

$$\begin{aligned} & \text{tonnes of sulfur from coal combustion in 1980} \\ &= \frac{90 \times 10^{18} \text{ J}}{29.3 \times 10^9 \text{ J/tonne(coal)}} \times 0.025 \text{ tonnes(S)/tonne(coal)} \quad (3) \\ &= 7.7 \times 10^7 \text{ tonnes(S)}. \end{aligned}$$

A mole of any material has a mass of M grams, where M is the molecular mass of the substance (number of protons and neutrons in a molecule). The following units conversion is used to convert tonnes to moles for any material, A :

$$\text{moles of } A = \frac{\text{tonnes}(A) \times [10^6 \text{ g}(A)/\text{tonne}(A)]}{M[\text{g}(A)/\text{mole}(A)]} \quad (4)$$

Using the fact that the atomic (and molecular) mass¹¹ of S is 32, and substituting the actual numbers into Eq. 4, we get:

$$\begin{aligned} & \text{moles(S) from coal combustion in 1980} \\ &= \frac{[7.7 \times 10^7 \text{ tonnes(S)}] \times [10^6 \text{ g(S)/tonne(S)}]}{32 \text{ g(S)/mole(S)}} \quad (5) \\ &= 2.4 \times 10^{12} \text{ moles(S)}. \end{aligned}$$

EXERCISE 1: Using additional data from the Appendix (VII.3), calculate the number of tonnes of cadmium, lead, zinc, selenium, mercury, and arsenic contained in the coal combusted worldwide 1980. Compare the rates at which these substances are emitted into the atmosphere worldwide from coal combustion with the natural background rates of mobilization to the atmosphere given in the Appendix (IX), under the assumption that all the trace substances found in fossil fuel are emitted into the atmosphere when the fuel is burned. In practice, some portion of the trace substances in fuels is left behind as solid waste in the form of ash when the fuel is burned. The pathways that the substances in fuel follow (through air, water, soil, and living organisms) and the chemical transformations they undergo in the environment (including reactions that can render them more or less toxic than they were in their initial emitted form) depend on many factors. Specific examples will be described later in this book.

EXERCISE 2: For further practice at converting units, use the data in the Appendix on the energy content of specified quantities of fossil fuels to calculate the present world's resources of petroleum, coal, and natural gas in units of barrels, metric tons, and cubic meters, respectively.

11. For a substance like molecular oxygen (O_2) consisting of two identical atoms, the molecular mass is twice the atomic mass; but for S or any other molecule consisting of a single atom, the molecular mass equals the atomic mass.

Chapter II

Tools of the Trade

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... having a good question, a fundamental question, and having some tools of inquiry that allow you to take the first step toward an answer—those are the conditions that make for exciting science.

—Herbert A. Simon

Here you will be handed some of the tools that form the core of environmental science. They include residence-time methods and box models, practical methods in thermodynamics and chemical equilibrium kinetics, and a few relatively simple differential equations. (If you are typical, you were probably paralyzed with fear when you read the previous sentence. Relax—we will take it slowly.)

From: "Consider a Spherical Cow" by

John Harte

University Science Books, 1998.

or

$$r = \left(\frac{4.5\eta v}{\rho_p g} \right)^{1/2}. \quad (9)$$

Using Eq. 3 and the values of η and g from the Appendix (V.1), we calculate

$$r = 0.0005 \text{ cm} = 5 \text{ microns}. \quad (10)$$

EXERCISE 1: Is the required condition on the Reynolds number satisfied in our case?

EXERCISE 2: (a) If all the falling aluminum originated with local biomass fuel combustion, and if the aluminum composition of biomass is taken from the Appendix (VIII), how much fuel per unit area would have to be burned in this region of Nepal in order to account for the observations? (b) Making a reasonable assumption about per capita fuel consumption in Nepal, what population density does this correspond to?

EXERCISE 3: What assumptions were made in deriving a flow of $0.0027 \mu\text{g(Al)}/\text{cm}^2\text{-day}$? Estimate, qualitatively, for each assumption listed, what effect relaxing that assumption would have on the final result.

11. An Indoor Risk

Radioactive radon gas (Rn^{222}) enters an average building at the rate of one picocurie per second per square meter of foundation area. Consider a house with a foundation area of 200 m^2 and an air volume of 1000 m^3 . Assume that the house is well designed for energy conservation so that the ventilation rate is low and only one tenth of the air in the house is exchanged with outdoor air every hour. (a) What will be the average steady-state concentration of Rn^{222} in the house? (b) In the steady state, what whole-body radiation dose, in rads/yr, will an adult male receive directly from Rn^{222} decay if he spends 12 hr a day in the house and derives the entire dose from the decay of radon in the inhaled air in his lungs?

.....

First a note on units and radioactive decay is in order.¹⁴ Every radioactive isotope has a characteristic time constant, called the half-life. It is usually denoted by the symbol $T_{1/2}$. Suppose that at some time, $t = 0$, there are N atoms of an isotope in a closed box. After a period of length $T_{1/2}$ has elapsed, there will be $N/2$ atoms left. The other half will have decayed to form some other atomic species. At time $t = 2T_{1/2}$, $N/4$ will remain, and so on. In each time interval equal to one half-life, half of the radioactive atoms of that isotopic species present at the start of the interval will decay. The Appendix (XI.1) provides values of $T_{1/2}$ for a number of important radioactive isotopes.

Consider a collection of atoms of a particular isotope with half-life $T_{1/2}$. Suppose at time t there are $N(t)$ atoms present. The rate of decay of these atoms is proportional to N itself. If twice as many atoms of the isotope are present then twice as many will decay per unit time. In fact, this is the feature of radioactive decay that makes it possible to assign a constant half-life to each isotope, regardless of the number of atoms of the isotope present. The rate of decay is called the activity and it can be written

$$\text{activity}(t) = \lambda N(t). \quad (1)$$

14. For an introduction to the science of radioactivity and radiation in an environmental context, see Harte and Socolow (1971), Eisenbud (1963), and Ehrlich et al. (1977).

Here, λ is a rate constant related to the half-life by¹⁵

$$\lambda = \frac{\ln 2}{T_{1/2}} = \frac{0.693}{T_{1/2}}. \quad (2)$$

Note that activity is expressed in units of number (of decaying atoms) per unit time. The curie (Ci) is a unit of activity, corresponding to 3.7×10^{10} decays per second. A picocurie (pCi) is 10^{-12} curie or 0.037 decays per second (see Sections I.1 and I.14 of the Appendix). If, for example, at $t = 0$ there are $N = 10^5$ atoms of an isotope with $T_{1/2} = 20$ sec, then the activity at time $t = 0$ is $(0.693/20) \times 10^5$ or 3,465 decays/sec. To convert this to units of curies, we divide by 3.7×10^{10} ; to convert to units of pCi, we divide by 0.037. Thus, there would be 9.4×10^4 pCi of activity in that particular sample. Twenty seconds later, the number of atoms of the isotope that remain will be reduced in half and the activity would then also be reduced by a factor of 2.

(a) Returning to our problem, we must choose sensible units to measure the stock of Rn^{222} in the indoor air. Any of several units—picocuries, molecules, grams, or moles—could be used to describe our variable. Or we could divide any of these by cubic meters or by kilograms of air to obtain a variable expressed in units of concentration.

It is conceptually easiest to work with the number, N , of atoms of Rn^{222} in the house. Converting back and forth between N and activity is easily done using Eq. 1. Similarly, converting either N or activity to units of household concentration is straightforward.

The equilibrium value of N is determined by setting the rate of inflow of Rn^{222} atoms equal to the rate of outflow (see Figure II-12). The rate of inflow of Rn^{222} is determined by the source term, 1 pCi/m²sec. For a house with a foundation area of 200 m², this is 200 pCi/sec or $200 \times 0.037 = 7.4$ decays/sec². That is, Rn^{222} activity enters the house at a rate of 7.4 decays per second per second. We denote by F_{in} the rate at which atoms of Rn^{222} enter the house. Eq. 1 tells us that the number of atoms of an isotope equals λ^{-1} times the activity of that isotope. Therefore, F_{in} equals λ^{-1} times the rate at which activity due to Rn^{222} enters the house. Using the value of $T_{1/2}$ for Rn^{222} (see Section XI.1 of the Appendix) of 3.8 days, or 3.3×10^5 sec, we obtain a rate constant, λ , for Rn^{222} of $0.693/(3.3 \times 10^5 \text{ sec})$ or $2.1 \times 10^{-6}/\text{sec}$. Therefore, we determine that

$$F_{in} = \frac{7.4}{\lambda} = 3.5 \times 10^6 \text{ atoms/sec}. \quad (3)$$

15. The reason for this relation will be explained in Problem III.3. You may be able to see where it comes from by referring back to Problem I.5.

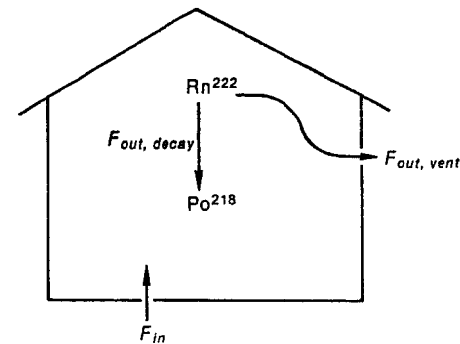


Figure II-12 The inflow and outflow of Rn^{222} for a house. There are two outflow terms: $F_{out, decay}$ describes the loss of Rn^{222} by decay to its first daughter, Po^{218} ; and $F_{out, vent}$ describes the loss of Rn^{222} with the airflow in the house as indoor and outdoor air are exchanged. F_{in} is the source term.

The outflow rate consists of two terms. The first describes loss of Rn^{222} by radioactive decay in the house. This decay rate is simply the activity $\lambda N = 2.1 \times 10^{-6} N/\text{sec}$. The second describes outflow resulting from ventilation. The ventilation rate is 0.1 air exchanges per hour. If the Rn^{222} is well mixed throughout the house, then one tenth of the Rn^{222} in the house is removed every hour as well. Hence, the second term in the outflow rate is 0.1 N/hr or $2.8 \times 10^{-5} N/\text{sec}$. Combining the two outflow terms, we find

$$\begin{aligned} F_{out} &= F_{out, decay} + F_{out, vent} \\ &= (2.1 \times 10^{-6} + 2.8 \times 10^{-5}) N \\ &= 3.0 \times 10^{-5} N/\text{sec}. \end{aligned} \quad (4)$$

The steady-state value of N can now be calculated by equating F_{in} and F_{out} :

$$3.5 \times 10^6/\text{sec} = 3.0 \times 10^{-5} N/\text{sec}. \quad (5)$$

Hence,

$$N = 1.17 \times 10^{11} \text{ atoms}. \quad (6)$$

This is the number of atoms of Rn^{222} present in the house in the steady state. The steady-state concentration, C , will equal N/V , where V is the volume of air in the house. Hence,

$$C = 1.17 \times 10^{11}/1000 = 1.17 \times 10^8 \text{ atoms/m}^3. \quad (7)$$

Multiplying by λ , the steady-state activity concentration is $2.1 \times 10^{-6} \times 1.17 \times 10^8$, or 246 decays/m³-sec. Using the definition of the curie, this is equivalent to 6.6×10^{-9} Ci/m³.

(b) The dose of radiation received in the lung of an occupant of the house depends upon the activity of the isotope in the lung. This, in turn, depends on the average number of Rn²²² atoms in the lung, which is in turn determined by the concentration of Rn²²² atoms in the indoor air. Section XV of the Appendix indicates that a typical adult male inhales 7.5 liter/min while resting and 20 liters/min while engaged in light activity. The breathing rate at rest is about 7 breaths/min, and so each breath contains about 1 liter of air. During light activity, a person takes about 13 breaths/min and so inhales about 1.5 liters of air with each breath.

Let us then assume that during the 12 hr indoors, the adult male typically has at any time about 1.2 liters of freshly breathed air in his lungs. Eq. 7 tells us that this much air will contain $1.2 \times 10^{-3} \times 1.17 \times 10^8$ or 1.4×10^5 atoms of Rn²²². Ignoring old air in the lungs, the activity of the lung air is $\lambda N = 2.1 \times 10^{-6} \times 1.4 \times 10^5$ or 0.29 decays/sec. Thus during a typical year of 12-hr days in the home, our subject's lungs will endure $365 \times 12 \times 3600 \times 0.29$, or 4.6×10^6 Rn²²² decays.

A rad of radiation dose corresponds to 100 ergs deposited per gram of tissue. To estimate the whole-body dose, we must determine the number of ergs deposited in the body and divide by the number of grams of body weight. The Appendix (XI.1) tells us that each Rn²²² decay produces an α -particle with 5.5 MeV of energy. One MeV is equivalent to 1.6×10^{-6} ergs, so 4.6×10^6 decays/yr deposits $4.6 \times 10^6 \times 5.5 \times 1.6 \times 10^{-6}$ or 40.5 ergs/yr. A typical adult male has a mass of 7×10^4 g, so the whole-body dose, in rads, is $40.5/(100 \times 7 \times 10^4)$ or 5.8×10^{-6} rads/yr.

The whole-body radiation dose received from all sources by an average person is about 0.2 rads/yr (see Section XI.2 of the Appendix). In comparison, the indoor whole-body exposure from Rn²²² calculated above is extremely small. However, the indoor Rn²²² dose is somewhat unusual. The isotope is a gas that emits α -particles. The dose we calculated is deposited entirely in the lungs, where α -particles are particularly dangerous.

The source term used here, 1 pCi/m²sec, is an average over a very wide range of conditions. Rn²²² is produced from the decay of U²³⁸, which produces a series of intermediate isotopes in a decay chain that leads to Rn²²². Because the ground distribution of U²³⁸ is heterogeneous, so is the rate at which Rn²²² enters buildings. Moreover, the rate at which Rn²²² penetrates building materials depends on the nature of those materials and the type of construction. Source rates as low as 0.1 and as high as 100 pCi/m²-sec have been observed. The effect of choosing a different source rate or a different ventilation rate can easily be analyzed with the methods presented here. (see Exercise 3, following)

A more serious difficulty with our approach to estimating the radiation dose from Rn²²² is that the major dose will result not directly from Rn²²² decay but from decay of its daughter isotopes. (The decay sequence is provided in the Appendix, (XI.1)) Po²¹⁴, an α -emitter near the end of the Rn²²² daughter sequence with a 1.6 msec half-life, poses this problem's greatest health risk. The dose from the daughters of Rn²²² is difficult to estimate because it depends significantly on their distribution within the house. While Rn²²², a gas, tends to mix uniformly throughout indoor air, the daughters do not. They are reactive and can attach to particles. By settling to the floor on large particles or attaching to walls, they escape being vented out of the house and may also escape being inhaled. On the other hand, if the daughters attach to particles of submicron dimensions, they may be breathed deeply into the lung and attach there, thus increasing the dose. All in all, reliable estimates of realistic daughter concentrations and of total doses to indoor occupants are difficult to make and require specification of more information (particularly indoor particle concentrations) than we have provided.¹⁶ Exercise 4 looks at one limiting case.

The issue of regulatory standards for indoor Rn²²² concentrations is currently under debate. Discussion is focused on the appropriateness of a permissible level of 3×10^{-9} Ci/m³. In addition, energy conservationists, aware of the potential hazards of indoor Rn²²², have become interested in heat-exchange systems for buildings that would permit air ventilation without loss of indoor heat.

EXERCISE 1: In working out our solution to the problem, what did we implicitly assume about the concentration of Rn²²² in the air outside the house? Give a qualitative argument why that approximation ought to be a good one.

EXERCISE 2: Our dose estimate did not depend on how long air remains in the lungs but only on the average amount of air that is in the lungs at any one time. Why was that the case? Under what circumstances would that independence from time not hold true?

EXERCISE 3: Consider two other houses with the same dimensions as the one here: (a) One has a higher ventilation rate of one air exchange per hour; (b) the other permits no air exchange at all, so that the only exit pathway for Rn²²² is radioactive decay. Calculate the steady-state concentration of Rn²²² activity (in Ci/m³) in these houses. Although a condition of no air exchange is unrealistic (a rate of 0.1 air exchanges per hour requires very airtight house construction and avoidance of unnecessary open-door time by the occupants), it provides a limiting case for which the Rn²²² exposure will be maximum.

16. For an excellent review of the health risks associated with indoor Rn²²², see the entire issue of *Health Physics* 45, No. 2, particularly the article by Nero (1983).

EXERCISE 4: The first daughter of Rn^{222} (i. e., its immediate decay product) is Po^{218} , with a three-minute half-life. Being the decay product of Rn^{222} , Po^{218} is formed at precisely the rate of Rn^{222} decay. In the house with a 0.1/hr ventilation rate, what will be the steady-state quantity of Po^{218} , expressed first in units of number of atoms and then in units of curies, under the assumption that none of the Po^{218} is vented from the house? Is it a numerical accident that the number of curies of Po^{218} equals the number of curies of Rn^{222} ?

* **EXERCISE 5:** If, on the average, the emission of Rn^{222} to the atmosphere from the continents is $1 \text{ pCi/m}^2\text{-sec}$ and from the oceans is zero, estimate the average concentration of Rn^{222} in the atmosphere. Qualitatively, how will the vertical distribution of Rn^{222} compare with that of N_2O ? (See Exercise 2 of Problem II.4.)

B. *Thermodynamics and Energy Transfer*

Thermodynamics is primarily the study of energy and its interaction with matter. Energy can take many forms: the energy an object has by virtue of its motion is called kinetic energy; the kinetic energy of molecules moving randomly is called heat energy; the energy required to lift or shove an object that is acted on by such forces as gravity and friction is called work; the energy available for release by dropping an elevated object is called potential energy; the energy available for release by burning substances such as coal is called chemical energy; and chemical energy, when released, often takes the form of heat energy.

The ways energy can interact with matter are likewise numerous. Energy can warm matter, melt it, freeze it, boil it, expand or contract it, scramble or unscramble it, or mutate it. The results depend on what kinds of energy and matter are involved. Despite the apparent complexity, however, a few simple and universal physical laws have been discovered that allow us to make sense of the whole story. Among these are the laws of thermodynamics. The first law states that the total amount of energy in a closed system (i.e., one which energy cannot enter or leave) remains constant, regardless of the transformations among energy types within the system. This law plays a central role in modeling both meteorological phenomena and physiological aspects of animal interactions with their environment.¹⁷ The second law, which describes constraints on the conversion of one type of energy to another, is particularly useful for evaluating the

17. Schmidt-Nielsen (1972) has written a delightful and informative book on animal physiology and physics. An excellent introduction to the subject of thermodynamics is the terse text by Van Ness (1969). *Entropy for Biologists* by Morowitz (1970) is also highly recommended.

performance of technological devices designed to convert one form of energy to another. The first six problems that follow illustrate various applications of thermodynamics. The last problem in this section, on the multiple scattering of solar radiation in the atmosphere, illustrates concepts about energy transfer in the atmosphere that are widely used in climate research.

12. Electricity from Junk Mail

At about what rate could electricity be produced by burning everybody's junk mail in the United States, assuming a conversion efficiency from heat to electricity of 30%?

.....

Three sequential questions lurk in this problem: How much junk mail would be burned, how much heat would be produced from that fuel, and how much electricity would be produced from that heat? We tackle each in turn.

In the United States we number about 7×10^7 households. Let's assume each receives as much junk mail as mine does. After weighing the ads and pleas in my mailbox for two weeks, I estimate that I am delivered about 2.0×10^4 g of paper junk mail per year. Hence, in the United States, about $2.0 \times 10^4 \times 7 \times 10^7$ or 1.4×10^{12} g/yr of paper are available for conversion to electricity.

According to Section VII.4 of the Appendix, burning paper produces about 2×10^4 J/g. U.S. junk mail would thus produce heat at an annual rate, R , of about

$$\begin{aligned} R &= 1.4 \times 10^{12} \text{ g/yr} \times 2 \times 10^4 \text{ J/g} \\ &= 2.8 \times 10^{16} \text{ J/yr.} \end{aligned} \quad (1)$$

How much electric power would this produce? The problem states that the conversion of heat to electricity proceeds at 30% efficiency.¹⁸ This means that

$$\text{rate of electricity production} = (0.3)(\text{rate of heat production}). \quad (2)$$

Electricity would be produced at a rate, R' , given by

$$\begin{aligned} R' &= (0.3)(2.8 \times 10^{16} \text{ J/yr}) \\ &= 8.4 \times 10^{15} \text{ J/yr.} \end{aligned} \quad (3)$$

A more familiar unit for the rate of electricity production (or conservation) is the watt (W), a unit of power. Power is the rate of energy flow, and a watt is defined as the flow of one joule per second. If you conserve a watt of power for a period of one second, you have conserved one joule of energy. Since there are 3.15×10^7 seconds

18. Problems II.15 and 16 delve more deeply into the subject of conversion efficiency and explain why heat-to-electricity conversion efficiency cannot be 100%.

in a year, electric energy would be produced at a rate of $8.4 \times 10^{15} / 3.15 \times 10^7 = 2.67 \times 10^8$ W. This is roughly one fourth the power output from one typical, modern, nuclear or coal-fired electric power plant.

EXERCISE 1: What fraction of the total rate of U.S. electricity production in 1980 does the answer above correspond to?

EXERCISE 2: What percentage of total world net primary productivity would have to be harvested and burned, at 30% conversion efficiency, to meet all the world's electricity needs, at the rate of electricity consumption in 1980?

* **EXERCISE 3:** In addition to his many discoveries in pure science and his useful inventions, Benjamin Franklin also was responsible for numerous social innovations. Indeed, junk mail is delivered by a postal system that was initiated in the American colonies by Franklin. He also was a pioneer in what is now called energy-impact analysis: Specifically, in his wise and jocular manner, Franklin proposed that Paris switch from standard time to daylight savings time, based on his estimate that such a scheme would save candle wax (Goodman 1956). The next time your area switches to or from daylight savings time, keep track of the amount of electric energy you use for lighting each day in your home during the week before and after the switch. (The electric energy used to light a W -watt bulb for S seconds is WS joules.)

13. How Hot Is Planet Earth?

What is the temperature of planet Earth? This is a complex question because Earth's temperature varies with time and especially with location. So, to be more specific, imagine a space traveler viewing our planet from afar. What temperature would she say Earth is?

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At the level of analysis in this problem, a precise answer to the question "How hot is Earth?" is derived. However, the answer will not be of direct relevance to our experience on Earth's surface. In later problems (III.6-9), more realistic models will be used to calculate more pertinent information, such as Earth's average surface temperature. These models will build upon the simple "core model" presented here.

Earth, continually receiving energy from the sun, would get hotter and hotter if it did not radiate energy back to space. This insight suggests that an energy conservation equation, balancing the rate of energy flow arriving at Earth against the rate of energy flow departing, might allow a calculation of the earth's temperature. To carry out this balancing act, the input and output rates are needed. Because only inputs and outputs are involved at this stage, you can ignore the complexities of atmospheric convection and the hydrocycle, which serve to redistribute energy on the wet, airy, planetary skin but do not affect the overall energy balance of the planet. Only radiant energy can be transmitted to any appreciable degree through the nearly empty space beyond Earth's atmosphere.

Consider, first, the solar input. On a flat disc perpendicular to the unimpeded sun's rays and 150×10^6 km from the sun, where Earth resides, the solar flux is $1,372$ W/m². For future reference, this important number will be denoted by the symbol, Ω . Across an average square meter above the atmosphere the flow of solar energy will not be this large. On the night side of Earth the flow will obviously be zero, and only on the point of Earth directly under the sun (for example, the equator at high noon on the equinox) will the energy flux from the sun equal Ω . The flux above the atmosphere, averaged over day and night and over all latitudes, is equal to $\Omega/4$. To see why this is so, note, first, that the ratio of the area of a sphere to the area of a disc of the same radius is $4\pi r^2/\pi r^2 = 4$. Thus, if you imagine the sun's rays making dots on the imaginary disc as they cross it, and then stretch the disc around the sphere, the dots will be one fourth as densely packed (see Figure II-13).

We must now determine the rate of outgoing energy, per unit area of the Earth's surface. If you looked at the earth from space, you

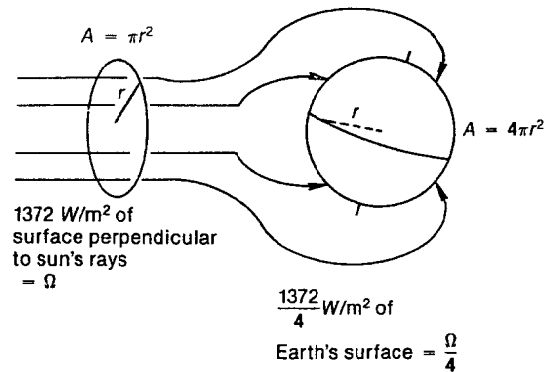


Figure II-13 The solar flux on Earth. The factor of four arises because the surface area of Earth is four times the area of a disc with a diameter equal to that of Earth. The solar flux on Earth, averaged over all latitudes and longitudes, is $\Omega/4$. The sun's rays do not, of course, strike the Earth from behind. Rather, Earth turns and the radiation is distributed over all longitudes.

would see a moon-like glow on its sunlit side. This is reflected solar radiation. Earth has a reflection coefficient, called the albedo, of about 0.30, which means that about 30% of the incident solar flux is reflected directly back to outer space. (Most of this radiation is reflected by Earth's clouds rather than the planet's surface.) The remaining 70% of the solar flux is absorbed, either in the atmosphere or by materials at Earth's surface. This absorbed solar energy is converted to infrared energy by the absorbing material. It is then emitted from Earth and radiated away to space in a form called "infrared radiation."

Thus, the outgoing energy takes two forms: reflected solar energy, and infrared radiation by objects that have absorbed such energy. The rate at which an object radiates energy away from itself depends on its temperature; the hotter the object, the greater the rate of radiation. Objects that are maximally effective radiators of energy are called blackbodies. (A glowing lump of coal is a good example.) Such objects are also perfect absorbers, which is why they are called black. The Stefan-Boltzmann Law describes the relation between the temperature of such objects and their rate of radiation. It states:

$$F = \sigma T^4. \quad (1)$$

Here, F is the radiant energy output, with units of energy per unit time per unit area, and T is the absolute temperature of the object in kelvins. The fundamental constant, σ , is given by

$$\sigma = 5.67 \times 10^{-8} \text{ J/m}^2 \text{ sec K}^4 \quad (2)$$

To a good approximation, Earth is a perfect emitter and absorber of infrared radiation, and so Eqs. 1 and 2 can be used to describe the outgoing infrared radiation.¹⁹ Thus, as shown in Figure II-14, the incoming and outgoing energy fluxes are:

$$F_{in} = \Omega/4 \quad (3)$$

$$F_{out} = a\Omega/4 + \sigma T^4,$$

where the albedo is denoted by a . Equating incoming flux to outgoing flux,

$$\Omega/4 = a\Omega/4 + \sigma T^4. \quad (4)$$

Eq. 4 implies

$$T^4 = \frac{(1-a)\Omega}{4\sigma}. \quad (5)$$

The solution to this equation is often denoted by T_0 , a quantity referred to as the blackbody temperature of Earth. Using the numerical values of Ω , a , and σ , the result is $T_0 = 255 \text{ K}$.

T_0 is not equal to the measured average temperature of Earth's surface, which is about 290 K. Earth's surface does emit infrared radiation upward, but that radiation is largely absorbed in the atmosphere

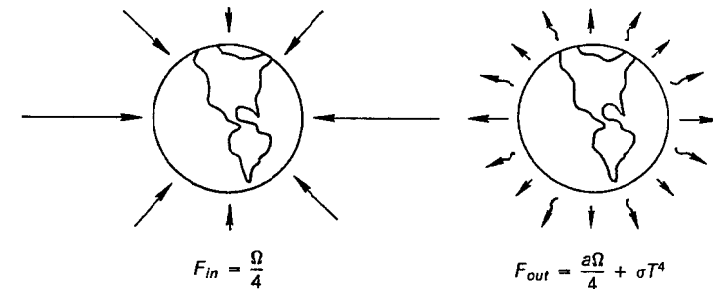


Figure II-14 The inflow and outflow of energy on Earth. Straight arrows are solar flux and wiggly ones are infrared radiation. Arrow lengths are roughly proportional to actual flows. Note that the total outflow from the polar regions is greater than the inflow, whereas the outflow from the tropics is less than the inflow. Poleward flow of heat in the oceans and atmosphere on Earth accounts for this.

19. More generally, any object radiates at a rate $\epsilon\sigma T^4$ where ϵ is a function of the wavelength of the radiation and is always ≤ 1 . An object is a blackbody in that portion of the spectrum of wavelengths for which $\epsilon = 1$.

and then reradiated within the atmosphere (see Problem III.6). Radiation emitted higher in the atmosphere has a greater chance of being radiated directly to outer space. The zone of the atmosphere that radiates directly to outer space consists of air from the mid-troposphere upward, and the density-weighted mean temperature of this zone is about 250 K, which is quite close to our calculated value of 255 K. Observed from far away, the infrared earthglow has a spectrum roughly like that of a 250-K blackbody, and thus our assumption that this planet is thermodynamically "black" is not a bad one. It must be emphasized, however, that Earth is nearly black only in the infrared range of the spectrum, not in the spectral range of sunlight. A planet that was a blackbody in the solar spectrum would have zero albedo because it would be a perfect absorber of sunlight; in contrast, Earth's albedo in sunlight is about 30%.

EXERCISE 1: Verify that Eq. 5 yields the result: $T_0 = 255$ K.

EXERCISE 2: Using the procedures presented here, we calculate an infrared blackbody temperature for Jupiter of 98 K; the measured value is 130 K. It is the only planet with such a large discrepancy. The reason is that the gravitational collapse of Jupiter's interior produces a sizeable amount of internal heat energy. Estimate the internal energy flux on Jupiter from the data above and compare it to Earth's geothermal flux, which is determined from data given in the Appendix (VII.1).

EXERCISE 3: Throughout Earth's history there have been cycles and fluctuations in the planet's average temperature. Changes in Earth's solar orbit have been proposed as one cause of these variations.²⁰ While the most important orbital modification of Earth's climate is most likely due to changes in the orientation of the tilt of Earth's axis with respect to orbital perihelion and aphelion (an effect too complicated to study with the globally averaged model presented here), a simpler phenomenon—change in the mean distance between Earth and the sun—can be studied. Assuming a circular orbit, by how much would the distance from Earth to the sun have to change in order to bring about a 1 K increase in T_0 ? Later, in the second section of Chapter III, other possible causes of climate alteration will be discussed.

EXERCISE 4: Derive the fact that the sun's blackbody temperature is 5,750 K, given the values of Ω and σ quoted above, and the information from the Appendix (IV) on the distance from the sun to Earth and the radius of the sun.

²⁰ See Ruddiman and McIntyre (1981) and Kerr (1983a) for further discussion of this hypothesis.

* *EXERCISE 5:* Imagine a very accurate, high-resolution light meter capable of measuring the light intensity reaching Earth's surface at night from the bright half of a half moon and, separately, the very faint light intensity from the "dark" half. How could you calculate Earth's albedo, knowing these two light intensities and some relevant distances?

14. Milk and Muscle

How high can you climb on a liter of milk?

.....

The chemical energy contained in the food you eat serves many functions. Some of it is used to maintain body temperature and drive bodily metabolic processes. Some is used to produce new biomass, either for net growth or to replace worn-out tissue. Some is used to perform mechanical work such as climbing a hill or pushing a wheelbarrow. And, of course, some of the chemical energy is excreted, playing a further ecological role but no longer available directly to your body. These energy expenditures are linked in a number of interesting ways. For instance, the performance of mechanical work generates internal heat; new biomass cannot be produced without the aid of energy-consuming metabolic processes; and much muscular activity performs internal work to drive circulation, digestion, and excretion.

What fraction of the energy in the food we eat can be converted to muscular work? The following qualitative argument suggests that the fraction of the food energy converted to mechanical work is small. Suppose you engage in mild exercise or physical work after a hearty breakfast. Chances are you will be hungry again in three or four hours. If you drive an automobile for three or four hours after the same breakfast, you will probably be about equally hungry. A sedentary activity burns food about as fast as a muscular one, and thus a large fraction of our caloric intake is used for "maintenance" and is not available for muscular work. Physiologists tell us that rarely is more than 25% of our caloric intake convertible to muscular work (see Exercise 4 below). To solve our present problem, I will assume a 15% conversion. The important thing is to learn how to set up the problem; if you find a better conversion rate you can redo the calculations later.

A liter of milk has an energy content of about 2.4×10^6 J (see Appendix, VII.4). To lift a mass, m , to a height, h , against the acceleration of gravity, g , on Earth requires an amount of work, W , given by

$$W = mgh. \quad (1)$$

With a conversion efficiency labeled ϵ , the amount of work that can be performed, W , is related to the food energy input, Q , by

$$W = \epsilon Q. \quad (2)$$

Assuming a mass of 50 kg, and a conversion efficiency of 15%, and using $g = 9.8 \text{ m/sec}^2$, the result is

$$\begin{aligned} h &= (\text{conversion efficiency}) (Q)/mg \\ &= \frac{(0.15)(2.4 \times 10^6) (\text{kg m}^2/\text{sec}^2)}{(50 \text{ kg}) (9.8 \text{ m/sec}^2)} = 700 \text{ m}. \end{aligned} \quad (3)$$

This is a plausible result. After an average meal (which has about 1.5 times the calorie content of a liter of milk) if you quickly climb only a few hundred vertical meters you will not feel hungry right away, whereas if you climb a thousand vertical meters in three or four hours you will feel as if you have *more* than burned up that last meal!

EXERCISE 1: (a) Express the rate at which a typical adult human being produces body heat, in units of watts, assuming 80% of the ingested calories are metabolized. (b) Using Table XV in the Appendix, calculate the resting metabolic rate of an average adult human being.

EXERCISE 2: A typical adult Alaskan brown bear (*Ursus arctos*) will enter "hibernation" weighing about 450 kg and emerge six months later having burned up about 100 kg of fat. Using Table VII in the Appendix, estimate the wintertime metabolic rate of the bear.

EXERCISE 3: It has been observed (see Schmidt-Nielsen 1972 for a review) that the resting metabolic rate of animals is proportional to the three-fourths power of body weight. Assuming that scaling relation and using the resting metabolic rate of human beings from Exercise 1, estimate the resting metabolic rate of the bear and compare that value with the metabolic rate during "hibernation" from Exercise 2. True hibernators, such as rodents, will metabolize during hibernation at a rate well below half their normal resting metabolic rate. Is the Alaskan brown bear a true hibernator?

* **EXERCISE 4:** The human body gets rid of heat produced by metabolic activity via radiation, evaporation of water (perspiration), and conduction to the surrounding air. Knowing the rate at which water is evaporated, we can estimate the rate of cooling by that process, as discussed later in Problem II.16. The Stefan-Boltzmann Law (see Problem II.13) can be used now, however, to describe radiation from a blackbody at temperature 310 K (98.6° F) to a surrounding environment. Hence, a lower limit on sedentary heat losses is obtained. It is a lower limit because only one mechanism of heat removal (radiation) is estimated. With a lower limit on heat loss, we obtain an upper limit on the fraction of our daily caloric intake available for mechanical work. Doing so is not easy, but the ambitious reader may want to attempt it. Consider that the exposed (unclad) areas of the body do most of the radiating. In addition to radiation loss from the body to the surrounding environment, there is also a radiation input to the body. Keep in mind, however, that although

sunlight can help maintain body temperature, it cannot power the tissue-building process or fuel muscular work; these processes require chemical (food) energy.

EXERCISE 5: How high can you climb on a pint of whiskey?

15. Debunking a Dynamo

Suppose somebody claims: "I have developed a heat engine that will operate by using the temperature difference between the top and bottom waters of a lake. It is a solar-powered device, since the sun's energy sustains this temperature difference. Using a lake that is 10^4 m^2 in area, and in which the temperature of the top and bottom waters are 25°C and 15°C , respectively, the engine will run for centuries. It will generate, on the average, a megawatt of electricity." Is the person telling the truth?

.....

When someone proposes a technical advance and you want to evaluate it (let alone invest in it!) it is sensible to check first whether it is compatible with the laws of nature. It is generally much easier to determine whether an hypothesized gadget violates physical principles (such as the law that information cannot be transmitted faster than the speed of light, or the law of conservation of energy) than to determine whether it will be unacceptable to society for reasons such as cost. This problem invites you to prove *unequivocally* that the engine promoter is a liar, not by showing that the proposed engine would be outrageously expensive or that it would require a backup system during a period when the lake was not stratified, but by identifying a fundamental law of nature that would be violated if the hypothesized engine existed.

Because the issue here is energy, you should look for a violation of the laws of thermodynamics. The first law states that energy is conserved, which assures us that the maximum sustained electric power output from the heat engine cannot exceed the rate at which solar energy strikes the lake surface. A megawatt of power produced over an area of 10^4 m^2 corresponds to a power density of 100 W/m^2 . This is less than the average solar flux at Earth's surface, and thus the first law of thermodynamics is not violated.

But before you reach for your checkbook and invest in the device, make sure the second law is upheld. This law takes many forms. In this case, the clue to knowing which form to use is in the statement that the device is a heat engine (such engines are also called Carnot engines) operating between two given temperatures. The device takes in heat energy from the warmer portion of the lake, at the temperature $T_H = 25^\circ\text{C}$, discharges some heat to the colder portion of the lake, at a temperature $T_C = 15^\circ\text{C}$, and produces electricity at a rate equal to the difference between the rate of heat input and the rate of heat discharge.

The efficiency, ϵ , of such an engine, is defined as

$$\epsilon = \frac{\text{rate of electric energy output from engine}}{\text{rate of heat energy input to engine}} \quad (1)$$

Dividing both the numerator and denominator by the lake area, we can use Eq. 1 to express ϵ in terms of input and output power density.

The second law of thermodynamics states that the *maximum* efficiency, ϵ_{\max} , of a Carnot engine is

$$\epsilon_{\max} = \frac{T_H - T_C}{T_H} \quad (2)$$

when T_H and T_C are absolute temperatures measured in K. This yields a maximum efficiency of the engine of $(298 - 288)/298 = 0.034$.

At this point we know the maximum value of ϵ and the power density output as predicted by the inventor. Using these data and rearranging Eq. 1, we can calculate the minimum power density input required to run the engine and compare it with the actual power density input (which must be less than or equal to the solar flux on the lake if the engine is to work). In terms of power density and rearranged, Eq. 1 becomes

$$\begin{aligned} \text{minimum power density input} &= \frac{\text{power density output}}{\epsilon_{\max}} \\ &= \frac{100 \text{ W/m}^2}{0.034} = 2941 \text{ W/m}^2. \end{aligned} \quad (3)$$

This minimum input is much higher than the daily averaged solar flux at Earth's surface, which rarely exceeds 500 W/m^2 . The inventor is not telling the truth.

EXERCISE 1: Suppose that the inventor is more modest and claims to be able to produce only 0.02 megawatts of electricity (MWe). In this case, the second law doesn't forbid the device. What efficiency would the device be working at? [Use the value for $(\Omega/4)(1 - a)$, as given in Problem II.B.13, for average surface solar flux.] If the inventor claims the device will produce 0.02 megawatts for years and years, what technical problem should you then worry about and investigate before investing in the device?

16. Cooling Off Hot Plants

At what rate is water used to cool a 1000-megawatt coal-fired power plant?

.....

Most coal-fired electricity generating plants produce electricity by means of a steam turbine. The same is true, in fact, for oil, gas, nuclear, and many solar-powered electricity generating plants. The heat from the burning coal produces steam under pressure, which is directed at turbine blades, causing them to rotate. In this way, heat energy is converted to mechanical energy. The remaining step—conversion of mechanical energy to electricity—is accomplished by taking advantage of a remarkable property of electricity: When a conducting wire is moved across the flux lines of a magnetic field, electric current flows in the wire. To take advantage of this fact, the rotating turbine shaft is wrapped with conducting wires and surrounded by a strong magnetic field. The device, called a generator, produces an electric current.

The laws of thermodynamics tell us that the first step—conversion of heat to mechanical energy—cannot be, even in principle, 100% efficient, whereas the second conversion (from mechanical to electrical energy) can be. The maximum efficiency of the heat-to-mechanical energy conversion is given by the equation (see also Problem II.14)

$$\epsilon_{\max} = \frac{T_H - T_C}{T_H} \quad (1)$$

where the hotter temperature, T_H , is the temperature of the pressurized steam, and T_C is the temperature at which condensed, "spent" steam emerges from the turbine as liquid water. If $T_C = T_H$, the efficiency would be zero, which is another way of saying that if the emerging water is as hot as the steam entering the turbine, the turbine will not turn. The steam must be cooled and thereby depressurized at the back end of the turbine if there is to be a net pressure on the turbine blades, causing them to rotate.

The actual efficiency of such a power plant will be less than the ideal, ϵ_{\max} . Inefficiencies in both conversion processes, resulting from mechanical friction, electrical resistance, loss of heat up the smoke stack, etc., result in energy loss.

For a typical coal-fired electric generating plant T_H is about 800 K, and T_C is about 300 K. The ideal efficiency, ϵ_{\max} , is thus equal to 500/800 or 62.5%. The actual conversion efficiency for a modern coal-fired electricity generating plant is about 40%, which means that

$$\frac{\text{electric power output}}{\text{rate of heat input from coal burning}} = 0.40. \quad (2)$$

The difference between the heat input and the electric output is waste heat. The rate at which this waste heat is produced, R , is

$$R = (\text{rate of heat input}) - (\text{rate of electrical energy output}). \quad (3)$$

Using Eq. 2 we can rewrite this as

$$R = \frac{(\text{electric power output})}{0.40} - (\text{electric power output}). \quad (4)$$

For a 1000-megawatt (MWe) electricity generating plant,²¹ this becomes

$$\begin{aligned} R &= 1500 \text{ MW} \\ &= 4.7 \times 10^{16} \text{ J/yr.} \end{aligned} \quad (5)$$

Typically, about 15% of this waste heat is removed via the smoke-stack, in the form of hot effluent gases. The remaining 85%, or 4.0×10^{16} J/yr is the heat that must be discharged from the turbine by some cooling process in order to maintain T_C at 300 K (see Figure II-15). Three methods are available to accomplish this cooling:

(1) Once-Through Cooling In this process, cool water flowing past the power plant and through the turbine condenser is warmed by the waste heat and then discharged to the environment. Sea, river, or lake water is used for such a purpose. If the cooling water enters at, for example, an average temperature of 290 K, then it will typically be heated by about 10 K (to 300 K) as it passes through the turbine condenser. The rate at which such water must flow through the system can then be calculated. It takes 1 cal, or 4.18 J, to heat 1 g of water 1 K. The 4.0×10^{16} J ($= 9.6 \times 10^{15}$ cal) that must be discharged every year will heat 9.6×10^{15} g of water by 1 K, or 9.6×10^{14} g of water by the required 10 K. In other words, about 10^{15} g of water per year ($32 \text{ m}^3/\text{sec}$) will flow through the turbine condenser and then be returned, warmed, to the local environment.

(2) Wet-Cooling Tower In this process, water is evaporated from the fins of a huge tower. Heat is expended to evaporate liquid water; this heat is removed from the site where the liquid water was, and therefore this site is cooled. Because the heat used to evaporate water is far more than one calorie per gram, a much smaller quantity of water is needed for this process than for once-through cooling. The water used is not returned to the local environment. Most of the evaporated water is likely to condense from vapor back to liquid and precipitate far downwind, and only a small fraction appears as fog in

21. The unit, MWe, is often used for the power output of an electricity generating plant. MWe stands for megawatts of electricity.

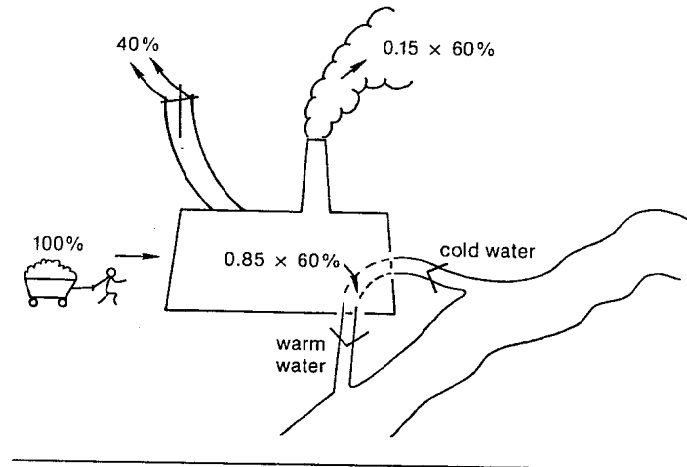


Figure II-15 The energy budget for a coal-fired electricity generating plant.

the vicinity of the cooling tower.²² The rate at which water will be consumed in the wet-cooling-tower process roughly equals the rate of waste-heat removal, 9.6×10^{15} cal/yr divided by the number of calories per gram of water evaporated. The latter is called the heat of vaporization of water. The Appendix (VI.1), gives this constant as 587.7 cal/g if the liquid water is at a temperature of 290 K. Hence, 9.6×10^{15} cal/yr divided by 587.7 cal/g(H_2O), or 1.6×10^{13} g(H_2O)/yr must be consumed by this process for a 1000-MWe coal-fired electricity generating plant.

(3) Dry-Cooling Tower In this process, the only water that is used flows in a closed cycle in the cooling tower. The scheme operates somewhat like the cooling system in an automobile, in which the water is cooled by air blown past the water in a radiator.

The environmental and economic trade-offs among these three processes are important. Once-through cooling results in thermal pollution—the returned water is 10 K warmer than the source water. Because the river or lake to which the water is returned will be warmer as a result of the thermal discharge, biological effects may occur. Also, the rate of evaporation from that water body will increase somewhat as a result of the higher temperature. Because the volume of water needed to flow past the power plant is large, large numbers of aquatic organisms in that water may be physically damaged during their passage through the cooling condenser. If an adequate year-round water supply is not present, a reservoir may have to be constructed, at potentially enormous ecological risks. The wet-cooling-tower approach is more costly and results in the local consumption of

22. When the vapor later condenses back to liquid water, the heat used to evaporate the water reappears at the site of condensation.

water, which may be more harmful, environmentally, than the withdrawal and return of water to a local source. On the other hand, this cooling technique results in no discharge of heat to local waters (i. e., no thermal pollution). Moreover, the lower withdrawal requirements of the wet-tower method are less likely to necessitate reservoir construction. Dry cooling is the most expensive and the most environmentally benign of the three approaches, although it does slightly lower the overall efficiency of the power plant, thus necessitating the burning of more fuel to produce a given amount of electricity.²³

EXERCISE 1: What percentage of the total annual runoff from the 48 coterminous states of the United States (the "lower 48") would have to be withdrawn for once-through cooling if all U.S. electricity demand in 1980 were to be met by coal-fired power plants using this cooling process?

EXERCISE 2: About 10 cm of precipitation falls each year in much of the dry southwestern United States, where new coal-fired power plants are being constructed. The rate at which water is consumed by a 1000-MWe coal-fired, wet-tower-cooled power plant corresponds to the precipitation rate over what land area?

EXERCISE 3: A nuclear power plant of the light-water reactor variety operates at about 32% efficiency. (The reactor is less efficient than a coal-fired plant because, for safety reasons, it uses a lower T_H .) Such a nuclear plant ejects practically none of its waste heat to the atmosphere, while in contrast a fossil-fuel fired plant ejects about 15% of its waste heat out the smokestack. For a given electrical power output, and for either wet-tower or once-through cooling, what is the ratio of the water requirement of the nuclear plant to that of the coal-fired plant?

EXERCISE 4: A once-through-cooled power plant would require far less cooling water if the water it did use were heated by much more than 10 K. What thermodynamic consideration tends to make this strategy unattractive?

EXERCISE 5: It takes energy to pump non-artesian groundwater up to the surface. Is it possible that an electrical power plant could require more water to cool it than could be pumped out of the ground by the plant's electrical output? To be specific, consider a wet-tower-cooled, coal-fired power plant and calculate the maximum water-table depth from which the cooling water requirement of the plant could be pumped if all of the electrical output were used only to pump groundwater for cooling. Assume that electric pumps can lift water with 90% efficiency.

23. These issues are discussed in more detail in Harte and El-Gasseir (1978).

17. When Waters Mix

If Mediterranean Sea water were allowed to flow into the Dead Sea, electric power could be derived in two ways. First, because the surface of the Dead Sea is about 400 m below the surface of the Mediterranean Sea, electrical energy could, in principle, be produced from falling water. Second, because on a weight-per-weight basis the Dead Sea is about 28% saline (only about 30% of which is common NaCl) and the Mediterranean Sea is about 3.8% saline, energy could, in principle, be derived from "entropic mixing." Suppose Mediterranean Sea water were to flow into the Dead Sea at a rate of $10^9 \text{ m}^3/\text{yr}$ and that the two energy conversion processes could be tapped at maximum thermodynamic efficiency. At what rate could electricity be derived from each?

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The notion of "entropic mixing" may be unfamiliar to you, but it will be explained shortly. Let's begin with the first method of deriving electric power because it is easier to understand. The rate at which electrical energy can be derived from falling water is deducible from Eq. 1 of Problem II.14. We need simply recall that the work needed to lift a mass, m , to a height, h , is equal to the energy that can be tapped when that mass falls the same vertical distance. The energy will be in the form of kinetic energy, which is convertible under ideal circumstances (no heat losses from, for example, friction) to electrical energy at 100% efficiency. In our problem the amount of energy that can be generated in one year by this gravitational source, E_{grav} , is given by

$$E_{grav} = mgh. \quad (1)$$

Substituting numerical values,

$$\begin{aligned} E_{grav} &= 10^9 \text{ m}^3(\text{H}_2\text{O}) \times \frac{10^3 \text{ kg}(\text{H}_2\text{O})}{\text{m}^3(\text{H}_2\text{O})} \times 9.8 \frac{\text{m}}{\text{sec}^2} \times 400 \text{ m} \\ &= 3.9 \times 10^{15} \text{ kg m}^2/\text{sec}^2 = 3.9 \times 10^{15} \text{ J}. \end{aligned}$$

Because this much electric energy is producible in one year, the rate of electricity production, p_{grav} , is

$$p_{grav} = \frac{3.9 \times 10^{15} \text{ J}}{3 \times 10^7 \text{ sec}} = 1.3 \times 10^8 \text{ W}. \quad (2)$$

Calculation of the rate of production of energy from entropic mixing, p_{ent} , is a bit less straightforward. The idea is as follows. Entropy is a measure of how well mixed things are. Seawater is a mixture of salt and water (plus other chemicals that we can ignore here). It has a higher entropy than the water and salt would have if they were separated from each other. One form of the second law of thermodynamics states that it requires energy to reduce the entropy of a system. This is the reason why a desalination plant requires energy to operate: It converts high-entropy seawater into a lower entropy state consisting of pure water plus salt. By the same token, the mixing of salt and water (or water of two different salinities) can generate energy.

How large is the effect? Let's first take a little detour to calculate the minimum amount of energy needed to remove salt from a sample of salt water. One procedure for doing so consists of pushing the salt out with a semipermeable membrane through which water, but not salt, passes (see Figure II-16). The salt ions in the water behave as the molecules of a dilute gas; they obey the gas law

$$PV = nRT, \quad (3)$$

where P equals the pressure of the ions (called the ionic pressure), V is the volume of the sample of seawater, n is the number of moles of salt ions present, R is a fundamental physical constant equal to 8.31 J per mole per K, and T is the temperature in K.

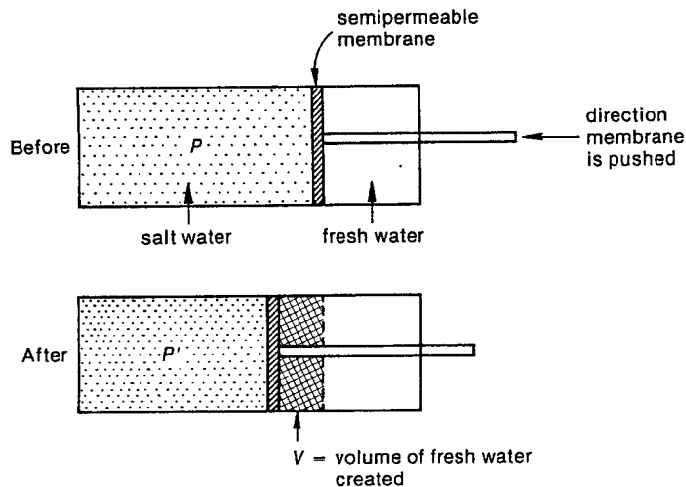


Figure II-16 Idealized representation of a desalination apparatus. As the piston with the semipermeable membrane is pushed to the left, salt and water are separated. If the volume of salt water is large compared to the volume of fresh water created, then the ion pressure, P , before will be nearly equal to the ion pressure, P' , after. Hence, the amount of work needed to push the piston in will equal PV .

Consider 1 m^3 of typical seawater, which has a salt content of 35 parts per thousand or 3.5% (by weight) and a density of $1.025 \times 10^3 \text{ kg/m}^3$. This sample will have a mass of 1,025 kg while the mass of salt ions in the cubic meter of seawater will be $1,025 \times 0.035$ or 36 kg. Suppose the only salt in the water is common table salt, NaCl. NaCl has a molecular weight of about 58.5, and there will be one mole of Na^+ and one mole of Cl^- for every mole of NaCl. Thus²⁴

$$n = 2 \times \frac{36 \times 10^3 \text{ g/m}^3}{58.5 \text{ g/mole}(\text{NaCl})} = 1.23 \times 10^3 \text{ moles}(\text{Na}^+, \text{Cl}^-)/\text{m}^3. \quad (4)$$

Therefore, at the average surface temperature on Earth, 290 K,

$$P = \frac{\left(1.23 \times 10^3 \frac{\text{moles}}{\text{m}^3}\right) \times \left(8.31 \frac{\text{J}}{(\text{mole})(\text{K})}\right) \times (290 \text{ K})}{1 \text{ m}^3} \quad (5)$$

$$= 2.96 \times 10^6 \text{ J/m}^3.$$

Since a newton-meter is a joule, this can be rewritten as a more familiar expression for pressure in units of force per unit area:

$$P = 2.96 \times 10^6 \text{ N/m}^2. \quad (6)$$

Atmospheric pressure at Earth's surface is $1.013 \times 10^5 \text{ N/m}^2$, so the pressure we have calculated is 29 times that of the atmosphere at sea level. In other words, the pressure of salt ions in seawater would be approximately 29 times the pressure of the atmosphere at sea level if all the salt were NaCl.

From Eq. 6 an approximate value for the minimum energy needed to desalinate seawater can be calculated. The amount of work required to push against a pressure, P , through a volume, V , is PV . Therefore, to clear the ions out of a cubic meter of seawater by pushing a semipermeable membrane through the water sample requires $2.96 \times 10^6 \text{ J/m}^3 \times 1 \text{ m}^3$ or $2.96 \times 10^6 \text{ J}$. This is equivalent to 2.9 J/g (seawater).

Why is this the *minimum* energy required to desalinate water? If a semipermeable membrane is pushed through an isolated cubic meter of seawater, then the salt concentration will gradually increase on the forward side of the membrane. Eqs. 5 and 6 will then be incorrect, because the concentration will continually increase forward of the membrane, exceeding the value of 3.5% salt concentration on which the calculation was based. The higher salt concentration will lead to a greater pressure, thus requiring more work to push it out of

24. Seawater actually contains other salts besides NaCl, so Eq. 4 is only approximate (see Exercise 1).

the way with the membrane. The value calculated here, $2.96 \times 10^6 \text{ J/m}^3$, is an ideal thermodynamic limit. It is most realistic when the total volume of seawater (of which the cubic meter sample to be desalinated is a part) is very large. In that case, the salt ions pushed forward by the membrane are diluted by a large volume of water, and the increase in pressure is negligible.²⁵

Now back to our problem. The difference in ionic pressure between the Mediterranean Sea water and the Dead Sea water can, in principle, be used to produce energy. A number of schemes for doing so are described in the technical literature [see, for example, Olsson et al. (1979) and references therein]. Details about the scheme are not important to us, though, because we only want to know the theoretical *maximum* rate at which energy can be derived. A thermodynamic process like desalination that uses energy requires the least energy when the process is carried out slowly in a reversible manner. Similarly, the amount of energy that can be derived from a process such as the mixing of solutions with different salinities is maximum when that process is carried out slowly and in a reversible manner. Because the mixing of solutions with different salinities is the reverse of the process of desalination, the *maximum* rate at which energy can be derived from the mixing of solutions equals the *minimum* energy needed to unmix those solutions. Hence, we can use the result above on the minimum energy required for desalination to derive the maximum energy that can be obtained from entropic mixing of waters with different salinities.

The difference in salt concentration between the Mediterranean and Dead Sea waters is 28% - 3.8%, or about 24%. This is 24/3.5 or 6.9 times the difference between the concentration of ions in seawater and fresh water. Using our calculated seawater ionic pressure of 29 atmospheres, the Mediterranean-Dead Sea ionic-pressure difference is 29×6.9 , or 199 atmospheres.²⁶

Next, we have to determine the rate at which energy can be derived from this pressure difference. To do this, we will calculate the height to which a column of water could be raised by the energy the pressure difference represents. One atmosphere of pressure corresponds to the pressure of a column of fresh water of height, h , where

$$\rho gh = 1.013 \times 10^5 \text{ N/m.} \quad (7)$$

25. For further discussion of this, see Harte and Socolow (1971). Van Ness (1969) gives a good general discussion of the conditions under which ideal thermodynamic limits apply.

26. The proportions of the various salt species in the Dead Sea are different from those in the Mediterranean Sea or in typical ocean waters. Moreover, as salt concentration gets large, ionic pressure is not simply linearly proportional to that concentration. For these reasons, the estimate of 199 atmospheres and the calculation in Eq. 9 are only approximate.

In this expression, ρ is the density of water (10^3 kg/m^3) and g is the acceleration of gravity (9.8 m/sec^2). Solving Eq. 7 for h , we obtain

$$h = \frac{1.013 \times 10^5}{9.8 \times 10^3} = 10.3 \text{ m.} \quad (8)$$

Therefore, a pressure difference of 199 atmospheres corresponds to a water-column height of 199×10.3 or 2,048 meters, which is 2,048/400 or 5.1 times as high as the elevation difference between the two seas. In other words, 5.1 times more power can, in principle, be derived from entropic mixing of these two waters than directly from falling water as calculated in Eq. 2. Hence

$$\begin{aligned} p_{ent} &= 5.1 \times p_{grav} \\ &= 5.1 \times 1.3 \times 10^8 \text{ W} \\ &= 6.6 \times 10^8 \text{ W.} \end{aligned} \quad (9)$$

Actually, tapping the energy from entropic mixing is much more difficult than tapping energy directly from the elevation difference. Membranes exist that can accomplish the task of converting a salinity difference into a pressure difference, but they cannot function at the ideal thermodynamic limit we have calculated. By the same token, if water were to be channeled and tunneled from the Mediterranean to the Dead Sea, frictional losses along the way would reduce the power derived from that source as well. What we have calculated here is an ideal thermodynamic limit for each of the two processes. Technology today is far closer to tapping p_{grav} than p_{ent} at an efficiency close to the thermodynamic limit.

EXERCISE 1: Correct Eqs. 4 and 5, by including the total Na, Cl, Mg, and S concentrations of seawater (see Appendix (VIII)).

EXERCISE 2: Water bodies like the Dead Sea have a high salt concentration because they have no outlet. Water flows into them, in the form of runoff bearing salts from the surrounding land, and exits mainly by evaporation. This exiting water is extremely pure (distilled). Thus, salts are left behind and become quite concentrated over time. If the Jordan River, historically the main inflow to the Dead Sea, is to be partially diverted for irrigation water, leaving Mediterranean inflow as the Dead Sea's major water source, what factors would govern the maximum allowable rate of inflow of Mediterranean water? First consider maintenance of water volume. The area of the Dead Sea is about $1,050 \text{ km}^2$. (a) Using the fact that 1.5 m of water evaporates from the Dead Sea's surface each year, determine what fraction of the Jordan River inflow would have to be diverted if there is inflow of Mediterranean water at a rate of $10^9 \text{ m}^3/\text{yr}$ and water volume remains

constant. (b) Next consider salt buildup in the Dead Sea. The volume of water in the Dead Sea is 136 km^3 . In how many years would inflow of Mediterranean seawater at a rate of $10^9 \text{ m}^3/\text{yr}$ result in a doubling of the salt content of the Dead Sea?

18. Bouncing Sunbeams

A layer of clouds has a light reflection coefficient (albedo) of 0.5 and a transmission coefficient of 0.4. It lies above a patch of Earth's surface with an albedo of 0.1. The air between clouds and earth transmits solar radiation perfectly. What is the albedo of the combined cloud-surface system?

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When solar radiation strikes a layer of material in the atmosphere, it can undergo three possible processes. Some of the incident flux will be reflected back to outer space from the material; some will either be transmitted unaffected through the material or will scatter off the material without a change in wavelength; and some will be absorbed in the material and converted to infrared radiation. Denote the fractions of the incident flux that are reflected, transmitted, and absorbed by symbols R , T , and A , respectively. The sum of $R + T + A$ is equal to one because reflection, transmission, and absorption are the only fates that can befall the incident light. R , the reflection coefficient of the layer, is often called the albedo; T is the transmission coefficient; and A is the absorption coefficient. All three are called optical coefficients.

Layers of material above or below a given layer also reflect, transmit, and absorb light. A pair of layers will bounce light back and forth between them like kids playing catch. However, some of the throws (to pursue the analogy) are not returned (i.e., not reflected) because the ball is either missed (i.e., transmitted) or caught and transformed into another condition (i.e., absorbed). To calculate the total reflection, transmission, or absorption by the two layers requires a mathematical summation of a series of sequential effects. The procedure used is the multiple scattering method illustrated below for the case where the top layer is a cloud layer and the bottom one is Earth's surface (see Figure II-17).

First let's estimate upper and lower bounds to the answer. The albedo of the combined system is the ratio of the rate at which light is reflected back to space to the rate at which light is incident on the combined system. Because the top layer has an albedo of 0.5 and the combined system cannot reflect less light than the top layer does, we expect that the albedo of the combined system will be greater than 0.5. A lower bound is thus 0.5. The rate at which light is reflected from Earth's surface is the albedo of that surface times the rate at which light hits it. Because the top layer both prevents some of the incident light from striking Earth's surface and also absorbs some of the light reflected from that surface (so that not all the reflected light

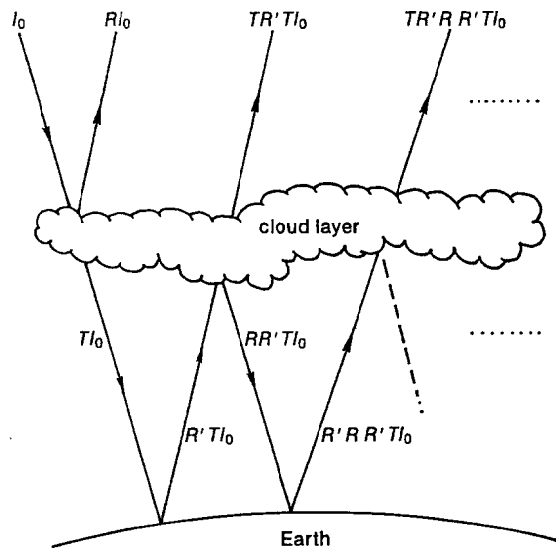


Figure II-17 The multiple scattering of the solar flux between Earth's surface and a cloud layer. I_0 is the incoming flux; R and R' are the reflection coefficients of the layer and of Earth's surface, respectively; T is the transmission coefficient of the layer.

reaches outer space), the albedo of the clouds and earth combined should be less than $0.5 + 0.1 = 0.6$. An upper bound is therefore 0.6. To obtain more precise values than these we must set up the problem properly.

Let R , T , and A be the optical coefficients for the top layer (clouds) and R' , T' , and A' be the optical coefficients for the bottom layer (Earth's surface). According to the problem statement, $R = 0.5$ and $T = 0.4$; thus $A = 1 - 0.5 - 0.4 = 0.1$. Because no light penetrates through Earth's surface, $T' = 0$. Since $R' = 0.1$, A' must equal 0.9.

Consider, now, an incident solar flux of intensity I_0 . On its first pass through the cloud layer, a flux of strength RI_0 will be reflected directly back to outer space and a flux of strength TI_0 will be transmitted to Earth's surface. Of the flux TI_0 transmitted to Earth's surface on the first pass, a fraction, R' , will be reflected and A' absorbed. Thus, a flux of strength $R'TI_0$ will hit the cloud layer from below. At this point we have to assume that the optical properties of the cloud are the same whether measured from the top or the bottom (see Exercise 4). Assuming this, a portion of this upward flux, of magnitude $TR'TI_0$, will be transmitted through the cloud to outer space and will contribute, along with that first reflected flux, RI_0 , to the albedo of the combined system. At this point, the reflected flux is $RI_0 + TR'TI_0$.

As Figure II-17 shows, a fraction, R , of the upward flux, $R'TI_0$, is reflected back down to Earth's surface. Again, some of this is absorbed and some reflected back up. Continuing in this way, the total flux, F , sent back to outer space is²⁷

$$F = RI_0 + TR'TI_0 + TR'RR'TI_0 + TR'RR'RR'TI_0 + \dots \quad (1)$$

This infinite sum can be written in the form

$$F = RI_0 + TR'[1 + (RR')^1 + (RR')^2 + \dots]TI_0. \quad (2)$$

A commonly used notation for the term in brackets is

$$[1 + (RR')^1 + (RR')^2 + \dots] = \sum_{i=0}^{\infty} (RR')^i. \quad (3)$$

In general, the following relation holds:

$$\sum_{i=0}^{\infty} (X)^i = \frac{1}{1 - X}, \quad (4)$$

if X is less than 1. Because optical coefficients like R and R' are fractions, they, and therefore their product, are less than 1. So, we can write

$$\begin{aligned} F &= RI_0 + \sum_{i=0}^{\infty} (RR')^i T^2 R' I_0 \\ &= RI_0 + \frac{T^2 R' I_0}{1 - RR'}. \end{aligned} \quad (5)$$

The albedo of the combined system is the ratio of the total flux reflected to outer space, F , to the incident flux, I_0 . Thus, dividing the above by I_0 , we obtain

$$\text{combined albedo} = R + \frac{T^2 R'}{1 - RR'}. \quad (6)$$

Upon insertion of numerical values, this yields

$$\text{combined albedo} = 0.5 + \frac{(0.4)^2(0.1)}{1 - (0.5)(0.1)} = 0.52.$$

27. We follow here the approach of Rasool and Schneider (1971).

EXERCISE 1: For our rough guess, we argued that the combined albedo should be greater than or equal to R and less than or equal to $R + R'$. Show that, indeed, Eq. 6 implies a combined albedo that satisfies these inequalities for any values of the optical coefficients R , R' , and T .

EXERCISE 2: Suppose a cloud layer with the same optical coefficients as above ($R = 0.5$, $T = 0.4$) lies above a region of Earth with a surface albedo of 0.8 instead of 0.1. What is the combined albedo of the cloud-surface system? Referring only to this albedo effect, consider how reflecting material in the atmosphere influences Earth's surface temperature. In particular, how does this influence differ between the polar regions and the temperate zone? What considerations other than albedo effects might be relevant to this difference?

EXERCISE 3: Derive general formulas for the fraction of the incident solar flux (a) absorbed at Earth's surface (f_s) and (b) absorbed in the cloud layer (f_c), and evaluate those quantities for the special case in which $R = 0.5$, $T = 0.4$, and $R' = 0.1$. Show that, in general, the total reflected flux plus the total absorbed flux equals the incident flux.

EXERCISE 4: Suppose two cloud layers (or a cloud layer and a layer of particles in the atmosphere) lie one above the other. One has optical coefficients of R , T , and A and the other of R' , T' , and A' . Ignore Earth's surface and considering the two layers as an isolated system (or, equivalently, let the absorption coefficient of Earth's surface equal 1), calculate the albedo of the two-layer system for two cases: (a) with the light encountering first the unprimed (R , T , A) system, with the primed (R' , T' , A') system behind it, and (b) the other way around. Does the albedo of the combined system depend on which layer the incident flux strikes first? Without doing any calculations, show how you could have reached your conclusion by considering a limiting case. To solve Problem II.18, we assumed that the optical coefficients of the cloud layer were the same, whether viewed from the top or the bottom. What does the result of this exercise tell you about the conditions under which that assumption would be invalid?

* **EXERCISE 5:** Pollution of the atmosphere with carbon soot particles of roughly a micron or smaller diameter is a major concern today.²⁸ In areas of the world once thought to be free of pollution, such as the Arctic, the atmospheric concentration of these fine particles of carbon soot is comparable to that in some urban areas of the United States. Arctic soot is believed to be produced by combustion

28. See, for example, Rosen et al. (1981).

of fossil fuel in the northern hemisphere. Soot in the atmosphere absorbs sunlight. If the soot lies above a region of Earth with high albedo (such as a region with low-lying clouds or the icy Arctic), it lowers the overall albedo of the region (see Exercise 2) by absorbing some sunlight before it gets a chance to reflect off the shiny surface below and by allowing less of the sunlight that penetrates to the surface to reach outer space again after reflection off the shiny material below. This tends to warm the Earth. On the other hand, if the high soot absorbs much of the incident sunlight, then less reaches the surface and the surface cools down. If the soot lies below the reflecting materials in the atmosphere, then the overall decrease in albedo should be less than if it lies above them.

To explore the interplay of these possibilities, consider a region of Earth with a surface reflection coefficient, R'' , and an absorption coefficient, $A'' = 1 - R''$. Let the atmosphere have a reflection coefficient, R' , equal to 0.26 and an absorption coefficient, A' , of 0.23. (Both these values are good averages for Earth's atmosphere.) Finally, let a layer of particulates with a reflection coefficient, R , of zero and an absorption coefficient, A , reside in the atmosphere. Consider the following cases:

	High particles			Low particles		
	$A = 0$	$A = 0.1$	$A = 0.5$	$A = 0$	$A = 0.1$	$A = 0.5$
$R'' = 0.16$						
$R'' = 0.5$						

The case of the high particles can be treated by letting the unprimed layer lie above the primed; for the low-particle case, these are reversed. The case $R'' = 0.16$ corresponds to the globally averaged surface reflectivity, while an R'' of 0.5 is typical for the north polar region. For all 12 cases, calculate (a) the value of the total albedo, a , of the region, and (b) the fraction of the region's incident sunlight that is absorbed at the surface.

From your results, what can you say about the effects of surface albedo and particulate altitude on the changes in total albedo and fraction of sunlight absorbed at Earth's surface? Remember that when $A = 0$, no particles are present. Would high or low particles be more likely to warm the Earth?

Later on, after reading Problem III.6, you will have access to a climate model that will enable you to analyze quantitatively the effect of the interplay of albedo and surface absorption on surface temperature.

* **EXERCISE 6:** Our treatment in Problem II.18 of multiple scattering between a cloud layer and the surface of Earth involved one major oversimplification, alluded to in the opening paragraph. As