Bioenergetics

In Chapter 8 (Thermodynamics), we find the maximum theoretical efficiency of a heat engine, in turning heat to work\(^1\), to be

\[ \eta_{\text{Carnot}} = \frac{T_\text{H} - T_\text{L}}{T_\text{H}}. \]

Since the upper temperature (body internal temperature) is about 310 °K and the exterior temperature is—in cold weather—about 273 °K, the absolute maximum efficiency is about 12%. Including the effects of heat leaks, friction and the need to have a reasonable power-to-weight ratio, the expected efficiency would be no better than half that (and worse on hot days!). However, from measurement of work output and food input, we discover the human being is about 25% efficient in converting food energy to work. The conclusion is inescapable: living organisms are not heat engines.

1. **Energy input to living organisms**

   How does a living organism get its energy? As with all other things biological, Nature provides a small machine (actually, a series of small machines). In this case it is an energy-storing molecule called adenosine tri-phosphate (ATP) that is constructed in the cellular energy factory (the mitochondrion, a tubular organelle present in all cells) using the energy from oxidation of sugar (glucose). The ATP molecule gives up one of its phosphate groups to a molecule that needs to be promoted to a higher energy state, thereby becoming adenosine bi-phosphate (ADP). About 11.5 kcal/mol can be provided by this maneuver, or about 0.5 eV per reaction\(^2\).

The oxidation of food provides energy as shown in the table below:

<table>
<thead>
<tr>
<th>Food</th>
<th>Kcal/gm(food)</th>
<th>L(CO(_2))/gm(food)</th>
<th>Kcal/L(O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipid (fat)</td>
<td>9.3</td>
<td>139</td>
<td>4.7</td>
</tr>
<tr>
<td>Protein</td>
<td>4.0</td>
<td>0.75</td>
<td>4.5</td>
</tr>
<tr>
<td>Alcohol</td>
<td>7.1</td>
<td>0.97</td>
<td>4.9</td>
</tr>
<tr>
<td>Sugar</td>
<td>3.8</td>
<td>0.74</td>
<td>5.1</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>4.1</td>
<td>0.81</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The interesting column is the energy output per liter of oxygen consumed: the numbers are almost constant. This is the reason why oxygen consumption can be used to measure basal metabolism, the rate of energy consumption needed to just sustain the processes of life, with no significant muscular or cognitive activity taking place\(^3\).

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1. In principle stoechiometric combustion of food with oxygen is 100% efficient in converting chemical energy to heat, so we neglect inefficiencies in the burners of heat engines.
2. An electron volt is the energy gained by letting an electron move across a potential difference of one volt. Since the electron charge is \(1.6 \times 10^{-19}\) Coulombs, and since \(1\) Coulomb \(\times 1\) Volt = 1 Joule, 1eV is \(1.6 \times 10^{-19}\) J.
3. As we shall see subsequently, the brain consumes significant amounts of energy during periods of intense concentration.
2. **Energy demand of organs**

We can easily estimate the power required to run the human heart. Basically we use the enthalpy, which for a moving fluid is

\[ h = \frac{1}{2} \rho v^2 + p + \rho gz. \]

The stream of blood leaving the heart has net pressure increment 60 mm (of Hg) or about \( 8 \times 10^4 \) dyne/cm\(^2\). When blood returns to the heart through the vena cava, its pressure is is basically the diastolic (gauge) pressure of the body and the speed of flow is roughly the same as that of the exiting blood. The height is the same so there is no change in potential energy. Therefore the amount of work done per unit time must be

\[ P = \Delta p \frac{dV}{dt}. \]

The volume of the ventricle is about 100 cm\(^3\) so assuming 60 beats per minute (that is, one contraction per second) we get

\[ P = 8 \times 10^4 \times 100 = 10^7 \text{erg/sec} = 1 \text{ Watt}. \]

Larger hearts, faster beats or higher blood pressures can double this. If we multiply by 4 or 5 to account for the inefficiency of converting chemical energy to work we find about 5-7 Watts or 90-120 Calories per day is needed to keep the heart pumping. This is only a few percent of our basal metabolic power demand.

What about the energy demand of kidneys? The thermodynamic potential of a concentration difference across a permeable membrane\(^4\) is

\[ \Delta E = RT \ln \left( \frac{c_2}{c_1} \right) \]

so that if the rate of transfer of material (in moles per unit time) is \( \frac{dv}{dt} \), the power needed is

\[ P = \frac{dv}{dt} RT \ln \left( \frac{c_2}{c_1} \right). \]

The logarithm of concentration ratio is a number of order 1; the average flow through the kidneys is 125 cm\(^3\)/sec, or about 1/8 of a liter of fluid per second. Assuming the material that must be either held back (or eliminated into the bladder) is about 0.1 molar in concentration, we get

\[ \frac{dv}{dt} = 0.0125 \text{ gm–mol/sec}. \]

Thus the average power demand is about 30 W, or about 660 Cal/day. That is, the energy required to operate our kidneys is a non-trivial fraction of the total energy budget of the human body.

Suppose we apply a different method for estimating energy requirements, based on the measured blood flow to various organs in the resting human being.

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4. That is, the energy needed to maintain a concentration gradient against the process of diffusion in the opposite direction.
If we assume the energy requirements of each organ system in the table below is proportional to the blood volume that circulates through it, then we find the results shown in the third column of the table:

<table>
<thead>
<tr>
<th>System</th>
<th>Flow* (ml/min)</th>
<th>Metabolism (Kcal/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liver, intestines, spleen</td>
<td>1400</td>
<td>480</td>
</tr>
<tr>
<td>Kidneys</td>
<td>1100</td>
<td>380</td>
</tr>
<tr>
<td>Brain</td>
<td>750</td>
<td>260</td>
</tr>
<tr>
<td>Heart</td>
<td>250</td>
<td>90</td>
</tr>
<tr>
<td>Skeletal muscles</td>
<td>1200</td>
<td>410</td>
</tr>
<tr>
<td>Skin</td>
<td>500</td>
<td>170</td>
</tr>
<tr>
<td>Other organs</td>
<td>600</td>
<td>210</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>5800</strong></td>
<td><strong>2000</strong></td>
</tr>
</tbody>
</table>


We see that our estimate for the heart (based on work output) is very close to that based on blood flow through the coronary arteries feeding the heart muscle. Our estimate for the kidneys was somewhat high, but considering that the concentration ratio \( c_2 / c_1 \) and the absolute concentration of dissolved substances were only “guess-timates”, the agreement seems remarkably good.

The energy demand of the resting brain, 12 W or 260 Kcal/day seems rather small. Measurements of blood flow to various parts of the brain, as well as of its heat output, yield comparable numbers for energy demand. However, when the brain is most active, as during periods of intense concentration on difficult problems (for example, the homework in this course), its demand rises 20-fold.

3. **Heating and cooling**

There are three mechanisms of heat loss by the body:

a) radiation;

b) conduction;

c) convection/evaporation.

Bodies radiate and absorb electromagnetic energy (black-body radiation) according to the Stefan-Boltzmann law,

\[
P = \sigma A T^4
\]

where \( A \) is the radiating area, \( T \) the absolute temperature (in °K), and the Stefan-Boltzmann constant \( \sigma \) is

\[
\sigma = \frac{2\pi^5 k^4}{15 \hbar^3 c^2} = 5.7 \times 10^{-8} \text{ Watts/m}^2/°\text{K}^4.
\]

A perfect (“black”) radiator can be shown theoretically to be a perfect absorber. Thus if an object of area \( A \) and temperature \( T_2 \) is situated with an enclosure whose temperature is \( T_1 \), it will radiate energy at a rate


6. One of the early triumphs of quantum mechanics was the calculation of \( \sigma \) from first principles, in terms of the speed of light, \( c \), Boltzmann’s constant \( k \) and Planck’s constant \( \hbar \). Because this derivation is important, it is repeated in the Appendix to this chapter.

7. Otherwise the Second Law of Thermodynamics will be violated.
\[ P_{\text{out}} = \sigma A T_2^4 \]

and absorb at the rate
\[ P_{\text{in}} = \sigma A T_1^4 . \]

Since the surface area of a typical human body is 1.5 m\(^2\), the net rate of radiation loss from a naked body at surface temperature 37 °C, into a room at 70 °F (21 °C) is
\[
P_{\text{net}} = \sigma A \left( T_2^4 - T_1^4 \right)
= 5.7 \times 10^{-8} \times 1.5 \times (310^4 - 294^4) \\
= 150 \text{ Watts} .
\]

It is therefore not surprising that we can feel a "chill" radiating from a cold surface such as an open refrigerator or a large window on a cold day. For example, suppose the surface is at 0 °C instead of room temperature. The additional radiated power is
\[
\Delta P = 5.7 \times 10^{-8} \times 1.5 \times (294^4 - 273^4) \\
= 164 \text{ W} .
\]

In this case our net radiation rate more than doubles (because the thermal radiation absorption from our surroundings is greatly decreased) which we interpret as a sudden chill.

What about thermal conduction across the fatty layer under the skin? Heat is conducted one-dimensionally through a uniform material according to Newton's law of heat conductivity
\[
j_x = -\kappa \frac{\partial T}{\partial x} .
\]

The constant \(\kappa\) is the thermal conductivity, often given in calories per centimeter per unit time, per degree Celsius. For fat the value in these units is \(5 \times 10^{-4}\), so assuming the thickness of the fatty layer is 1 cm and the area is 1.5 m\(^2\) as before, we find that a naked body loses heat by conduction in a room at 70 °F, at the rate
\[
P = 5 \times 10^{-4} \times 1.5 \times 10^4 \frac{\text{cal}}{\text{cm} \cdot \text{oK}} \times \frac{310 - 294}{1} \\
= 500 \text{ Watts} .
\]

That is, conduction is much more important than radiation as a mechanism by which we lose heat.

Finally, if the air is moving we can lose heat a lot faster, by convection. This is why even a mild breeze leads to a substantial "wind chill" on a cold day. And of course any form of evaporation (perspiring) removes large amounts of heat because of the large heat of vaporization of water (540 cal/gm).

Note that if we were unclothed, we would need to eat about 13,000 Cal daily just to maintain our core temperature against radiation and conduction into a rather warm environment.

Most animals avoid this problem by maintaining some form of insulation (blubber, feathers or fur). Our closest hominid relatives (chimpanzees) have considerable body fur, despite living in a much warmer (tropical or sub-tropical) climate, to provide insulation against the night chill.

The absence of human body hair, by and large, points to the fact that because of our adaptive strategies—clothing and fire—we have not needed fur for at least a half-million years.

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8. They also huddle together for warmth.
9. There are wide variations in pilosity (hairiness), known from antiquity: "My brother Esau is a hairy man, but I am a smooth man."
Blackbody radiation is by definition the electromagnetic radiation emitted by a perfectly “black” object—a perfect absorber of radiation (and consequently, by the Second Law of thermodynamics, a perfect emitter) at a definite temperature \( T \). A very good approximation to a blackbody is a container with a small hole in it, as shown below:

If the container is a good thermal conductor the heat source will maintain it at a constant temperature; what comes out of the hole is radiation with a spectrum like that shown below:

Quantum mechanics began with Max Planck’s successful derivation of the spectrum of this radiation by means of one remarkable new idea: the quantum hypothesis. The object of this Appendix is to give the highlights of Planck’s results, in modern language.

Electromagnetic radiation in free space is described by two of Maxwell’s equations:

\[
\begin{align*}
\nabla \times \vec{E} &= -\frac{1}{c} \frac{\partial \vec{B}}{\partial t} \\
\nabla \times \vec{B} &= \frac{1}{c} \frac{\partial \vec{E}}{\partial t},
\end{align*}
\]

Taking the curl of the first and the time derivative of the second, and using the identity

\[
\nabla \times (\nabla \times \vec{E}) \equiv \nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E}
\]

we find (in the absence of charge, \( \nabla \cdot \vec{E} = 0 \))

\[
\frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} - \nabla^2 \vec{E} = 0;
\]

that is, the electric vector satisfies a wave equation. Suppose we now try plane wave solutions of the form

\[
\vec{E}(\vec{x}, t) = \vec{E}(t) e^{i(\vec{k} \cdot \vec{x})};
\]

if we choose the wave vector \( \vec{k} \) suitably, this solution to the wave equation can be made to satisfy appropriate boundary conditions at the sides of

10. We use Gaussian units rather than SI to exhibit explicitly the speed of light, \( c \).
11. — for example, periodic boundary conditions.
Now with this form of the solution, the wave equation reduces to
\[ \frac{d^2 E}{dt^2} + k^2 c^2 E(t) = 0 \]
which is the equation for a simple harmonic oscillator of angular frequency
\[ \omega = kc. \]

In classical physics, a harmonic oscillator can have any energy at all. As we have seen in our discussion of Brownian motion, a (damped) classical harmonic oscillator in thermodynamic equilibrium with a heat bath at temperature \( T \) has average energy \( kT \). Thus to find the energy of electromagnetic radiation in a box of volume \( \Omega = L_x L_y L_z \)
we need to count the number of oscillators and multiply by the average energy of each:
\[ E = N_\text{osc} kT, \]
where
\[ N_\text{osc} = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} \rightarrow \frac{2 \Omega}{8\pi^3} \int d^3 k. \]
That is, for each mode there are two polarizations, the wave numbers appropriate to periodic boundary conditions are
\[ k_x = \frac{2\pi n_x}{L_x}, \text{ etc.} \]
and we take the limit as the dimensions of the box become large (which permits replacing the sum by an integral).

This means the total energy in a finite box is infinite.

What about the frequency spectrum of energy in the box? If we integrate over angles only, and note that
\[ k^2 dk = \frac{1}{c^3} \omega^2 d\omega \equiv \frac{(2\pi)^3}{c^3} v^2 dv \]
we find that if the harmonic oscillators behave classically, their energy density in the frequency range \( [\nu, \nu + d\nu] \) is
\[ dU = \frac{dE}{\Omega} = \frac{8\pi k_B T}{c^3} v^2 dv \equiv 8\pi k_B T \frac{d\lambda}{\lambda^4}. \]
However, while the blackbody radiation spectrum looks like this formula\(^\text{12}\) at long wavelengths, at short wavelengths it resembles the observed spectrum not at all.

At short wavelengths, as Planck knew, the radiation spectrum is well fit by the formula\(^\text{13}\)
\[ dU = \alpha e^{-\beta/\lambda T} \frac{d\lambda}{\lambda^5} \]
where \( \alpha \) and \( \beta \) are constants. He therefore guessed a formula that had the correct short- and long wavelength behavior—and that, incidentally, agreed very well with all the data. Planck’s formula was
\[ dU = \frac{8\pi h c^3}{e^{h\nu/k_B T} - 1} \]
where \( h \) is a new constant of nature, now called Planck’s constant. If Planck had left matters there, he still would be famous for proposing the correct formula describing blackbody radiation. However, he felt impelled to find some kind of underlying reason for the formula to work.

\(^{12}\) due to Rayleigh, among others.
\(^{13}\) W. Wien, Annalen der Physik 58 (1896) 662.
So he worked backward. The number of oscillators per unit volume, per unit frequency, was certainly as given above,
\[ d_n = \frac{8\pi k_B T}{c^3} \nu^2 d\nu. \]
Thus what must be wrong was the equipartition assumption, that gave an oscillator at temperature \( T \) the average energy \( \langle \epsilon \rangle = k_B T \), independent of frequency. Planck’s formula clearly indicates that the average energy depends on frequency;
\[ \langle \epsilon_\nu \rangle = \frac{\hbar \nu}{e^{\hbar \nu/k_B T} - 1}; \]
we can rewrite this as
\[ \langle \epsilon_\nu \rangle = \frac{\hbar \nu}{e^{\hbar \nu/k_B T} - 1} = \left( \frac{e^{\hbar \nu/k_B T} - 1}{e^{\hbar \nu/k_B T} - 1} \right)^2 \]
\[ \sum_{n=0}^{\infty} n \hbar \nu e^{-n\beta \hbar \nu} = \sum_{n=0}^{\infty} e^{-n\beta \hbar \nu} \]
where we have set \( \beta = 1/k_B T \). This is just the Boltzmann formula for the average energy of a system at temperature \( T \), where the possible energies do not take on continuous values but rather are restricted to a discrete set of values
\[ \epsilon_\nu^{(n)} = n \hbar \nu, \ n = 0, 1, 2, \ldots \]
That is, the energies are restricted to integer multiples of a fundamental energy, \( \hbar \nu \).
This hypothesis, central to the black body radiation formula, was called the quantum hypothesis\textsuperscript{14} by Planck.

Planck also realized immediately several implications of his formula: first, it permits us to calculate the the intensity of emitted radiation from a blackbody—that is, to obtain the Stefan Boltzmann constant, in terms of other quantities. The total energy density of radiation in a box is
\[ U = \int_0^\infty dU = \frac{8\pi \hbar}{c^3} \int_0^\infty \nu^3 \frac{d\nu}{e^{\hbar \nu/k_B T} - 1} = \frac{8\pi \hbar}{c^3} (k_B T)^4 \int_0^\infty x^3 \frac{dx}{e^x - 1}. \]
The integral can be evaluated in closed form, for example by expanding, integrating term-by-term, and comparing with the Reimann zeta function; or else by contour integration techniques. The result is \( \pi^4/15 \).

To get the power radiated per unit area, convert the energy density to a flux (pretending it is a fluid):
\[ \vec{j} = U \vec{v} \equiv U c \hat{v}. \]
Averaging the normal component over a half-space gives the net radiated flux as
\[ \langle \vec{j} \rangle = U \vec{v} \equiv U c/4 \]
so the result for the Stefan-Boltzmann constant is
\[ \sigma_{SB} = \frac{2\pi^5 h^2 k_B^4}{15c^2}. \]

Planck also realized that fitting his formula to the blackbody radiation measurements yields both \( h \) and \( k_B \); from the latter one can calculate Avogadro’s number from the formula
\[ N_A = \frac{R}{k_B} \]

14. \( \ldots \)from the Latin word, meaning “how much”.
as well as the charge on the electron \( F \) is the Faraday, about \( 2.9 \times 10^{14} \text{ esu} \), or 96,500 Coulombs, per gram-mol):

\[
e = \frac{F}{N_A}.
\]