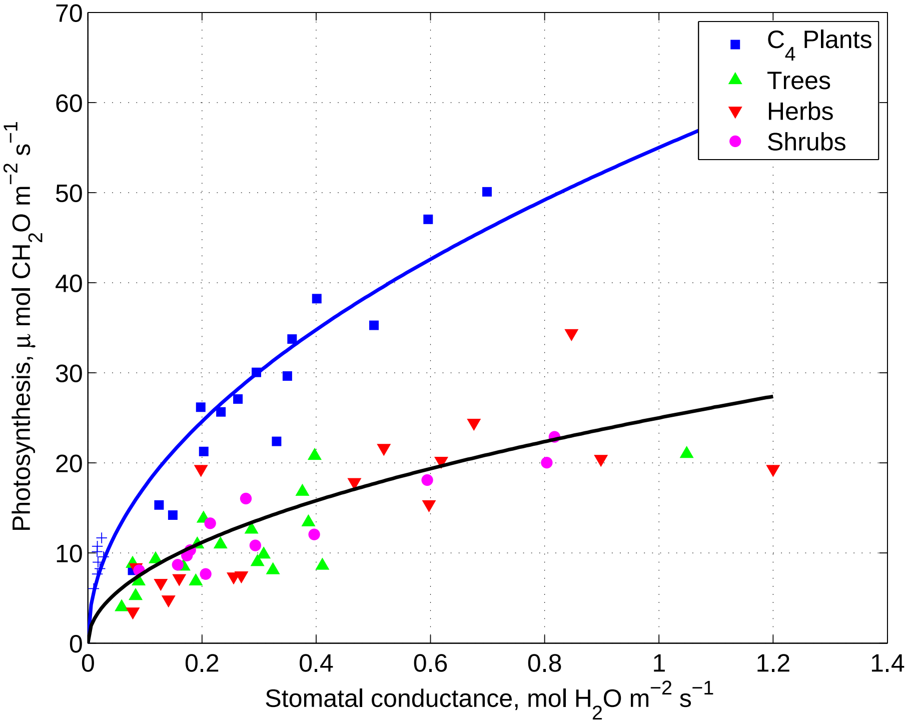


Figure 19.3: Maximum biomass production fluxes vs. maximum stomatal conductance flux in C_4 and C_3 plants. The data are from multiple sources listed in (Hetherington and Woodward, 2003). The crosses are for sugarcane. Note that water requirements calculated from these fluxes are about 10 times higher than those listed in Table 1.

19.5 Problems

1. Given the assumptions in Section 19.3.2, determine the minimum ratio of H_2O and CO_2 fluxes in the leaves of C_3 and C_4 plants. Find out and summarize the differences in photosynthetic pathways in these two types of plants.

   Hint: The water saturation pressure at 30^0 C is 42560 Pa (4.2×10^{-2} atm). Use DALTON's law, to replace molar concentrations of water and carbon dioxide with their partial pressures.

2. Given the time series of corn water requirements between 1911 – 1917: $368, 280, 399, 368, 253, 495, 346$ kg/kg, and the time series of evaporation $48.8, 37.75, 43.06, 41.86, 33.40, 47.17, 42.7$ inches, generate Figure 19.2.

   Answer: $a = 1.48$ and $b = 5.87$.

3. Suppose that the density of biomass sequestered as corn plants is 3000 g m^{-1} $crop^{-1}$.

   (a) If corn growth season is 120 days, and there is about 10 hours of sunlight per day, calculate the crop-average sequestration flux in μmol CH_2O m^{-2} s^{-1}

   Answer: 23 μmol CH_2O m^{-2} s^{-1}.

   (b) Given the average C_4 curve in Figure 19.3, how many kilograms of water was transpired from each square meter of the field during the growth season?

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Chapter 20

Post Scriptum

The Builders from *The Seaside and the Fireside*
by Henry Wadsworth Longfellow (1807 – 1882)

All are architects of Fate,
Working in these walls of Time;
Some with massive deeds and great,
Some with ornaments of rhyme.

Nothing useless is, or low;
Each thing in its place is best;
And what seems but idle show
Strengthens and supports the rest.

For the structure that we raise,
Time is with materials filled;
Our to-days and yesterdays
Are the blocks with which we build.

Truly shape and fashion these;
Leave no yawning gaps between;
Think not, because no man sees,
Such things will remain unseen.

In the elder days of Art,
Builders wrought with greatest care
Each minute and unseen part;
For the Gods see everywhere.

Let us do our work as well,
Both the unseen and the seen;
Make the house, where Gods may dwell,
Beautiful, entire, and clean.

Else our lives are incomplete,
Standing in these walls of Time,
Broken stairways, where the feet
Stumble as they seek to climb.

Build to-day, then, strong and sure,
With a firm and ample base;
And ascending and secure
Shall to-morrow find its place.

Thus alone can we attain
To those turrets, where the eye
Sees the world as one vast plain,
And one boundless reach of sky.

Appendix A

Availability and Irreversibility in Thermal Systems

Because the earth can export entropy by infrared radiation from the outer layers of the atmosphere, in this appendix I define any thermodynamic system on the earth as interacting with the atmosphere only. The atmosphere will be treated as being in stable dynamic equilibrium, and characterized by the constant absolute temperature T_0, volume V_a, and the hydrostatic pressure, $p_0 = 1$ atm, at sea level. By including within the system as much surface land area, surface water, groundwater, minerals, material, plants, machinery, etc.[1], as affected by the process of interest, one is always able to construct the system that interacts with the atmosphere only. For simplicity, chemical entropy generated by the system is not considered here.

GIBBS[2] showed that for any process which can occur under these circumstances the quantity defined as

$$\Phi = E + p_0 V - T_0 S \tag{A.1}$$

decreases

$$\Delta\Phi \leq 0 \tag{A.2}$$

where E is the total energy of the system, V its volume, S its entropy, and the increment of Φ, $\Delta\Phi$, is taken in the direction of increasing chronological Time.

The process of interest can only occur until the system pressure is uniformly hydrostatic and its uniform temperature is T_0. Therefore, the state from which no *spontaneous* change can occur is the state in which the system has the hydrostatic pressure (p_0 at sea level) and the atmospheric temperature T_0, and for which Φ has the smallest possible value, $\Phi_{\min}$. If only one state of the system

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[1] The entire globe, if necessary.

[2] (Gibbs, 1994), p. 40.

results in this minimum value, the system is in *stable equilibrium.* Otherwise, if there are several states corresponding to the minimum value of $\Phi_{\min}$, the system is in *neutral equilibrium* of maximum stability.

GIBBS[3] referred to the difference

$$\Phi - \Phi_{\min}, \tag{A.3}$$

where Φ corresponds to the state in question, as the "... available energy of the body (*our system*) and the medium (*our surroundings*)."

JOSEPH H. KEENAN (1951) later showed that for the system undergoing change from an *earlier* state 1 to a *later* state 2, the amount of useful work W_u is

$$W_u \leq \Phi_1 - \Phi_2 \leq \Phi_1 - \Phi_{\min} \tag{A.4}$$

Therefore, for any state 1, the maximum possible useful work done by the system is $\Phi_1 - \Phi_{\min}$. KEENAN proposed to call this maximum value *availability*, Λ. It may be said[4] that for any system in the stable atmosphere

$$\Lambda \geq 0 \tag{A.5}$$

and that for the most stable state of the system

$$\Lambda = 0 \tag{A.6}$$

From Eq. (A.4) it also follows that

$$\begin{aligned} \Delta\Lambda &= \Delta\Phi \\ W_u &\leq W_{u,\max} = \Phi_1 - \Phi_{\min} = -\Delta\Phi = -\Delta\Lambda \end{aligned} \tag{A.7}$$

KEENAN also quantified the *irreversibility*[5], I, of a process executed by the system-atmosphere combination:

$$\begin{aligned} I =& W_{u,\max} - W_u \\ =& -\Delta\Phi - W_u \\ =& -\Delta\Lambda - W_u \end{aligned} \tag{A.8}$$

and showed that

$$\begin{aligned} I =& T_0\Delta S + \Delta E_a + p_0\Delta V_a \\ =& T_0\Delta(S_a + S) \end{aligned} \tag{A.9}$$

Of course, KEENAN's irreversibility was discovered much earlier and independently by GOUY (1889) and STODOLA (1898; 1927)[6]. Regardless, the irreversibility of a process is equal to the increase of entropy of everything involved in the process multiplied by the temperature of the atmosphere.

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[3] (Gibbs, 1994), p. 53; my comments in italics.

[4] (Keenan, 1951), Eqs. (12) and (13).

[5] (Keenan, 1951), Eqs. (31) - (36).

[6] In particular, Volume II of STODOLA's monograph (1927), pp. 1271-1330, brings a thorough discussion of *The Highest Possible Conversion into Work on the Basis of the Second Law of Thermodynamics.*

One may use Eq. (A.9) in the differential form, and per unit area of the earth surface, by writing

$$\begin{aligned} \frac{1}{A_e}\frac{\mathrm{d}I}{\mathrm{d}t} =& T_0\left(\frac{1}{A_e}\frac{\mathrm{d}S_a}{\mathrm{d}t} + \frac{1}{A_e}\frac{\mathrm{d}S}{\mathrm{d}t}\right) \\ \sigma_I =& T_0(\sigma_a + \sigma) \end{aligned} \tag{A.10}$$

where σ_I is the specific rate of irreversibility, σ_a is the specific rate of entropy increase in the atmosphere generated by the process, and σ is the specific rate of entropy increase of the system. Note that as the atmospheric temperature increases, so does the irreversibility of any process on the earth.

From Chapter 16 it follows that we can treat the atmosphere as an open system that exports entropy to the universe with the flux j_S^E calculated from Problem 2. The energy transport through the atmosphere generates entropy at the specific rate of σ_t, calculated from Eq. (16.6) to be ~0.2 W m^{-2} K^{-1}.

Thus, we may rewrite Eq. (A.10) as

$$\sigma_I^{\text{net}}/T_0 = \underbrace{(\sigma_a + \sigma)}_{\substack{\text{Thermal entropy from} \\ \text{Earth processes}}} + \underbrace{(-j_S^E + \sigma_t)}_{\substack{\text{Thermal entropy from} \\ \text{Solar processes}}} \tag{A.11}$$

Using equation (A.11), we can define sustainability as

$$\begin{aligned} &\sigma_I^{\text{net}} \le 0 \\ &\sigma_a + \sigma - j_S^E + \sigma_t \le 0 \\ &\text{For all places on the earth, and at all times} \end{aligned} \tag{A.12}$$

For *sustainability*, equation (A.12) requires that the net rate of increase of entropy of everything at every place on the earth and for all times be less or equal to zero! Note that the process and energy transport increase the entropy of the earth and the atmosphere, and low-temperature heat radiation decreases it.

Remark 4 As derived, Eq. (A.12) is quite deceiving. The anthropogenic part of the thermal entropy generation rates, $\sigma + \sigma_a$, can only be sustainable if this entropy is generated in cycles in which all process materials are completely recycled, and all chemical entropy is transformed into thermal entropy. If we rely on a finite stock of fossil energy, then even if the entropy generation rate in a process is much lower than the entropy export flux, the process is *never* sustainable. Therefore, sustainability can only be discussed in the context of *cyclic processes.* □

Over an arbitrary time interval $[\tau_1, \tau_2]$, we can write the global condition of *sustainability* of all cyclic processes on the earth as

$$\begin{aligned} &\underbrace{[S_a(\tau_2) - S_a(\tau_1)]}_{\substack{\text{Increase of atmospheric entropy} \\ \text{from earth processes}}} + \underbrace{[S(\tau_2) - S_(\tau_1)]}_{\text{Increase of earth entropy}} - S^E(\tau_1, \tau_2) + S_t(\tau_1, \tau_2) \le 0 \\ &\text{For the entire earth, and arbitrary } \tau_1,\ \tau_2 \end{aligned} \tag{A.13}$$

where $S^E(\tau_1, \tau_2) = j_S^E A_e(\tau_2 - \tau_1)$ is the total thermal entropy exported by the earth over the time interval $[\tau_1, \tau_2]$, and $S_t(\tau_1, \tau_2) = \sigma_t A_e\,(\tau_2 - \tau_1)$ is the corresponding thermal entropy generated in the atmosphere by the steady-state energy transport to the universe.

Appendix B

Efficiency of a Fuel Cell System

In their Science paper, Deluga et al. (2004) claim the following:

> . . . Further, combustion used for transportation has ∼20% efficiency as compared with up to 60% efficiency for a fuel cell. . . The efficiency of these processes for a fuel cell suggests that it may be possible to capture >50% of the energy from photosynthesis as electricity in an economical chemical process that can be operated at large or small scales. (p. 996).

Following Deluga et al.'s paper and common chemical engineering knowledge, I will assume the following:

1. The catalyst is made of a rare-earth metal, rhodium[1], and a Lanthanoid, cerium[2].
2. The catalytic reaction has 100% selectivity and >95% conversion efficiency. I will assume here the conversion efficiency $\eta_1 = 0.96$.
3. The ethanol-water reactant mixture for the catalytic conversion to hydrogen is ultra pure (on the order of 99.9999% pure C_2H_5OH and H_2O). Otherwise, any and all of the impurities listed in Footnotes 3 and 4, and carbon deposition, will destroy the catalyst and reactor. Therefore, one must separate all impurities from the $8 - 10\%$ alcohol[3]-yeast-rest beer[4] by multiple distillations, rectification, and molecular sieve exclusion (Maiorella,

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[1] Rhodium is a precious metal whose price is about US$30 000/kg, 3×more expensive than gold, http://www.kitco.com/charts/rhodium.html.

[2] The nanoparticles of cerium dioxide are called *ceria*, and cost $250/kg, http://www.advancedmaterials.us/58N-0801.htm

[3] Alcohol dissolves a large number of substances insoluble in water and acids, such as many inorganic salts, phosphorus, sulphur, iodine, resins, essential oils, fats, coloring matters, etc. (Wright, 1994).

[4] The beer obtained by mashing and fermenting consists of volatile components, such as

1985). As described in Part II, all these processes consume irreversibly large amounts of free energy.

4. The reaction products are hydrogen, carbon dioxide, carbon monoxide, water vapor, plus whatever other impurities. The hydrogen fuel separation from all other components of reactor effluent is almost perfect. Compared with the reference hydrogen of 99.9999999% purity, even tiny amounts of impurities can cause a noticeable drop in performance of a fuel cell[5]. Some of these impurities are CO (at 5-10 ppm), SO_2 (at 2 ppm), H_2S (at 1-2 ppm), HCHO (at 10-20 ppm), and HCOOH (at 50-100 ppm).

5. In summary, by the time we are ready to use the ethanol-derived hydrogen in a fuel-cell/electric car, we have spent a lot of free energy on picking ethanol, water, and hydrogen molecules; *much* more than on distilling the relatively dirty ethanol to be mixed with gasoline. The latter free energy expenditure is $\sim$15 MJ L^{-1} EtOH, or >50% of the ethanol's high heating value.

After Bossel (2003a), I will summarize efficiency of a Proton Exchange Membrane (PEM) fuel cell as follows. In fuel cells, gaseous hydrogen is combined with oxygen to water. This process is the reversal of the electrolysis of liquid water and should provide an open circuit voltage of 1.23 V (Volts) per cell. Because of polarization losses at the electrode interfaces the maximum voltage observed for PEM fuel cells is between 0.95 and 1.0 V. Under operating conditions the voltage is further reduced by ohmic resistance within the cell. A common fuel cell design voltage is 0.7 V. The mean cell voltage of 0.75 V may be representative for standard driving cycles. Consequently, the average energy released by reaction of a single hydrogen molecule is equivalent to the product of the charge current of two electrons and the actual voltage of only 0.75 V instead of the 1.48 V corresponding to the hydrogen high heating value[6]. Therefore, in automotive applications, PEM fuel cells may reach mean voltage efficiencies of

$$\eta_2 = \frac{0.75 \text{ V}}{1.48 \text{ V}} = 0.50 \tag{B.1}$$

However, there are more losses to be considered. The fuel cell systems consume part of the generated electricity. Typically, automotive PEM fuel cells consume

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water, alcohols (mostly ethyl, but also traces of methyl, propyl, butyl, amyl, and other alcohols – depending on the impurities in glucose), essential oils, and a little acetic acid; and of non-volatile substances, such as cellulose, dextrine (an intermediate product of starch hydrolysis), unaltered sugar and starch, mineral matter, lactic acid, glycerol, etc.

[5] Japan Automotive Research Institute (JARI), DOE Hydrogen Codes and Standards, Coordinating Committee Fuel Purity Specifications Workshop, April 26, 2004, http://-www.eere.energy.gov/hydrogenandfuelcells/pdfs/fuel_purity_notes.pdf

[6] According to Faraday's Law, the standard enthalpy of combustion of hydrogen, $\Delta H_f^0 = -285.9$ kJ mol^{-1}, can also be expressed as an electrochemical potential ("standard potential") $U^0 = -\Delta H_f^0 / n_e F = 1.48$ V with $n_e = 2$ being the number of electrons participating in the conversion and $F = 96485$ Coulomb mol^{-1} the Faraday constant.

10% or more of the rated stack power output to provide power to pumps, blowers, heaters, controllers, etc. At low power demand the fuel cell efficiency is improved, while the relative parasitic losses increase. The small-load advantages are lost by increasing parasitic losses. Let us assume optimistically that for all driving conditions the net power output of an automotive PEM fuel cell system is about $\eta_3 = 0.9$ of the power output of the fuel cell stack.

Depending on the chosen drive train technology, the DC power is converted to frequency-modulated AC or to voltage-adjusted DC, before motors can provide motion for the wheels. Energy is always lost in the electric system between fuel cell and wheels. The overall electrical efficiency of the electric drive train can hardly be better than $\eta_4 = 0.9$.

By multiplying the efficiency estimates, one obtains for the maximum possible tank-to-wheel efficiency of a hydrogen fuel cell vehicle

$$\eta = \eta_1 \eta_2 \eta_3 \eta_4 = 0.96 \times 0.50 \times 0.90 \times 0.90 = 0.38, \tag{B.2}$$

or 38%. This *optimistic* estimate agrees with another analysis (31-39%) (Fleischer and Ørtel, 2003), and is significantly less than the 60% used by the promoters of a hydrogen economy and hydrogen fuel cell vehicles.

Appendix C

Basic Units and Their Conversions

Table C.1: Prefixes for units in the International System

Prefix	Symbol	Power	Example	USA/Other
exa	E	10^{18}		quintillion
peta	P	10^{15}	petagram (Pg)	quadrillion/billiard
tera	T	10^{12}	terawatt (TW)	trillion/billion
giga	G	10^{9}	gigawatt (GW)	billion/milliard
mega	M	10^{6}	megawatt (MW)	million
kilo	k	10^{3}	kilgoram (kg)	
hecto	h	10^{2}	hectoliter (hl)	
deka	da	10^{1}	dekagram (dag)	
deci	d	10^{-1}	decimeter (dm)	
centi	c	10^{-2}	centimeter (cm)	
milli	m	10^{-3}	millimeter (mm)	
micro	m	10^{-6}	micrometer (mm)	
nano	n	10^{-9}	nanosecond (ns)	
pico	p	10^{-12}	picofarad (pf)	
femto	f	10^{-15}	femtogram (fg)	
atto	a	10^{-18}		

Length: 1 meter = 100 cm = 1,000 mm = 3.281 ft = 39.37 inches (in)

1 foot = 12 inches (in) = 30.48 cm = 1/3 yard (yd)

1mile = 5,280 ft = 1.609 km

1 micron (μm)= 10^{-6} m

1 angström (Å) = 10^{-10} m

1 nanometer = 10 Å

1 Astronomic Unit (AU) = 1.496×10^8 km

Area: 1 m^2 = 10^{-2} are (a) = 10^{-4} hectare (hecto-are, ha) = 10.76391 ft^2

1 acre = 43,560 ft^2 = 4,046.86 m^2 = 0.4047 ha

1 ha = 2.4711 acre = 10^4 m^2 = 10^{-2} km^2

Volume: 1 m^3 = 10^6 cm^3 = 10^3 liters (l) = 1.056688×10^3 quart (qt) = 264.1721 gal (U.S.)

1 liter (l) = 1.056688 quart (qt) = 0.2641721 gal (U.S.)

1 gallon (U.S.) = 4 qt = 3.785412 l = 0.1336806 ft^3

1 barrel (bbl) = 42 gal (U.S.) = 159 l = 5.6146 ft^3

Time: 1 year (yr) = 3.1536×10^7 seconds (s)

1 day (d) = 86,400 s

Mass: 1 kg = 2.2046 pounds (lbs) = 10^{-3} metric ton (tonne) = 1000 grams

1 lb = 0.4535924 kg

1 metric ton = 0.9842 long ton = 1.102311 short ton

1 short ton = 2,000 lbs = 0.9071847 metric ton

1 long ton = 2,240 lbs = 1.016047 metric ton

Energy: 1 joule (J) = 0.2390057 calorie (cal) = 9.478172×10^{-4} British thermal unit (Btu)

1 cal = 4.184 J = 3.965667×10^{-3} Btu

1 Btu = 1055.056 J = 252.1644 cal = 2.930711×10^{-4} kilowatt-hour (kWh)

1 kWh = 3.6 megajoule (MJ) = 0.8604207 Mcal = 3412.142 Btu

Power. 1 W = 1 J/sec = 0.9478×10^{-3} Btu/s = 3.41214 Btu/hr

Pressure: 1 pascal (Pa) = 1 newton/m^2 (N/m^2)

1 physical atmosphere (atm) = 101325 Pa = 760 mm of mercury (mm Hg) = 14.69 lb-force/in^2 (psi)

1 technical atmosphere (at) = 1 kilogram-force/cm^2 (kG/cm^2)= 9.806650×10^4 Pa

Miscellaneous Useful Units and Conversions: An odd collection of physical quantities follows.

- The Avogadro number 6.0225×10^{23} molecules/mole

- 1 barrel (bbl) of oil = 42 US gallons = 5.516 ft^3 = 136 kg for 35 ^{0}API crude oil
- Boltzmann's constant $k = 1.3806503 \times 10^{-23}$ J K^{-1}
- Earth radius (equal area value) $R_{\text{earth}} = 6.371 \times 10^6$ m
- Earth-Sun distance (annual mean value) $d_{SE} = 149.598 \times 10^9$ m
- Planck's constant, $h = 6.626068 \times 10^{-34}$ J s
- Specific gravity of oil γ = oil density/water density at 60 ^{0}F

$$\text{API gravity} = 141.5/\gamma - 131.5$$

- Speed of light in vacuum $c = 299792458$ m s^{-1}
- Sun radius $R_{\text{sun}} = 6.955 \times 10^8$ m
- Universal gas constant, R = 8.314510 Pa m^3 K^{-1} mol^{-1} = 82.5 atm cm^3 K^{-1} mol^{-1} = 10.73 psi ft^3 lb-mol^{-1} $^0\text{R}^{-1}$